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# Roadmap for integrating deep eutectic solvents into adsorption processes: A critical review & design blueprint

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ABSTRACT

The adoption of green chemistry and sustainable engineering approaches into various processes became a trending, proactive practice. On this front, mature and well-developed processes, such as adsorption, have been complemented with different nuances in green chemistry and neoteric solvents, such as Deep Eutectic Solvents (DESs). This review provides a detailed reading of the adsorption studies that incorporated DESs for the development of adsorption materials, referred here as DES-based Adsorbents (DES-ADS).

The first part of this review summarizes the different DES-ADS in the literature under specific themes, namely, (i) applications, (ii) adsorbent materials, and (iii) DES components. The majority of DES-ADS are investigated for application in water/wastewater treatment (55.1%), followed by applications in protein isolation (12.7%), food (12.7%), biomass (7.6%), medical (3.4%) and other application (8.5%). The adsorbents were prepared from different base materials, and two or more base materials are often used as hybrids. As for the DES constituents, hydrogen bond acceptors were mainly chosen as choline chloride or other quaternary ammonium salts, while hydrogen bond donors include ethylene glycol, glycerol, urea in addition to other organic acids, polymerizable monomers, and sugars.

The second part of the review traces the different methodologies used within DES-ADS field through homogenization of different terms in the literature and categorizing each methodology based on the role of the DES within the different DES-ADS development schemes. Accordingly, three main synthesis routes were identified, namely, (i) Mixing, (ii) Dispersion, and (iii) Solvothermal methods. The discussion includes a critique about certain generalizations, assumptions, and shortcomings with regard to the DES's nature and intrinsic properties during the development of such DES-ADS. This includes using improper reaction environments and dismissing the basic thermal properties of DES during the synthesis/functionalization of DES-ADS. Lastly, an alternative bottom-up framework is proposed for developing functional and task-specific DES-ADS.

This work provides a detailed mapping of trends and trajectories in the field of DES-based adsorbents and a critical discussion on the different methodologies used within the field. The

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framework devised in the light of such meticulous reading is a methodical, bottom-up approach that considers the principles from both fields (Adsorption and DES). Ultimately, this framework allows researchers to take the necessary steps towards answering the research question(s) imposed by the need for DES-ADS development. The framework can be also extrapolated into other fields in order to develop various DES-based adsorbents, membranes or other functional materials.

**Abbreviations**

*Used as Hydrogen Bond Acceptors (in this review)*

| | |
|---|---|
| DMEA | 2-Dimethylaminoethanol |
| APTMACl | 3-Acrylamidopropyl trimethyl ammonium chloride |
| ATECl | Allyl triethylamine chloride |
| ATMACl | Allyl trimethyl ammonium chloride |
| ATPPBr | Allyl triphenyl phosphonium bromide |
| Bet | Betaine |
| BS-12 | Amphiprotic surfactant (BS-12) |
| BTBACl | Benzyl tributyl ammonium chloride |
| BTMACl | Benzyl trimethyl ammonium chloride |
| BTPCl | Benzyl triphenyl phosphonium chloride |
| ChCl | Choline Chloride |
| Cl-ChCl | Chloro Choline Chloride |
| CTEABr | Cetyl trimethyl ammonium bromide |
| DEACl | N,N-diethylethanolammonium chloride |
| – | $FeCl_3$ |
| Fru | Fructose |
| GA-HCl | Guanidine hydrochloride |
| Glu | Glucose |
| HTMABr | Hexadecyl trimethyl ammonium bromide |
| – | LiCl |
| L-pro | L-proline |
| MalA | Malic Acid |
| MATACl | Methacryloxyethyl trimethyl ammonium chloride |
| Men | Menthol |
| - | $MgCl_2{\cdot}6H_2O$ |
| MTPPB | Methyltriphenylphosphonium bromide |
| NGA-HCl | Amino guanidine hydrochloride |
| - | $NiCl_2{\cdot}6H_2O$ |
| P-ChCl | Phospho ChCl |
| Poly(VP) | Poly(Vinyl Pyrolidone) |
| Si-surf | Silicone Surfactant |
| TarA | L-(+)-tartaric acid |
| TBABr | Tetrabutyl ammonium bromide |
| TBACl | Tetrabutyl ammonium chloride |
| TEACl | Tetraethyl ammonium chloride |
| TEAOH | Tetraethylammonium hydroxide |
| TMACl | Tetramethyl ammonium chloride |
| VBTMACl | 4-vinyl benzyl trimethyl ammonium chloride |
| VP | Vinyl Pyrolidone |

*Used as Hydrogen Bond Donors (in this review)*

| | |
|---|---|
| AcrTMA | (3-Acrylamidopropyl) trimethylammonium |
| dmU | 1,3-Dimethylurea |
| 1,3-PD | 1,3-Propanediol |
| 1,4-BD | 1,4-Butanediol |
| BuIM | 1-Butylimidazole |
| Naph | 1-Naphthol |
| 2,4,6-TCP | 2,4,6-Trichlorophenol |
| HMA | 2-Hydroxyethyl Methacrylate |

| | |
|---|---|
| VBenA | 4-Vinyl Benzoic Acid |
| ActIM | Acetamide |
| ActA | Acetic acid |
| AcrIM | Acrylamide |
| AA | Acrylic Acid |
| Arbidol | Arbidol |
| CafA | Caffeic Acid |
| CatOH | Catecol |
| CitA | Citric Acid |
| DodecA | Dodecanoic Acid |
| Sor | D-sorbitol |
| ED | Ethanediol |
| EthN | Ethanolamine |
| EG | Ethylene Glycol |
| Glu | Glucose |
| Gly | Glycerol |
| GlyA | Glycolic acid |
| HFIP | Hexafluoro isopropanol |
| IM | Imidazole |
| ItA | Itaconic acid |
| LacA | Lactic acid (Lac) |
| MalA | Malic Acid |
| MlnA | Malonic Acid |
| Cresol | m-Cresol |
| MA | Methacrylate |
| MAA | Methacrylic acid |
| OlcA | Oleic acid |
| OA | Oxalic acid |
| $OA{\cdot}2H_2O$ | Oxalic Acid dihydrate |
| PEG | Polyethylene Glycol |
| PhActA | Phenyl Acetic Acid |
| p-tsOH | p-Toluenesulfonic acid |
| Sor | Sorbitol |
| Suc | Sucrose |
| TEG | Tetraethylene Glycol |
| ThioU | Thio urea |
| Thy | Thymol |
| TFAI | Trifluoroacetamide |
| HTTA | Thenoyltrifluoroacetone |
| TPP | Triphenyl phosphate |
| TOPO | Trioctylphosphine oxide |
| U | Urea |
| Xyl | Xylitol |
| 1,2-PD | 1,2 propanediol |
| FA | Formic Acid |
| HFP | Hexafluoro isopropanol |
| MPrA | 3-Mercaptopropionic acid |
| 2,4,6-TCP | 2,4,6-Trichlorophenol |

*Target analytes*

| | |
|---|---|
| Epic | (−)-Epicatechin |
| Epig | (−)-Epigallocatechin |
| Cat | (+)-Catechin |
| BrP | 4-Bromophenol |
| NP | 4-Nitrophenol |
| OHMF | 5-Hydroxymethylfurfural |
| – | Acetaminophen |
| AB 74 | Acid Blue 74 |
| AB 80 | Acid Blue 80 |
| – | Amaranth |
| – | Arbidol |

| | |
|---|---|
| As | Arcenic |
| – | Aspartame |
| – | Atenolol |
| – | Avidin |
| – | Baicalein |
| BenzA | Benzoic acid |
| Bzyl peptides | Benzoylation peptides |
| BHb | Bovine hemoglobin |
| BPA | Bisphenol A |
| BPAF | Bisphenol AF |
| BPF | Bisphenol F |
| BSA | Bovine serum albumin |
| Cd | Cadmium |
| Caf | Caffeine |
| Cat | Catechin |
| CP | Cholorphenol |
| CAS | Chrome azurol S |
| CinA | Cinnamic acid |
| Cipro | Ciprofloxacin |
| CR | Congo red |
| – | Cortisone |
| Cr (VI) | Chromium |
| CV | Crystal Violet |
| Cyt c | Cytochrome *c* |
| – | Dexamethasone |
| DBrP | Dibromophenol |
| DCP | Dichlorophenol |
| – | Diclofenac |
| DCS | Dissolved and colloidal substances |
| DNA-T-Cs | DNA toxic compounds |
| EY | Eosin Y |
| – | Forchlorfenuron |
| GalA | Gallic Acid |
| Glur peptide | Glularylated peptide |
| HRP | Horseradish peroxidase |
| HylA | Hyaluronic acid |
| – | Hydrocortisone |
| IC | Indigo carmine |
| IB | Indigotin Blue |
| I3C | Indole-3-carbinol |
| – | Isorhamnetin |
| – | Kaempferol |
| – | Laminarin |
| La | Lanthanium |
| Aspr | L-Asparaginase |
| Lev | Levofloxacin |
| Lys peptides | Lysine acetylation peptides |
| Lyz | Lysozyme |
| MG | Malachite Green |
| Hg | Mercury |
| – | Methcathinone |
| MO | Methyle orange |
| MB | Methylene Blue |
| – | Metronidazole |
| – | Myricetin |
| – | Naproxen |
| Ni | Nickel |
| OflN | Norfloxacin |
| Ofl | Ofloxacin |
| OPP | Organophosphorus pesticides |
| OVA | Ovalbumin |

| | |
|---|---|
| OA | Oxalic acid |
| PTX | Paclitaxel |
| AnisA | p-anisic acid |
| – | Paracetamol |
| Cu | Copper |
| Pb | Lead |
| – | Pesticides |
| Phen | Phenol |
| – | Phthalate esters |
| PAHs | Polycyclic aromatic hydrocarbons |
| PPCPs | Pharmaceuticals and personal care products |
| – | Quercetagetin |
| Qrc | Quercetin |
| R70 | Red 70 |
| REE | Rare Earth Elements |
| RB | Rhodamine B |
| ST | Safranine T |
| Salb | Salbutamol |
| SalA | Salicylic acid |
| Schn | Schisandrin |
| – | Sertraline |
| SinpA | Sinapic acid |
| OflS | Sparfloxacin |
| Sr | Strontium |
| SY | Sunset Yellow |
| – | Tetracycline |
| – | Thiabendazole |
| – | Thidiazuron |
| Tfr | Transferrin |
| TBrP | Tribromophenol |
| Tryp | Trypsin |
| – | Vanillin |

## 1. Introduction

The perspective of the scientific community, with practitioners from both academic and industrial spheres, emphasizes the adoption of green chemistry & engineering approaches, and advocates their integration into various processes. This is particularly the case for water & wastewater treatment, in which several environmental and economic factors intertwine [1]. The treatment of natural and anthropogenic aqueous streams is usually conducted for different means: On one hand, protective measures are taken for the purification of water & wastewater to meet certain regulatory values (e.g. drinking or agricultural uses) [2]; On the other hand, productive measures are considered to recover value-added elements from aqueous streams (e.g., industrial uses) [3]. Nevertheless, both measures require sustainable and cost-effective technologies, and one of the recent technologies developed with such merits is deep eutectic solvents (DESs) [4].

In recent years, DESs have emerged as potential substitutes for ionic liquids (ILs) and a promising alternative for conventional organic solvents. DESs are basically a mixture of two or more components, a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA), of which the resulting eutectic mixture has a decreased melting point compared to its starting components [5]. This simplified definition has been later refined to distinguish the "*deep*" qualificative in DESs from other ideal liquid mixtures, thereby identifying DESs as *a mixture of pure compounds for which the melting point temperature is occurring below that of an ideal liquid mixture* [6]. Such temperature depression is associated with the hydrogen bond interactions between the compounds of the mixture. DESs have been portrayed as the new generation of "*designer solvents*", offering several unique features such as simplicity of preparation, biodegradability, tunability and cost-efficiency [7]. Moreover, stemming from the development made with their predecessors (i.e., ionic liquids), the possibilities of developing different DESs are huge due to the vast number of available HBAs and HBDs used to form DESs and their various molar combinations. These versatile characteristics facilitated the use of DESs in different fields, such as catalysis [8,9], separation [10–14], biochemistry [15], electrochemistry [16,17], and nanotechnology [18,19].

The properties of DESs, their fundamental interactions, and their mode of application are still being studied. Several reports have discussed the integration of DESs with other technologies (i.e., adsorption or membrane filtration), where DESs function as extractants, reaction solvents, phase modifiers, or functionalizing agents [20–22]. Attempts to incorporate DESs with different types of adsorbents only began to grow in 2016 but have recently gained considerable attention to practitioners from the adsorption community. The basic operating principle of adsorption is the preferential concentration of chemical species (adsorbate) onto the surfaces of solids

(adsorbents). Many adsorbents were developed from different materials and for diverse applications. Some of the most widely used adsorbents include activated carbon, silica, metal oxides, metal organic frameworks, and polymeric adsorbents, to name a few [23]. Selection of the adsorbent material for a given application represents perhaps one of the most essential tasks, and several factors are taken into consideration such as adsorption capacity, selectivity, recyclability and cost [23]. To qualify for practical use, adsorbents can be modified to incorporate different functional groups, thereby changing their affinity to certain species, altering their physical and chemical properties, or enhancing their adsorption capacity. In other instances, the functionalization of the adsorbent by a certain compound is done due to the difficulty of using this compound solely. For instance, ILs can be used for the treatment of wastewater when grafted onto the surface of different adsorbents, thereby overcoming certain drawbacks such as solubility and cost [24]. Likewise, adsorbents functionalized with hydrophilic DESs were investigated for the recovery of heavy metals, dyes, proteins, and other analytes from aqueous media [25–29].

While it is tempting to test the potential of DESs within the scope of other mature technologies, such as adsorption, it is essential to have a clear understanding of the nature of DESs and their associated molecular behavior when used within the parameters of these technologies. More importantly, the critical role (i.e., function) contributed by DES's components and the expected outcome (i.e., objective) of utilizing a particular DES must be clearly identified. With these two prerequisites (function and objective), knowledge-based criteria for the proper selection and application of DESs with other technologies can be acquired. It was noticed that, during the preparation of DES-based adsorbents, several studies appear to dismiss the basic principles governing the molecular interactions of DES's components. Moreover, analytical assessments to validate the stable formation of DESs onto the adsorbent material are lacking. Irrespectively, these practices seem to propagate in the literature, presumably due to the encouraging performance exhibited by these modified adsorbents.

This review aims to construct a reliable bottom-up framework approach for the design and application of DES-based adsorbents (DES-ADS) for the treatment of different feed streams. A thorough examination of the studies utilizing DES-ADS was conducted. After reflecting on the (i) relevant fields of application, (ii) adsorbent material and (iii) DES components used, the methods of incorporating DESs into the synthesis, functionalization or treatment of different adsorbents were scrutinized and critiqued. A more constructive framework for developing DES-ADS is postulated herein, considering the DESs' stability during the synthesis procedure and the individual influence of the DES's components (HBA and HBD) on the adsorption mechanism. In the light of these investigations, potential avenues of research and unexplored research ideas were highlighted.

## 2. Methodology & data collection

The relevant literature for this review was joined from two distinct fields: *Adsorption* and *Deep Eutectic Solvents*. To identify and collect such relevant articles, critical aspects related to the design and application of DES-functionalized adsorbents were targeted. These aspects are concerned with the (i) adsorbent material, (ii) DES components, and (iii) target analytes. The selected articles were compiled from the Scopus database, complemented with the Web of Science database, using the keywords: "*Adsorption*" AND "*Deep eutectic solvents*", with no bounds on a specific period (statistical analysis cutoff date: Jul-2023). It is worth noting that from nearly 600 + listed articles, ~120 articles fall within the scope of this review. Articles related to gas adsorption using DESs were disregarded as they do not share the same solid–liquid (adsorbent-adsorbate) kinetics but are rather categorized with other sorption technologies. Likewise, articles lacking rigorous analyses of the developed adsorbent, or using previously reported ones for the same application, were also excluded. Accordingly, the only articles included were those concerned with developing, modifying, or functionalizing adsorbents using DESs and applying these adsorbents to treat a certain–typically aqueous–feed.

The data collected from these articles were tabulated in one 120x35 Excel sheet (available in the ***Supplementary information***). The tabulated information from each article included a set of classifications in the following order: Article Title, Process, Application, Material, DES used, Feed properties, Performance, Regeneration/recyclability, and Synthesis route.

The *process* field describes the extraction techniques the authors used in each respective article. Most of the articles – conforming with the scope of this search – have used 'adsorption' as the main technique, which is identified here as: the mixing of a solid extractant (adsorbent) with an aqueous feed containing a target analyte (adsorbate) with the aim of concentrating the adsorbate within or on the surface of the adsorbent. Although most articles have used the same principle, different techniques have been tested, including Solid-Phase Extraction (SPE), Magnetic Solid Phase Extraction (MSPE), Solid Phase Micro Extraction (SPME), Liquid Phase Micro Extraction (LPME), Dispersive Liquid Phase Micro Extraction (DLPME), Magnetic Dispersive Liquid Phase Micro Extraction (MDLPME), among other methods. The use of these techniques was based on the scope of each article, and the aim of listing this information was to notify the reader of the different approaches considered in the synthesis of each adsorbent material and the corresponding achieved performance.

**Table 1**
Basic Types of DESs [32,33].

| Type | Formula | Terms |
|---|---|---|
| Type I | $Cat^{+}X^{-}zMCl_x$ | M = Zn, Sn, Fe, Al, Ga, In |
| Type II | $Cat^{+}X^{-}zMCl_x \bullet yH_2O$ | M = Cr, Cp, Cu, Ni, Fe |
| Type III | $Cat^{+}X^{-}zRZ$ | Z = $CONH_2$, COOH, OH |
| Type IV | $MCl_x + RZ = MCl^{+}_{x-1} \bullet RZ + MCl^{-}_{x+1}$ | M = Al, Zn and Z = $CONH_2$, OH |
| Type V | $RZ + RZ$ | Z = $CONH_2$, COOH, OH |

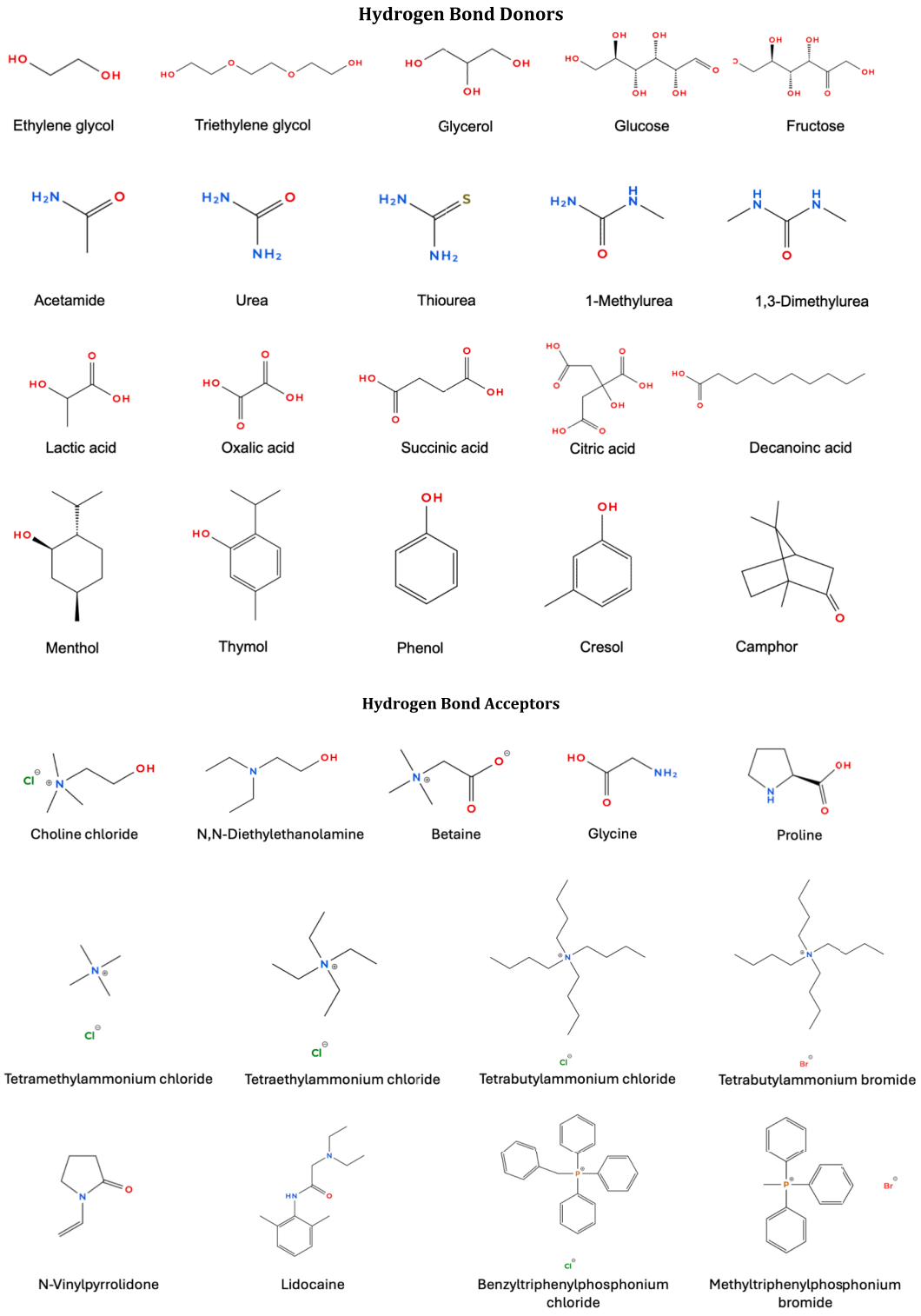


**Fig. 1.** List of commonly used HBDs and HBAs for DES preparation.

The *application* field describes the industry or the general theme that the conducted research work falls into. In this aspect, the reviewed articles were categorized into six different applications as follows: (1) Water/wastewater treatment, (2) Protein isolation, (3) Extraction from Food, (4) Extraction from biomass, (5) Medical/Pharmaceutical, and (6) "Other" applications. Due to the majority of

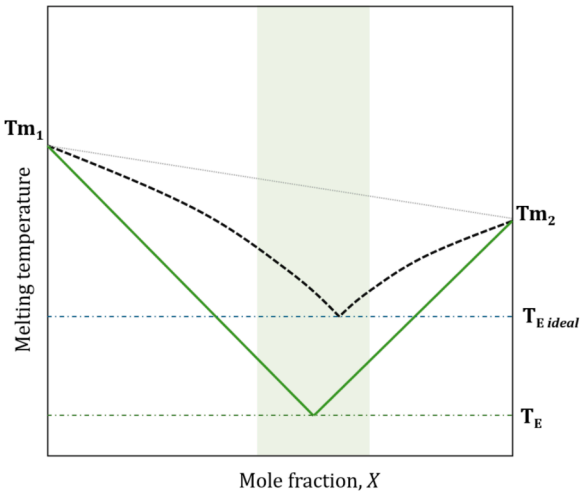


**Fig. 2.** Schematic representation comparing the Solid-Liquid phase diagram of a simple ideal eutectic mixture (black – dashed) and a deep eutectic mixture (green – continuous). Mole fraction, *X*, of one of the components with relevance to the other components in the mixture (x-axis); the melting temperature, Tm, of components (y-axes). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

papers dealing with water/wastewater applications, this category was sub-divided into further classifications which includes heavy metal extraction, pharmaceuticals removal, dye removal, phenol extraction, and 'other' aqueous applications. The uses of DES-ADS in different applications are summarized and discussed in *section 4*.

The adsorbent '*material*' field contains an abbreviated text describing the type of material or hybrid material(s) used as the substrate for the adsorbent. Overall, the reviewed papers were categorized into 12 categories based on the material(s) used including Ferric oxide ($Fe_3O_4$), Carbon nanotubes (CNT), Graphene oxide (GO), Molecularly imprinted polymers (MIPs), Metal organic frameworks (MOFs), Metal oxides/hydroxide (MO), Cyclodextrin (CD), biomass-based (Bio), Silica-based (Si), and *other* materials. Additionally, magnetic-based MIPs ($Fe_3O_4$-MIPs) were classified as a separate field due to their high occurrence, especially with tertiary substrate material. The materials used for DES-ADS preparation and the different composite options developed are detailed in *section 5*.

The '*Deep Eutectic Solvents*' field is straight forward, and it was subdivided into separate fields based on the '*HBA*', '*HBD*' ('HBD II' for ternary DESs), '*Molar ratio*', '*Role*', and '*Function*'. The '*role*' of the DES is mainly classified as either DES used for the *synthesis of* the adsorbent material or for its *functionalization*. Furthermore, the '*Function*' field gives more details into the functionality of the DES (e.g., monomer, reaction medium, solvent, precursor, and others). *Section 6* contains an in-depth discussion about the various DESs used to develop DES-based adsorbents.

The '*Feed properties*' field comprises different properties, including the type of the feed (e.g., stock solution, actual sample…etc.), the target analyte, concentration of analyte, and adsorbent-to-feed ratio. It should be noted that the adsorbent/feed ratio is stated as reported in the corresponding articles. However, another column containing a homogenized value of a specific amount of adsorbent per 1 mL of feed was added to the table.

The '*performance*' field states the adsorption capacity as reported in the corresponding article. Wherever possible, the maximum adsorption capacity ($Q_{max}$) was tabulated. Likewise, whenever possible, the isotherm and kinetic models were reported along with the optimum operating pH value of the feed. One of the crucial aspects of evaluating an adsorbent is its recyclability. Among the reviewed articles, nearly ~ 70 % considered regenerating the adsorbents after extraction. In this '*regeneration*' field, the type of the regenerant, the regeneration/recovery ratio after the 1st cycle, the regeneration/recovery ratio after the $n^{th}$ cycle, and the number of cycles is reported.

The '*synthesis routes*' field reports the different approaches used for the development of DES-ADS. It should be noted that across all the reviewed papers, it seems that different nomenclatures have been used to describe the preparation steps. Nevertheless, after further examining the methodology/methods adopted in each of the articles, the synthesis routes can be classified into one of three main routes: (1) dilution/mixing, (2) dispersion and (3) solvothermal methods. These three routes and their suitability for DES-ADS synthesis are scrutinized in *section 7*.

Lastly, the findings and insights from this review were used to construct a methodical, stepwise, bottom-up framework approach to be used for developing DES-based adsorbents. The framework was explained in *section 8* by detailing both the DES-related and adsorbent-related aspects to be considered during the synthesis/functionalization of such adsorbents. Overall, the framework allows for a practical, investigative approach for developing DES-ADS, whereby more fundamental insights can be acquired on the contribution of DESs, adsorbent materials, and their interactions.

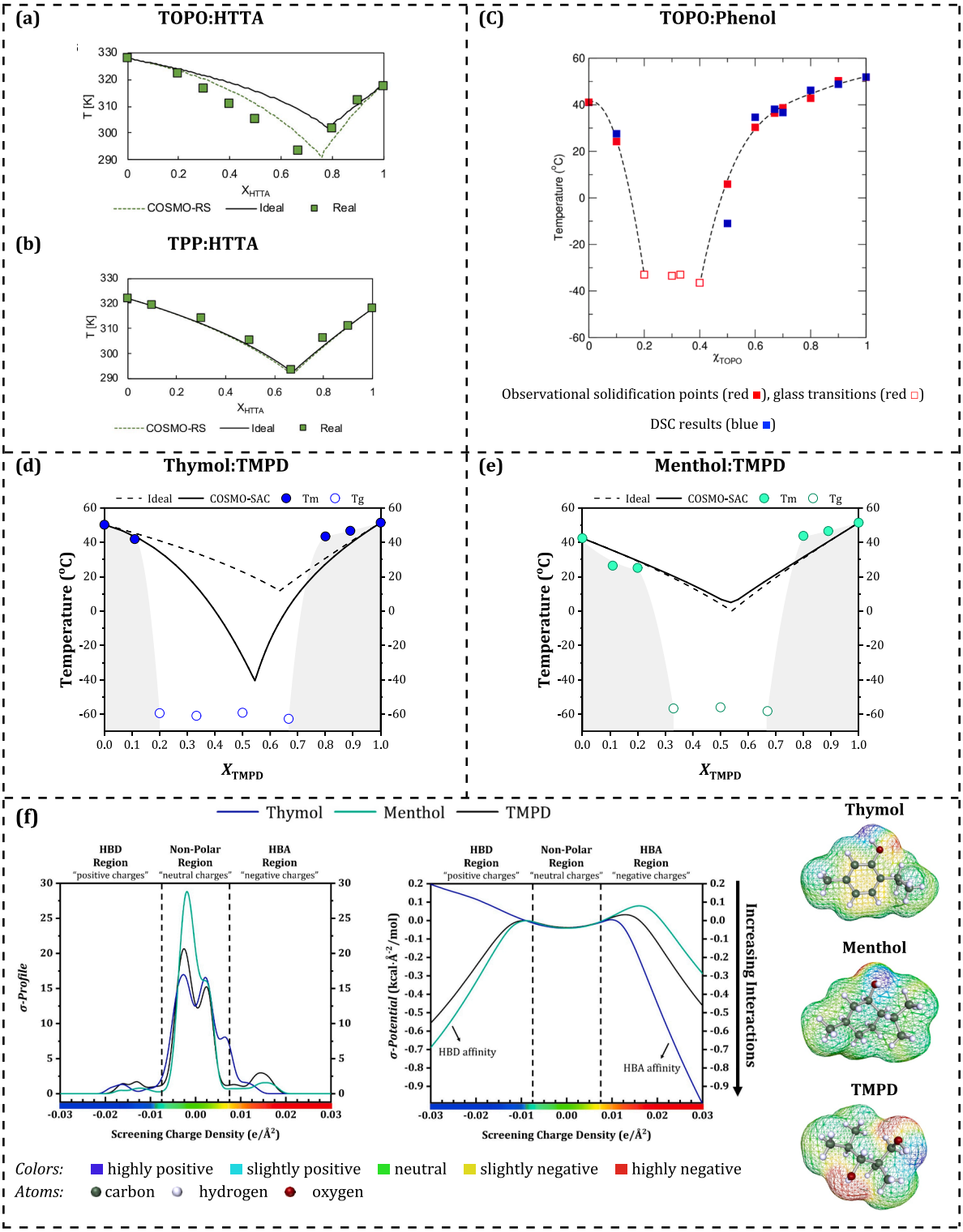


**Fig. 3.** Solid-liquid phase equilibrium for different DES systems; (a-b) TOPO:HTTA, TPP:HTT [40] Copyright 2021, American Chemical Society; (c) TOPO:Phenol [42] Copyright 2018 American Chemical Society; solidification point was measured through an observational method using a solid–liquid cell, and melting point with DSC. (d) Thymol:TMPD; (e) Menthol:TMPD; (f) molecular descriptors, i.e. σ-profile (left) and σ-potential (right) calculated via COSMO-RS [41]. Copyright 2021 Elsevier B.V.

**Table 2**
Basic principles and definition of DESs.

| What DESs are | What DESs aren't |
|---|---|
| • DESs are mixtures of two or more pure compounds associated through hydrogen bond interactions and prepared by a simple physical process. | • DESs are not novel or pseudo pure compounds. |
| • DESs can be composed of ionic species (s), non-ionic species, or both. | • DESs are not a new class of ionic liquids, as they have different molecular behavior. |
| • Many DESs can be prepared from cheap compounds | • DESs are not necessarily low cost, as this parameter depends on the starting materials. |
| • DESs can be prepared from natural, renewable and non-toxic compounds [48]. | • Not all DESs are "green" and non-toxic. This depends on the individual compounds and the toxicity profile of the resulting DES (irrespective of its individual compounds) [49,50]. |

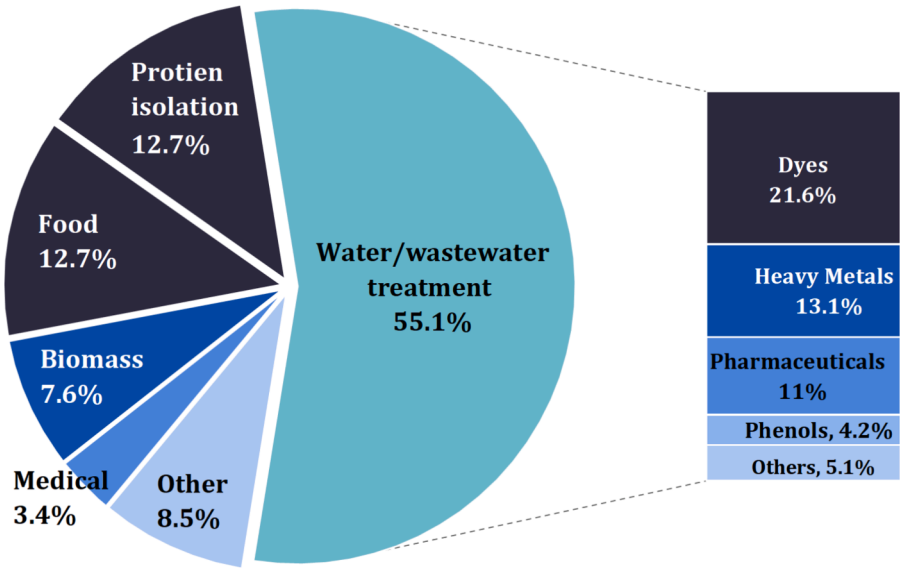


**Fig. 4.** Application categories of DES-based adsorbents from literature (from 2010 to 2024).

## 3. Fundamentals of Deep eutectic solvents

Eutectic mixtures –typically of binary components– refer to the occurrence of a composition with a lower melting point than that of any other composition, including that of the neat components. The liquefication and enhanced solubility of eutectic mixtures served many practical applications, especially for the pharmaceuticals and molten salts industries [6]. In regard to the term "*Deep eutectic solvents*", it was first introduced in the early 2000's by Abbott et al. [30] to describe eutectic mixtures of quaternary ammonium salts and amides, of which the melting point of the system was much lower than that of the individual components. This behavior was attributed to the association of the constituents through hydrogen bonding, resulting in lower lattice energy and, accordingly, notable depression in the melting point [31]. The general formula of a DES is usually a mixture of two (or more) components, of which one acts as the hydrogen bond donor (HBD) and the other as hydrogen bond acceptor (HBA). Different DESs were developed, and based on the starting components, several categories of DESs were initially defined using the general formula: $\boldsymbol{Cat^{+}X^{-}zY}$, with $Cat^{+}$ representing the cations of various ammonium, phosphonium, or sulfonium salts, $X^{-}$ is the halide anion of the salts, $Y$ is a Lewis or Brönsted acid, and $z$ is the number of $Y$ molecules.

The basic types of DESs initially proposed by Abbott and co-workers [32] (type I – IV) are listed in the upper part of Table 1. Amongst these, Type III DESs, usually prepared from quaternary ammonium salts with different alcohols as HBDs, received wide attention from the literature due to their attractive features, such as ease of preparation, biodegradability, and low cost of starting compounds.

Notably, the different types of DESs developed initially were hydrophilic. Beyond these types, and more recently, hydrophobic DESs were first reported in 2015 by van Osch et al. [34] and Ribeiro et al. [35] The former group combined quaternary ammonium salts and decanoic acid, while the latter used terpenoids (i.e. DL-menthol) with carboxylic acids; terpenoids include the naturally occurring non-ionic monoterpenes such as thymol and menthol [36]. The use of solely non-ionic species in the formation of hydrophobic eutectic mixtures–referred to as Type V DESs–has been well-received in the literature, as important features of these DESs include their low viscosity, reduced cost, and high potential for regeneration compared to DESs comprised from ionic components [33]. Hydrophobic DESs allowed various applications in aqueous media, which were not easily applicable to hydrophilic ones [36].

**Table 3**
Applications of DES-based adsorbents within the field of water & wastewater treatment, specifically for: Dye adsorption. (chronological order).

| Application | | Water & Wastewater treatment - Dyes | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Article info. | | Process | Material | DES | | Feed properties | | | Performance | Model | | Regeneration | | | |
| Ref | Year | Process | Composite | HBA:HBD | Ratio | Target | Conc.ppm [specified] | Adsorbent dose | Performancemg.g$^{-1}$ [specified] | Isotherm | Kinetic | Regenerant | R % | R %(last cycle) | Cycles |
| [1] | 2015 | Ads. | CoFe oxide | ChCl:U | 1:2 | Congo red | 100 ppm | 0.3 - 0.5 mg / 1 mL | 305 [95%] | | | Combusted at 280 C | | | 4 |
| [2] | 2019 | SPE | Cellulose monolith | ChCl:U | 1:2 | Red 70 | 70 ppm | 1-3 mL/min | 29.2^ [83.3%] | Thomas Yoon-Nelson | | EthOH, NaCl and H2O | | 72% | 5 |
| [3] | 2019 | Ads. | CNT | ChCl:EG | 1:2 | Methyle orange | 40 ppm | 7.45 mg / 50 mL | 310.2* | Langmuir | pseudo-2$^{nd}$ order | | | | |
| [3] | 2019 | Ads. | CNT | DEACl:EG | 1:3 | Methyle orange | 40 ppm | 9.77 mg / 50 mL | 263.14* | Langmuir | pseudo-2$^{nd}$ order | | | | |
| [4] | 2019 | SPE | $Fe_3O_4$-MOF (HKUST-1) | APTMACl:Sor | 1:1<br>2:1 | Malachite Green | 8480 ppm | 5 mg / 1 mL | 966.93 | Freundlich | | NaCl-MeOH | | ~450<br>~300 | 5 |
| [4] | | | | | | Crystal Violet | 3730 ppm | 5 mg / 1 mL | 788.90<br>833.33* | Langmuir | | NaCl-MeOH | | | |
| [5] | 2019 | Ads. | Biochar–clay | HTMABr:Gly | 2:1 | Acid Blue 74 | 20 - 100 ppm | [0.5 g in column] | 409.235* | Langmuir | pseudo-2$^{nd}$ order | | | | |
| [6] | 2019 | Ads. | CNF-halloysite | Amino GA-HCl:Gly | 1:2 | Chrome azurol S | 50 ppm | 50 [mg/L] | 19 [80%] | | | | | | |
| [7] | 2019 | Ads. | CNT-ZnCo2O4 | CTEABr:Gly | 1:2 | Eosin Y | 20-200 ppm | 500 mg / 250 mL | 412.497^<br>414.454* | Langmuir | pseudo-2$^{nd}$ order | Acetone (EthOH) | 96% (81%) | 65% (49%) | 5 |
| [8] | 2019 | Ads. | MnO2 | BTBACl:ActIM | 1:7 | Congo red | 20 ppm | 40 mg / 50 mL | 54.85* | Freundlich | pseudo 1$^{st}$ order | Thermal desorption (400 C) | | | |
| [9] | 2019 | Ads. | MgO | BTMACl:U | 1:2 | Congo red | 250 ppm | 40 mg / 80 mL | 666.7* | Langmuir | pseudo-2$^{nd}$ order | Annealed at 350 C | 97 | 91 | 5 |
| [9] | 2019 | Ads. | MgO | CTEABr:U | 1:2 | Amaranth | 250 ppm | 40 mg / 80 mL | 43.74* | Langmuir | pseudo-2$^{nd}$ order | Annealed at 350 C | 92.1 | 81.5 | 5 |
| [9] | 2019 | Ads. | MgO | BTBACl:U | 1:2 | Indigo carmine | 250 ppm | 40 mg / 80 mL | 54.32* | Langmuir | pseudo-2$^{nd}$ order | Annealed at 350 C | 89.8 | 79 | 5 |
| [10] | 2019 | Ads. | CNT | CTEABr:Gly | 1:2 | Crystal violet | 50 ppm | 30 mg / 30 mL | 385.27*<br>394.17^ | Freundlich | pseudo 1$^{st}$ order | | | | |
| [11] | 2020 | Ads.-Mem | $MnO_2$ | BTBACl:EG | 1:2 | Methylene Blue | 50 ppm | 50 mg/100 ml | 253 | | | Iso-propyl alcohol | >93% | >93% rejection (membrane) | 10 |
| [12] | 2020 | Ads. - LLE | L-amino acid gel | BTBACl: PhActA | 1:2 | Rhodamine B | $1.8\times10^{-4}$ [M] | 250 [mg/ 500 µL] | 1930^ | | | | | no loss in performance | 9 |
| [13] | 2020 | Ads. | Polyacrylamide-ϒ-$Fe_2O_3$ | BTMACl:ActA | 1:1 | Methylene Blue | 5-300 ppm | 50 mg/ 50 mL | 359.71* | Langmuir | | MeOH at pH = 2 | | 97.30% | 6 |
| [14] | 2020 | Ads. | $Fe_3O_4$-GO | CTEABr:U | 1:2 | Methylene Blue | 25 ppm | 0.3 mg / Ml | [~100%] | | | | | | |
| [15] | 2020 | Ads. | Chitosan beads | CTEABr:U | 1:2 | Malachite Green | 100 ppm | 20 mg /20 mL | 6.54, 6.59^, 1.34* | Freundlich | Intraparticle diffusion | $H_2SO_4$ | ~90% | | 3 |
| [15] | 2020 | Ads. | Chitosan beads | BTBACl:Gly | 1:2 | Malachite Green | 100 ppm | 20 mg /20 mL | 8.64, 3.776^, 17.86* | Langmuir | pseudo-2$^{nd}$ order | $H_2SO_4$ | ~90% | | |
| [16] | 2020 | Ads. | N-doped porous carbon | Glucose:U | 1:5 | Methylene Blue | 1000 ppm | 10 mg / 10 g | 439.9* | Langmuir | pseudo-2$^{nd}$ order | | | | |
| [17] | 2020 | Ads. | MgAl LDH | MgCl2·6H2O: U | 1:2 | Methyle Orange | 200 ppm | 20 mg / 40 mL | 1051.87* | Langmuir | pseudo-2$^{nd}$ order | NA | NA | NA | NA |

(*continued on next page*)

**Table 3** (*continued*)

| Application | | Water & Wastewater treatment - Dyes | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Article info. | | Process | Material | DES | | Feed properties | | | Performance | Model | | Regeneration | | | |
| Ref | Year | Process | Composite | HBA:HBD | Ratio | Target | Conc.ppm [specified] | Adsorbent dose | Performancemg.g$^{-1}$ [specified] | Isotherm | Kinetic | Regenerant | R % | R %(last cycle) | Cycles |
| [17] | 2020 | Ads. | MgAl LDH | MgCl2·6H2O:U | 1:2 | Congo red | 200 ppm | 20 mg / 40 mL | 889.76* | Langmuir | pseudo-2$^{nd}$ order | | | | |
| [17] | 2020 | Ads. | MgAl LDH | MgCl2·6H2O:U | 1:2 | indigo carmine | 200 ppm | 20 mg / 40 mL | 512.55* | Langmuir | pseudo-2$^{nd}$ order | | | | |
| [18] | 2021 | Ads. | COF | TBABr:IM | 3:7 | Methylene Blue | 50–600 ppm | 5 mg /10 mL | 407* | Langmuir | | THF and 1 M HCl (1: 1, v/v) | 98.90% | 94.70% | NA |
| [18] | 2021 | Ads. | COF | TBABr:IM | 3:7 | Safranine T | 50–600 ppm | 5 mg /10 mL | 1185* | Langmuir | | THF and 1 M HCl (1: 1, v/v) | 98.90% | 94.70% | NA |
| [19] | 2021 | Ads. | $Fe_3O_4$-polydopamine | TBACl :MAA | 1:2 | Malachite Green | 0.2 mg/ml | 5 mg /5 mL | 277.78 | Langmuir | | DMF and DMSO | unchanged capacity | | 6 |
| [19] | 2021 | Ads. | $Fe_3O_4$-polydopamine | TBACl :MAA | 1:2 | Sunset Yellow | 200 ppm | 5 mg /5 mL | 129.27 | Dubinin-Radushkevich | | DMF and DMSO | unchanged capacity | | 6 |
| [20] | 2021 | Ads. | Chitosan | ChCl:U | 1:2 | Malachite Green | 20 ppm | 20 mg / 20 mL | 78.13* | Langmuir | pseudo-2$^{nd}$ order | $H_2SO_4$ | >90% | ~80 | 5 |
| [20] | 2021 | Ads. | $Fe_3O_4$-Chitosan | ChCl:U | 1:2 | Malachite green | 20 ppm | 20 mg / 20 mL | 87.72* | Langmuir | pseudo-2$^{nd}$ order | $H_2SO_4$ | ~90% | ~60 | 5 |
| [21] | 2021 | Ads. | $Ni_2CO_3(OH)_2$-$SiO_2$ | NiCl2·6H2O : EG | 1:2 | Congo red | 20-1200 ppm | 10 mg / 50 mL | 2637* | Langmuir | pseudo-2$^{nd}$ order | | | | |
| [22] | 2022 | Ads. | Lignin | ChCl:EthN | 1:6 | Methylene Blue | 800 ppm | 2 mg / 1 mL | 258.5 | Langmuir | pseudo-2$^{nd}$ order | | | | |
| [23] | 2022 | Ads. | $NiSO_4$ | ChCl:EG | 1:2 | Methylene Blue | 10 ppm | 50 mg / 100 mL | 19.56-24.38 | Langmuir | pseudo-2$^{nd}$ order | | | | |
| [24] | 2022 | Ads. | halogenated dibenzylidene-D-sorbitol-Euteectogel | ChCl:EG | NA | Crystal violet | $1.0 \times 10^{-4}$ [M] | 400 mg / 1 mL | [>90%] | | | MeOH | | | 8 |
| [24] | 2022 | Ads. | halogenated dibenzylidene-D-sorbitol-Euteectogel | ChCl:EG | NA | MB | $1.0 \times 10^{-4}$ [M] | 400 mg / 1 mL | [>90%] | | | MeOH | | | 8 |
| [24] | 2022 | Ads. | halogenated dibenzylidene-D-sorbitol-Euteectogel | ChCl:EG | NA | RhB | $1.0 \times 10^{-4}$ [M] | 400 mg / 1 mL | [>90%] | | | MeOH | | | 8 |
| [25] | 2022 | Ads. | Carboxylated Cellulose | ChCl:OA: Water | 1:5 | Methylene Blue | 10 ppm | 100 mg / 10 mL | 111.039 | Langmuir | quasi-2$^{nd}$ order | Water/CAN (90/10) | ~95% | ~94% | 4 |
| [26] | 2023 | Ads. | FeO-Chitosan | ChCl:U | 1:2 | Acid Blue 80 | 100 ppm | 150 mg / 5 mL | 61.64 | Langmuir | pseudo-2$^{nd}$ order | NaOH | 98–100% | | 5 |
| [27] | 2024 | Ads. | GO-cellulose | ChCl:MlnA | 1:1 | Methylene Blue | 200-300 ppm | 500 mg / 1000 mL | 611.44 | Langmuir | pseudo-2$^{nd}$ order | | | | |
| [28] | 2024 | Ads. | ZnO | ChCl:LacA | 1:1 | Congo Red | 1 mM | 5 mg / 50 mL | [84%] | | pseudo-1$^{st}$ order | | | | |
| [28] | 2024 | Ads. | ZnO | ChCl:LacA | 1:1 | Crystal Violet | 1 mM | 5 mg / 50 mL | [99%] | | pseudo-1$^{st}$ order | | | | |

* Reported $Q_{max}$ value
^ Reported Qe value

**Table 4**
Applications of DES-based adsorbents within the field of water & wastewater treatment, specifically for: Heavy metal adsorption. (chronological order).

| **Application** | | **Water & Wastewater treatment – Heavy metals** | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Article info.** | | **Process** | **Material** | **DES** | | **Feed properties** | | | **Performance** | **Model** | | **Regeneration** | | | |
| **Ref** | **Year** | **Process** | **Composite** | **HBA:HBD** | **Ratio** | **Target** | **Conc.ppm [specified]** | **Adsorbent dose** | **Performancemg.g$^{-1}$ [specified]** | **Isotherm** | **Kinetic** | **Regenerant** | **R %** | **R %(last cycle)** | **Cycles** |
| [29] | 2016 | Ads. | CNT | ChCl:TEG | 1:3 | Pb (II) | 5 ppm | 10 mg / (Not reported) | 288.4* | Langmuir | pseudo-2$^{nd}$ order | | | | |
| [30] | 2016 | Ads. | CNT | MTPPB:Gly | 1:3 | $As^{3+}$ | 5 ppm | 10 mg / 50 mL | 23.4* | Langmuir Freundlich | pseudo-2$^{nd}$ order | | | | |
| [30] | 2016 | Ads. | CNT | BTPCl:Gly | 1:16 | $As^{3+}$ | 5 ppm | 10 mg / 50 mL | 14.23* | Langmuir Freundlich | pseudo-2$^{nd}$ order | | | | |
| [31] | 2017 | Ads. | CNT | DEthACl:Gly | 1:2 | $As^{3+}$ | 5 ppm | 10 mg / 50 mL | 17.085* | Langmuir | pseudo-2$^{nd}$ order | | | | |
| [32] | 2017 | Ads. | CNT | ATPPBr:Gly | 1:14 | $Hg^{2+}$ | 5 ppm | 5 mg / 50 mL | 186.97* | Freundlich | pseudo-2$^{nd}$ order | DI (pH 1.3) | 99% | 70% | 3 |
| [33] | 2017 | Ads. | CNT | TBABr:Gly | 1:4 | $Hg^{2+}$ | 5 ppm | 6 mg/ 50 mL | 177.76* | Langmuir | pseudo-2$^{nd}$ order | DI (pH 1.3) | | 96 mg/g | 5 |
| [34] | 2018 | SPE | Fe3O4-GO | ChCl:ItA: MPrA | 2:1:1 | $Hg^{2+}$ | 30 ppm | 10 mg / 50 mL | 215.1*[99.91%] | Langmuir | | EDTA 0.05M | 94.94% | 90.23% | 7 |
| [35] | 2019 | Ads. | Chondroitin sulfate | ChCl:EG | 1:2 | Pb (II) | 4 - 100 ppm | 10 mg / 5 mL | 55* | Langmuir | pseudo-2$^{nd}$ order | 0.01 M HNO3 | | | |
| [35] | 2019 | Ads. | Chondroitin sulfate | ChCl:EG | 1:2 | Cd (II) | 4 - 100 ppm | 10 mg / 5 mL | 51* | Langmuir | pseudo-2$^{nd}$ order | 0.01 M $HNO_3$ | | | |
| [35] | 2019 | Ads. | Fucoidan | ChCl:EG | 1:2 | Pb (II) | 4 - 100 ppm | 10 mg / 5 mL | 79* | Langmuir | pseudo-2$^{nd}$ order | 0.01 M $HNO_3$ | | | |
| [35] | 2019 | Ads. | Fucoidan | ChCl:EG | 1:2 | Cd (II) | 4 - 100 ppm | 10 mg / 5 mL | 40* | Langmuir | pseudo-2$^{nd}$ order | 0.01 M $HNO_3$ | | | |
| [14] | 2020 | Ads. | $Fe_3O_4$-GO | BTBACl:U | 1:2 | Pb (II) | 25 ppm | 10 mg / 10 mL | 120.3 | Langmuir (Lead (II)) | | | | | |
| [36] | 2021 | Ads. | N,S-codoped carbon | Fru:U:Thio U | 6:1:3 | Cr (VI) | 50-700 ppm | 1 [g/L] | 564.7 | Freundlich | pseudo-2$^{nd}$ order | | | loss 11.8% | 4 |
| [37] | 2021 | Ads. | CNT | TBABr:Gly | 1:4 | $Ni^{2+}$ | 50 ppm | 10 mg / 50 mL | 110.2-115.8* | Sips (25 - 55 C) | pseudo-2$^{nd}$ order | 0.1M NaOH | | | 7 |
| [38] | 2021 | Ads. | Biomass | ChCl:p-tsOH | 1:1 | Cr (VI) | 325 ppm | 50 mg / 25 mL | 270.3 | Langmuir | pseudo-2$^{nd}$ order | NaOH | 0.9367 | 40.01 | 4 |

(*continued on next page*)

**Table 4** (*continued*)

| Application | | Water & Wastewater treatment – Heavy metals | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Article info. | | Process | Material | DES | | Feed properties | | | Performance | Model | | Regeneration | | | |
| Ref | Year | Process | Composite | HBA:HBD | Ratio | Target | Conc.ppm [specified] | Adsorbent dose | Performancemg.g$^{-1}$ [specified] | Isotherm | Kinetic | Regenerant | R % | R %(last cycle) | Cycles |
| [39] | 2022 | Ads. | Biochar | FeCl3:U | 2:1 | Cr (VI) | 50 ppm | 0.025 g/ 50 mL | 133.33 | Langmuir | pseudo-2$^{nd}$ order | NaOH | | 51% | 5 |
| [40] | 2022 | Ads. | COF | ChCl: OA.2H2O | 1:1 | La$^{+3}$ Other REEs | 125 ppm | 5 mg / 5 mL | 84.67* | Langmuir | pseudo-2$^{nd}$ order | N/A | N/A | N/A | non-recyclable |
| [41] | 2022 | Ads. | LTO | ChCl:U | 1:2 | $Pb^{2+}$ | 100 ppm | 50 mg / mL | [96%] | Freundlich | pseudo-2$^{nd}$ order | 0.1M $HNO_3$ | 90% | | |
| [41] | 2022 | Ads. | LTO | ChCl:U | 1:2 | $As^{3+}$ | 100 ppm | 50 mg / mL | [74%] | Freundlich | pseudo-2$^{nd}$ order | 0.1M $HNO_3$ | 69% | | |
| [41] | 2022 | Ads. | LTO | ChCl:U | 1:2 | Cr | 100 ppm | 50 mg / mL | [71%] | Freundlich | pseudo-2$^{nd}$ order | 0.1M $HNO_3$ | 67% | | |
| [42] | 2022 | Ads. | Peanut shell | ChCl:U | 1:2 | Cr (VI) | 5-50 ppm | 4 [g/L] | 5.36 | Langmuir | pseudo-2$^{nd}$ order | NaOH | 8.77% | | |
| [43] | 2022 | Ads. | Chalcogenidometalates | TEACl:Thiourea | 1:2 | $Sr^{2+}$ | 1000 [mL/g] | 20 mg / 20 mL | 104.17 ± 23.53 | Langmuir–Freundlich | pseudo-2$^{nd}$ order | 2M KCl | | | |
| [44] | 2024 | Ads. | CNT | ChCl:Fru:W | 5:2:5 | $Pb^{2+}$ | | | 23.4* | Langmuir | | | | | |
| [44] | 2024 | Ads. | CNT | ChCl:Suc:W | 4:1:4 | $Pb^{2+}$ | | | 74.1* | Langmuir | | | | | |

ˆReported Qe value

* Reported Qmax value

**Table 5**
Applications of DES-based adsorbents within the field of water & wastewater treatment, specifically for: Pharmaceuticals adsorption. (chronological order).

| Application | | Water & Wastewater treatment – Pharmaceuticals (Ph) | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Article info. | | Process | Material | DES | | Feed properties | | | Performance | Model | | Regeneration | | | |
| Ref | Year | Process | Composite | HBA: HBD | Ratio | Target | Conc.ppm [specified] | Adsorbent dose | Performancemg. $g^{-1}$ [specified] | Isotherm | Kinetic | Regenerant | R % | R %(last cycle) | Cycles |
| [45] | 2018 | Ads. | Cellulose nanofibrils (anionic) | LiCl:U | 1:5 | Salbutamol | 200 ppm | 75[ mg / L] | 196 | Freundlich | | | | | |
| [5] | 2019 | Ads. | Biochar–clay | HTMABr: Gly | 2:1 | Acetaminophen | 20 - 100 ppm | [0.5 g in column] | 118.235* | Freundlich | pseudo-2nd order | | | | |
| [5] | 2019 | Ads. | Biochar–clay | HTMABr: Gly | 2:1 | Ciprofloxacin | 20 - 100 ppm | [0.5 g in column] | 140.273* | Langmuir | pseudo-2nd order | | | | |
| [46] | 2019 | Ads. | MIR | ChCl:EG | 1:2 | Ofloxacin | 100 ppm | 10 mg / 5 mL | 32.92* | Langmuir | pseudo-2nd order | | | | |
| [47] | 2020 | Ads. | MIP | ChCl: MAA | 1:2 | Levofloxacin | 50 ppm | 30 mg /1 mL | [98.3%] | | | | | | |
| [48] | 2020 | Ads. | $Fe_3O_4$-MOF | CTEABr: LacA | 1:2 | Ofloxacin | 1000 ppm | 5 mg / 1 mL | 50 | Langmuir | pseudo-2nd order | PBS pH=2 | | no decrease | 6 |
| [48] | 2020 | Ads. | $Fe_3O_4$-MOF | CTEABr: LacA | 1:2 | Mefenamic acid | 1000 ppm | 5 mg / 1 mL | 52.91 | Langmuir | pseudo-2nd order | isopropanol | | no decrease | 6 |
| [49] | 2021 | Ads. | $Fe_3O_4$-MIP | ChCl: BuIM | 1:1 | Naproxen | 40 ppm | 30 mg /10 mL | [96.3%] | Freundlich | pseudo-2nd order | ACN | >90.0% | 89.7%. | 6 |
| [50] | 2021 | Ads. | Keratin | ChCl:EG | 1:2 | Norfloxacin | 25 ppm | 2 [g/L] | 79.36* | Langmuir | | Acetone | >80% | | 7 |
| [51] | 2021 | Ads. | $Fe_3O_4$ | ChCl: BuIM | 1:1 | Diclofenac | 5-100 ppm | 10 mg / 10 mL | 58 [94.2−97.1%] | Freundlich and Halsey > Temkin | pseudo-2nd order | ACN | 90% | | 5 |
| [52] | 2021 | Ads. | Rice Husk Ash | ChCl: GlyA | 1:3 | Ofloxacin | 25 ppm | 400 mg / 100 mL | 25.097* | Langmuir, Temkin, and RP | pseudo-2nd order | Thermal desorption | ~70% | | 3 |
| [53] | 2022 | Ads. | HsGY | ChCl:m-Cresol | 1:4 | Chrysophanol acid | 160,000 ppm | 1 mg / 10 mL | 28.5 | | | | | | |
| [53] | 2022 | Ads. | HsGY | ChCl:p-Cresol | 1:2 | Chrysophanol acid | 160,000 ppm | 1 mg / 10 mL | 29.2 | | | | | | |
| [54] | 2022 | In-situ SPE | Chloromethyl polystyrene resin | DMEA: Arbidol | | Arbidol | 300 ppm | 100 m g/ 50mL | 12610% | Freundlich | pseudo-2nd order | anhydrous EthOH | 95% | 95% | 12 |
| [55] | 2022 | MSPE | $Fe_3O_4$-biochar | ChCl:Gly | 1:2 | Methcathinone | 0.5-1 ppm | 10 mg / 2 mL | [93.26-95.85%] | Freundlich | pseudo-2nd order | MeOH-FA (99:1, V/V) | 94.14% | 86.92% | 5 |
| [56] | 2022 | LPME | $Fe_3O_4$-GO | ChCl:EG | 1:2 | Ofloxacin | 10 ppm | 200 μL /10mL | [>70.3%] | Freundlich and Halsey | pseudo-2nd order | MeOH: $NH_4$ (8:2) | 70.0 to 105.2 % | | |

(*continued on next page*)

**Table 5** (*continued*)

| Application | | Water & Wastewater treatment – Pharmaceuticals (Ph) | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Article info. | | Process | Material | DES | | Feed properties | | | Performance | Model | | Regeneration | | | |
| Ref | Year | Process | Composite | HBA: HBD | Ratio | Target | Conc.ppm [specified] | Adsorbent dose | Performancemg. $g^{-1}$ [specified] | Isotherm | Kinetic | Regenerant | R % | R %(last cycle) | Cycles |
| [56] | 2022 | LPME | $Fe_3O_4$-GO | ChCl:EG | 1:2 | Sparfloxacin | 10 ppm | 200 µL /10mL | [>70.3%] | Freundlich and Halsey | pseudo-2nd order | MeOH: $NH_4$ (8:2) | 70.3 to 121.5 %. | | |
| [57] | 2022 | Ads. | Calix[4] pyrrole | L-(+)-TarA: dmU | 3:7 | Paracetamol | 30 ppm | 0.32 [g/L] | 479.3* | Freundlich | pseudo-2nd order | 0.5M HCl | 0.9312 | 0.5545 | 5 |
| [58] | 2023 | Ads. | Chitosan-MI (hydrogel) | ChCl:EG | 1:4 | Salicylic acid | 165 ppm | 1.2 [g/L] | 106.5 | Freundlich | pseudo-2nd order | HAc/MeOH (1/ 9, v/v) and DI water | 93.15% | 89.82% | 5 |
| [59] | 2024 | Ads. | MOF | ChCl: MAA | 1:2 | Diclofenac | 100 ppm | 10 mg / 1 mL | 19.39 | Freundlich | pseudo-1st and 2nd order | | | | |
| [60] | 2024 | Ads. | Lignocellulose | TEAOH: dmU | 1:2 | TetracyclineLevofloxacinNorfloxacin | 20 ppm | 100 mg / 100 mL | [~99%] | | | | | | |
| [61] | 2024 | MSPE | Fe3O4-Chitosan | ChCl:Fru | 1:1 | Diclofenac | 600 ppm | 5 mg/ 5 mL | 180.2 | Langmuir | pseudo-2nd order | 20% Acetic acid | ~99% | ~90% | 6 |

^Reported Qe value

* Reported Qmax value

**Table 6**
Applications of DES-based adsorbents within the field of water & wastewater treatment, specifically for: Phenol adsorption as well as other applications. (chronological order).

| **Application** | | **Water & Wastewater treatment – Phenols (P)** | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Article info.** | | **Process** | **Material** | **DES** | | **Feed properties** | | | **Performance** | **Model** | | **Regeneration** | | | |
| **Ref** | **Year** | **Process** | **Composite** | **HBA:HBD** | **Ratio** | **Target** | **Conc.ppm [specified]** | **Adsorbent dose** | **Performancemg.g$^{-1}$ [specified]** | **Isotherm** | **Kinetic** | **Regenerant** | **R %** | **R % (last cycle)** | **Cycles** |
| [62] | 2018 | Ads. | CNT | ChCl:EG | 1:2 | 2,4-dichlorophenol | 10 ppm | 10 mg / 50mL | 390.53 | Langmuir | pseudo-2$^{nd}$ order | / | / | / | / |
| [63] | 2019 | Ads. | CNT | (BS-12):1,3-PD:Gly | 1:1:1 | 4-bromophenol | 1.25 - 30 ppm | 2 [μg/mL] | 155.82<br>263.16 | Freundlich | pseudo-2$^{nd}$ order | / | / | / | / |
| [63] | 2019 | Ads. | CNT | (BS-12):1,3-PD:Gly | 1:1:1 | 2,4-dibromophenol | 1.25 - 30 ppm | 2 [μg/mL] | 267.42, 322.58^ | Freundlich | pseudo-2$^{nd}$ order | | | | |
| [63] | 2019 | Ads. | CNT | (BS-12):1,3-PD:Gly | 1:1:1 | 2,6-dibromophenol | 1.25 - 30 ppm | 2 [μg/mL] | 761.19, 909.09^ | Freundlich | pseudo-2$^{nd}$ order | | | | |
| [63] | 2019 | Ads. | CNT | (BS-12):1,3-PD:Gly | 1:1:1 | 2,4,6-tribromophenol | 1.25 - 30 ppm | 2 [μg/mL] | 1719.68, 1666.67^ | Freundlich | pseudo-2$^{nd}$ order | | | | |
| [10] | 2019 | Ads. | CNT | BTMACl:Gly | 1:2 | Phenol | 50 ppm | 30 mg / 30 mL | 274.51<br>298.54 | Freundlich | pseudo 1$^{st}$ order | / | / | / | / |
| [64] | 2020 | MSPE | $Fe_3O_4$-MIP-GO | CTEABr:2,4,6-TCP | 1:1 | Cholorphenol | 100 ppm | 20 mg /50 mL | 80.82 | / | Lagergren rate equation | / | / | / | 10 |
| [65] | 2024 | MSPE | $Fe_3O_4$-MIP-COF | ChCl:HFIP | 1:4 | bisphenol AF | 1-20 ppm | 2 mg / 2 mL | 243.1 | Langmuir | pseudo-2$^{nd}$ order | | | | |
| **Application** | | **Water & Wastewater treatment – Other (O)** | | | | | | | | | | | | | |
| [66] | 2020 | SPE | GO | ChCl:EG | 1:3 | Polycyclic aromatic hydrocarbons (PAHs) | 5 ppm | [1mgmonolith] | [90.8%] | / | / | ACN | / | / | / |
| [67] | 2021 | Ads. | MIP | ChCl:1,4-BD | 1:2 | Thidiazuron | 2-100 ppm | 2 mg / 2 mL | Qm 36.55 | Langmuir | pseudo-2$^{nd}$ order | 50% ACN–water | ~100% | ~83% | 26 |
| [67] | 2021 | Ads. | MIP | ChCl:1,4-BD | 1:2 | Forchlorfenuron | 2-100 ppm | 2 mg / 2 mL | Qm 62.34 | Langmuir | pseudo-2$^{nd}$ order | 50% ACN–water | ~100% | ~80% | 26 |
| [68] | 2021 | Ads. | COF | ChCl:HFP | 1:2 | Flavonoids:<br>Rutin<br>Myricetin<br>Quercetin<br>Luteolin<br>Morin<br>Quercetagetin<br>Apigenin<br>Kaempferol<br>Genistein<br>Soy isoflavone | 100 ppm | 2 mg / 2 mL | Flavonoids:<br>25.12<br>485.43<br>490.19<br>393.70<br>497.51<br>370.37<br>341.29<br>444.44<br>217.86<br>12.23 | Langmuir | pseudo-2$^{nd}$ order | ACN | >90% | >70% | 7 |
| [69] | 2022 | Ads. | lignocellulose nanofibers (CNF) | TEAOH :dmU | 1:2 | Polygalacturonic acid | 400 - 800 ppm | 0.5 mg / 1 mL | 1054 | Langmuir | pseudo-2$^{nd}$ order | / | / | / | / |
| [70] | 2022 | Ads. | β-cyclodextrin | ChCl:CitA | 1:2 | Atenolol | 1-10 ppm | 25 mg / 25 mL | [60.2- 66.5% ] | / | / | / | / | / | / |
| [55] | 2022 | MSPE | Fe3O4-biochar | ChCl:Gly | 1:2 | Methcathinone | 0.5-1 ppm | 10 mg / 2 mL | [93.26-95.85%] | Freundlich | pseudo-2$^{nd}$ order | MeOH:FA (99:1, V/V) | 0.9414 | 0.8692 | 5 |
| [71] | 2024 | Ads. | Poly(HMA) | ChCl:U | 1:2 | paracetamol | 50 ppm | 60 mg / 10 mL | 6.21 | Freundlich | | DI water | ~98% | ~40% | 4 |
| [71] | 2024 | Ads. | Poly(HMA) | ChCl:U | 1:2 | ciprofloxin | 50 ppm | 60 mg / 10 mL | 7.19 | Freundlich | | DI water | ~98% | ~32% | 4 |
| [71] | 2024 | Ads. | Poly(HMA) | ChCl:U | 1:2 | glyphosate | 50 ppm | 60 mg / 10 mL | 6.01 | Freundlich | | DI water | ~97.5% | ~80% | 4 |
| [71] | 2024 | Ads. | Poly(HMA) | ChCl:U | 1:2 | triton X-100 | 50 ppm | 60 mg / 10 mL | 6.99 | Freundlich | | DI water | ~98% | ~30-35% | 4 |

*Reported $Q_{max}$ value.
^ Reported $Q_e$ value.

A listing of commonly used HBAs and HBDs for preparation of DESs is shown in Fig. 1 and can be also found within the body of other specific reviews for both hydrophilic and hydrophobic DESs [32,36,37]. It should be noted that certain components might have the tendency to act as both an HBA or an HBD, such as the case with certain terpenoids or diols. This is predominately determined based on the types of interactions within the component itself as well as its interactions with its counterpart within the DES [33].

Given that the field is still under development and lacks a clear definition of DES, several reports attempt to introduce various novel DES combinations which might or might not be necessarily portray the same phenomenon exhibited by the earliest generation of DESs engineered previously. As more fundamental studies about the molecular interactions and phase behavior of DESs became available in the literature, a more exclusive description for DESs was referred. A deep eutectic solvent can be defined as a mixture of pure compounds for which the eutectic point temperature occurs below that of an ideal liquid mixture of these compounds [6,38]. Fig. 2 illustrates such melting point deviations from the ideal liquid behavior, of which the latter is usually described by classical thermodynamics with the following equation:

$$\ln(x_i\gamma_i) = \frac{\Delta H_{fus,i}}{R}\left(\frac{1}{T_{m,i}} - \frac{1}{T}\right) + \frac{\Delta C_{p,i}}{R}\left(\frac{T_{m,i}}{T} - ln\frac{T_{m,i}}{T} - 1\right) \quad (1)$$

where $x_i$ and $\gamma_i$ are the liquid mole fraction and activity coefficient for a compound $i$, respectively; $R$ is the gas constant, $\Delta H_{fus,i}$ is the fusion enthalpy of the pure compound, $T_{m,i}$ is the melting temperature, and $\Delta C_{p,i}$ is the difference between the molar heat capacity of the compound $i$ in the liquid and solid phases. In most cases, the last term of the equation can be neglected, especially when the melting temperature is close to the equilibrium temperature. Accordingly, the expression can be reduced to:

$$\ln(x_i\gamma_i) = \frac{\Delta H_{fus,i}}{R}\left(\frac{1}{T_{m,i}} - \frac{1}{T}\right) \quad (2)$$

Moreover, and with the aim of establishing a sound understanding of the field, the identification of the solid–liquid phase behavior over a representative range of compositions for any studied eutectic mixture is considered vital. This will not only help analyze the deviations from the ideal liquid mixture (if any), but it will also aid in identifying the exact eutectic point temperature of a DES rather than testing an arbitrary molar ratio of the starting compounds (e.g., 1:2 HBA:HBD), which is not necessarily appropriate ratio for certain mixtures. One of the predictive tools used to better describe the nonideality of DES systems *ab initio* is via certain statistical mechanics calculations using the Conductor-like Screening Model for Real Solvents (COSMO-RS), which basically relies on the pairwise interactions between the molecules in a mixture to evaluate their resulting activity coefficients [33,39]. This predictive tool is useful in gaining insight into the tendency of certain combinations of molecules forming a DES (Fig. 3**(a, b)**) [40]. Nevertheless, such calculations are not always necessary to capture the true deviations from ideality in a DES system, which still require conventional empirical methods (i.e., DSC) to be accurately described. This usually happens when the DESs does not undergo any crystalline phase upon freezing but rather goes through glass transition, as shown in Fig. 3**(c-e)** [41,42]. One of the features in using COSMO-RS modeling for estimating phase behavior of eutectic mixtures is the use of molecular descriptors such as σ-profiles, a mathematical translation of the molecule's surface polarity distribution. Supported by their quantum chemical background, σ-profiles are considered holistic representation of molecules given their ability to depict a molecule as a collection of quantitatively charged surface segments, in addition to capturing subtle effects such as polarizability and asymmetric electron densities. Moreover, these molecular descriptors can be also used to describe the affinity of molecules towards other HBDs, HBAs or non-polar molecules using the associated σ-potentials Fig. 3**(f)**. Further usage of σ-profiles as molecular descriptors extends beyond the theoretical/experimental data spectrum, as it can be effectively used for modelling different physicochemical properties [43–45], performance characteristics [46] and solvent design of novel solvent systems [39,46], especially when equipped with machine-learning approaches [47].

There is an emphasis on the importance of studying the thermal behavior of eutectic mixtures and its relevance to DES preparation [4,6,22]. Nevertheless, the number of articles concerned with the application of DESs surpasses those devoted to understanding their basic nature and behavior. This departs between understanding the DESs' definitive characteristics and their applications within other fields via different routes (processes), leading to misusing this class of neoteric solvents to their finest potential. To clarify the definition of a DES and its difference from other solvents, a summary of what DESs "are/aren't" is listed in Table 2.

The problem of using DESs in other applications without *a priori* reasoning could be resolved by delineating the fundamentals of this class of solvents, as we tried to summarize above. It is not expected to have everyone become an expert on DESs before using them in their respective field(s), but the proper practices for testing DESs should be at least outlined. Additionally, the integration of DESs with other technologies provides new grounds for testing and analysis in material science. This calls for collaborative research initiatives among experts from the DESs community and researchers from other fields of potential interest, whereby the former can help develop, validate, and characterize adequate DESs for the latter group to optimize based on their intended application/objective. Indeed, this is the status in a majority of scientific research areas; however, it needs to be stressed in the case of neoteric solvents as, again, the competency of these solvents is in their versatile tunability to match a specific target, thereby reaching even the most subtle niches in scientific research.

## 4. Applications of DES-based adsorbents

The emerging technology that combines unique properties of DESs with an efficient adsorbent is still not well-investigated, regardless of the increasing efforts in recent years to explore the performance of such a promising class of adsorbents. Due to their designability, DES-based functional adsorbents have the potential to be used in a variety of applications. The various functional groups

introduced by different HBAs and HBDs within the DES not only broaden the type of adsorbent and scope of application but can also enhance its stability. Moreover, the hydrophobic/hydrophilic nature of a certain DES is of paramount importance in endowing the final adsorbent, its chemical properties, and its behavior in surrounding media.

DES-based adsorbents have been extensively applied in different fields such as water and wastewater treatment, protein isolation, extraction from biomass, extraction from food and medical applications, and other applications. Fig. 4 displays the percentages of DES-based adsorbents utilized in the abovementioned fields based on the data analyzed in this review. It is evident that DES-based adsorbents find tremendous potential in the field of water and wastewater treatment with more than half of the studies (55.1 %) highlighting their application for the removal of different contaminants from water. This category encompasses within it a variety of applications, with the majority of studies focusing on the removal of dyes (21.6 %), heavy metals (13.1 %), pharmaceuticals (11 %), phenols (4.2 %), and other applications (5.1 %). On the other hand, 12.7 % of all the papers under study focused on using DES-based adsorbents for the isolation of proteins such as bovine serum albumin (BSA), bovine Hemoglobin (BHb), Ovalbumin (OVA), Transferrin and lysozyme. Another 12.7 % of the papers investigated the extraction of certain compounds from food substances for detection or separation purposes, while 7.6 % studied the same from biomass materials. DES-ADS have been also explored in medical and pharmaceutical applications (5.3 %). All details for the studies within the context of utilizing DES-ADS are tabulated in a categorized and pivoted spreadsheet in the **Supplementary Information** Document (in the "*Categorical*" tab). Moreover, in the following sections and subsections, further details will be summarized and discussed within relative context, including a tabulation of relevant information.

### *4.1. Water and wastewater treatment applications*

In the field of water and wastewater treatment, there is a predominant trend towards using DES-based adsorbents for the removal of organics, inorganics, and even emerging contaminants, with nearly a third of the studies within this category (i.e., 21.6 % of all studies) targeting the removal of toxic textile dyes from water. These studies confirmed the promising potential of DES-based adsorbents in the selective and efficient removal of several types of cationic and anionic dyes (Table 3). Furthermore, it can be noted that almost one-fourth of the studies within the water/wastewater treatment category (i.e., 13.1 % of all studies) investigated the application of such DES-functionalized adsorbents for heavy metals removal (Table 4), with a special focus on lead, arsenic, mercury, chromium, and nickel. Additionally, many pharmaceutical products such as levofloxacin, ofloxacin, mefenamic acid, naproxen, fluoroquinolone antibiotics, diclofenac, and salbutamol were reported to be successfully removed by DES-ADS as shown in Table 5. Other studies also targeted the removal of phenols (bromophenols and chlorophenols), polycyclic aromatic hydrocarbons (PAHs), thidiazuron, and flavonoids (Table 6).

#### *4.1.1. Dyes*

Wastewater streams containing toxic dyes pose severe public health concern and an environmental challenge. With adsorption being one of the mature technologies in this field, different DES-ADS were evaluated for the removal of cationic and anionic dyes from aqueous streams, including congo red (CR), methylene blue (MB), methyl orange (MO), malachite green (MG), rhodamine b (RhB), sunset yellow (SY), indigo carmine (IC), safranine T (ST), chrome azurol S (AS), eosin Y (EY), and others.

One of the trends observed in the literature is that all the DES-based adsorbents for the removal of CR were based on some metal oxides as a base material with the role of the DES in the synthesis of the precursors. For instance, Ge *et al.* [51] prepared a CoFe layered double hydroxide (LDH) in DES, which in turn was used for the preparation of spinal CoFe oxides. The CoFe oxides were used for the fast removal of CR of up to 305 $mg.g^{-1}$. Similarly, MgO microcubes were prepared from a precursor DES ($MgCl_2{\cdot}6H_2O$:Urea 1:2) for the removal of different anionic dyes, including CR, Amaranth, and IC, with adsorption capacities up to 666.7, 43.74 and 54.32 $mg.g^{-1}$, respectively [52]. A different study reported the synthesis of $Ni_2CO_3(OH)_2/SiO_2$ composites with a strong ability for CR adsorption. The maximum adsorption capacity of CR reached 2637 $mg.g^{-1}$ at neutral pH, primarily due to the high surface area of the new composite as well as to the strong electrostatic interactions, coordination effect, and hydrogen bonding [53].

For the removal of MB from aqueous solutions, DES-ADS from various starting components were used, mostly prepared from ChCl-based DESs. For instance, a ChCl:EG 1:2 DES was used mainly as a reaction medium – replacing conventional hazardous organic solvents – to prepare three different materials, namely, $MnO_2$, $NiSO_4$, and halogenated dibenzylidene-sorbitol (xDBS) eutectogels. The MB adsorption capacity of $MnO_2$ reached 293 $mg.g^{-1}$ with notable recyclability of up to 10 cycles without severe reduction in performance [54]. As for $NiSO_4$, different morphologies were synthesized based on the concentration of the reactants, with the highest maximum adsorption capacity of 24.38 $mg.g^{-1}$ for nano spherical $NiSO_4$ [55]. Here, the DES played dual functionalities as both a reaction medium and a template in the preparation of $NiSO_4$. Lastly, the xDBS eutectogel achieved high removal efficiency > 90 % for different dyes including MB, CV and RhB, with the ability to use the regenerated eutectogel for up to six cycles without significant loss in performance [56]. Similarly, a ChCl:OA 1:5 DES (+ 10 wt% DI water) was used to synthesize carboxylated cellulose with MB $q_{max}$ of 111.039 $mg.g^{-1}$. Moreover, a ChCl:U 1:2 DES was used to functionalize magnetic-graphene oxide (GO) adsorbent and, with a high adsorbent dose (1 mg/mL), the functionalized $Fe_3O_4$-GO adsorbent achieved complete recovery of MB from a 25 ppm MB stock solution [57]. The same DES-ADS was also used for lead removal (*section 4.1.2*). A similar functionalization of magnetic chitosan beads using ChCl:U 1:2 was also reported for MB removal, yielding an adsorption capacity of 61.64 $mg.g^{-1}$. Other DES-ADS with high potential for MB removals, such as Polyacrylamide-ϒ-$Fe_2O_3$, COF, and N-doped porous carbon, were also tested, having a $q_{max}$ of 359.71, 407, and 439.9 mg. $g^{-1}$, respectively [58–60].

The use of DES-ADS to remove other cationic dyes, such as MG and CV, was also investigated. For instance, a magnetic MOF (HKUST) was functionalized with a certain polymeric-based DES (APTMACl:Sorbitol 1:1); The modified HKUST MOF achieved MG and CV adsorption capacity of 966.93 and 788.90 $mg.g^{-1}$, respectively [61]. In another study, a TBACl:MAA 1:2 DES was used to modify

**Table 7**
Applications of DES-based adsorbents within the field of protein isolation and extraction. (chronological order).

| Application | | Protein isolation | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Article info. | | Process | Material | DES | | Feed properties | | | Performance | Model | | Regeneration | | | |
| Ref | Year | Process | Composite | HBA:HBD | Ratio | Target | Conc.ppm [specified] | Adsorbent dose | Performancemg.g$^{-1}$ [specified] | Isotherm | Kinetic | Regenerant | R % | R %(last cycle) | Cycles |
| [72] | 2016 | MSPE | Fe3O4-GO | ChCl:Gly | 1:1 | BSA | 1000 ppm | 10 mg / 1 mL | ~44.59 | | | Na2HPO4 0.1M in NaCl 1M | 98.73% | ~33-36 | 3 |
| [72] | 2016 | MSPE | Fe3O4-GO | ChCl:EG | 1:2 | BSA | 1000 ppm | 10 mg / 1 mL | ~44 | | | | | | |
| [72] | 2016 | MSPE | Fe3O4-GO | ChCl:Glu | 2:1 | BSA | 1000 ppm | 10 mg / 1 mL | ~37.5 | | | | | | |
| [72] | 2016 | MSPE | Fe3O4-GO | ChCl:Sor | 1:1 | BSA | 1000 ppm | 10 mg / 1 mL | ~41 | | | | | | |
| [73] | 2016 | Ads. | Fe3O4-MIP | ChCl:MAA | 1:2 | BHb | 1000 ppm | 5 mg / 1 mL | 175.44* | Langmuir | | SDS-HAc (2% W/V: 2% W/V) | | 7.93% or less. | 3 |
| [74] | 2018 | Ads. | Fe3O4-MIP | ChCl:AA | 1:2 | Transferrin | 150 ppm | 4 mg / 1 mL | 37.5* | Langmuir | | SDS-HAc (2% w/v:2% w/v) | | 23 | 6 |
| [75] | 2018 | MSPE | Fe3O4-MIP | ATECl:Gly | 1:1 | Lysozyme | 1200 ppm | 5 mg / 1 mL | 108 | Langmuir | | SDS-HAc (2% w/v:2% v/v) | | | 4 |
| [76] | 2019 | Ads. | Fe3O4-MIP | APTMACl: U | 1:2 | BHb | 1300 ppm | 5 mg / 1 mL | 172.48* | Langmuir | | SDS-HAc (2% w/v:2% v/v) | | 146.69 | 3 |
| [77] | 2020 | Ads. | $Fe_3O_4$-MIP-$SiO_2$ | BTBACl: OHMA | 1:2 | BHb | 1 [g/mL] | 5 mg / 1 mL | 229.54 | Freundlich | pseudo-2$^{nd}$ order | SDS-HAc (2% w/v:2% v/v) | 223.11 mg/g (after 3 cycles) | 271.71 mg/g | 6 |
| [77] | 2020 | Ads. | $Fe_3O_4$-MIP | BTMACl: AcrTMA | 1:1 | BHb | 1 [g/mL] | 5 mg / 1 mL | 229.54 | Freundlich | pseudo-2$^{nd}$ order | | | | |
| [78] | 2020 | SPE | $TiO_2$ nanotubes | BTBACl: MAA | 1:2 | BSA | 2000 ppm | [monolithic column] | 40 [ug/cm] | | | | 80% | | 24 |
| [78] | 2020 | SPE | $TiO_2$ nanotubes | BTMACl: MAA | 1:2 | OVA | 2000 ppm | [monolithic column] | [92.7 %] | | | | 80% | | 24 |
| [79] | 2021 | Ads. | $Fe_3O_4$-β-cyclodextrin | BTMACl: MAA | 1:2 | OVA | 2000 ppm | 5 mg / 1 mL | 151.62 | | | Buffer solution pH = 2 | / | 108 mg/g | 6 |
| [80] | 2021 | Ads. | $Fe_3O_4$-MIP-β-cyclodextrin | MATACl: ItA | 2:1 | BHb | 0.4– 1.6 [mg/g] | 5 mg / 1 mL | 195.94<br>192.3* | Langmuir | pseudo 1$^{st}$ order | SDS (2% W/V)-HAc (2% V/V) | | 71.63% | 5 |
| [80] | 2021 | Ads. | $Fe_3O_4$-MIP-β-cyclodextrin | ATMACl: EG | 1:1 | BHb | 0.4– 1.6 [mg/g] | 5 mg / 1 mL | 195.94<br>192.3* | Langmuir | pseudo 1$^{st}$ order | | | | |
| [81] | 2021 | Ads. | MIP-MOF | ChCl:MAA | 1:2 | BHb | 0–0.2 [mg/mL] | 5 mg / 1 mL | 151.28 | Langmuir | | SDS (2% W/V)-HAc (2% V/V) | | 118.53 mg/g | 5 |
| [82] | 2022 | SPE | MIP | ChCl:MAA | 1:2 | lysine acetylation peptides | 10 ppm | Monolith | 12.08* | Langmuir | Scatchard high affinity | HAC/ACN/ H2O (5/5/90, v/v) | 0.932 | 89.2 | 5 |
| [83] | 2022 | Ads. | MIP-molecular sieve (SBA15) | ChCl:EG | 1:16.725 | Glularylated peptide | 10-80 ppm | 5mg/1mL | 8.35* | Langmuir | | water-HAc (9/1, v/v) | 0.871 | | 5 |
| [84] | 2022 | SPE | MIP | ChCl:AA | 1:2 | benzoylation peptides | 5 [mM] | Monoloith | 19* | Langmuir | | water: HAc (7:3, v/v) | 93.00% | 86.30% | 5 |
| [85] | 2022 | Ads. | Monomer-Monolith | ChCl:MAA | 1:2 | BSA | 2000 ppm | Monolithic column | [95.5%] | | | NaCl | 95.50% | 85% | 30 |
| [85] | 2022 | Ads. | Monomer-Monolith | ChCl:MAA | 1:3 | OVA | 2000 ppm | Monolithic column | [29.4%] | | | NaCl | | | |
| [85] | 2022 | Ads. | Monomer-Monolith | ChCl:MAA | 1:4 | Cyt c | 2000 ppm | Monolithic column | [98.2%] | | | NaCl | | | |
| [85] | 2022 | Ads. | Monomer-Monolith | ChCl:MAA | 1:5 | Avidin | 2000 ppm | Monolithic column | [93.7%] | | | NaCl | | | |
| [85] | 2022 | Ads. | Monomer-Monolith | ChCl:MAA | 1:6 | Horseradish peroxidase (HRP) | 2000 ppm | Monolithic column | [0.61%] | | | NaCl | | | |

^Reported $Q_e$ value
* Reported $Q_{max}$ value

**Table 8**
Applications of DES-based adsorbents within the field of extraction and/or detection of certain substances in food. (chronological order).

| Application | | Extraction from Food | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Article info. | | Process | Material | DES | | Feed properties | | | Performance | Model | | Regeneration | | | |
| Ref | Year | Process | Composite | HBA:HBD | Ratio | Target | Conc.ppm [specified] | Adsorbent dose | Performancemg. $g^{-1}$ [specified] | Isotherm | Kinetic | Regenerant | R % | R % (last cycle) | Cycles |
| [86] | 2016 | Ads. / SPE | Silica-tris (indolyl) methane | ChCl:U | 1:2 | Benzoic acid | 60 ppm | 20 mg / 1 mL | 0.418 | | | KCl 0.2M in 85% MeOH | | 82 % | 14 |
| [86] | | | | | | p-anisic acid | 60 ppm | 20 mg / 1 mL | 0.33 | | | | | 82 % | 14 |
| [86] | | | | | | Salicylic acid | 60 ppm | 20 mg / 1 mL | 0.3332 | | | | | >100% | 14 |
| [86] | | | | | | Cinnamic acid | 60 ppm | 20 mg / 1 mL | 0.4073 | | | | | >100% | 14 |
| [87] | 2020 | SPME | MIP-MOF | BTBACl:Gly | 2:1 | Phthalate esters | 10 ppm | [3cmhollowfibers] | [95.5%] | | | n-hexane | | | |
| [88] | 2021 | Ads. | $Fe_3O_4$-MIP-zein | ChCl:CafA:FA | 1:6:3 | aspartame | 100 ppm | 10 mg /5 mL | 13.18<br>14.95* | Langmuir | pseudo-2nd order | | | | |
| [89] | 2021 | Ads. | $Fe_3O_4$-GO | TMACl:U | 1:1 (mass) | Indigotin Blue | 0.2 ppm | 10 mg / 50 mL | 312.5* | Langmuir | pseudo-2nd order | EthOH | 98% | | not reusable durability (6 months) |
| [90] | 2022 | In-situ DLPME | CNT (nanofluid) | ChCl:EG | 1:2 | Triazole in Juice {in Tea}:<br>paclobutrazol<br>myclobutanil<br>epoxiconazole<br>flusilazole<br>penconazole<br>hexaconazole<br>diniconazole | 1000 ppm | 300 µl/100 mL | Triazole in Juice {in Tea}:<br>4.55 {3.24}<br>7.36 {5.55}<br>11.48 {11.43}<br>14.83 {9.14}<br>10.77 {6.05}<br>17.98 {6.37}<br>15.49 {11.63} | Freundlich | pseudo-2nd order | MeOH | 70.03-107.14 | | |
| [91] | 2022 | Ads. | $Fe_3O_4$-MIP | Bet:CitA:Gly | 1:1:1 | oxalic acid | 150 ppm | 5mg/ 5mL | 18.73 | Langmuir | pseudo-2nd order | EthOH-glacialHAc (9:1, v/v) | | | 5 |
| [92] | 2022 | SPE | GO-Poly (DES) | ChCl:MAA | 1:2 | indole-3-carbinol | 1000 ppm | 3 mg /0.5 mL | 83.8 [µg/mg] | | | Ammonia water-ACN | 84.3–96.4 % | | |
| [93] | 2022 | Ads. | $Fe_3O_4$-MIP-$SiO_2$ | ChCl:MAA | 1:2 | Vanillin | 50 ppm | 20mg/10mL | 6.31 | Freundlich | pseudo-2nd order | MeOH-HAc | reduced from 6.31 to 5.64 mg/g | | 3 |
| [94] | 2022 | MSPE | Fe-MIP | ChCl:CafA:FA | 3:1:1.5 | organophosphorus pesticides:<br>CP<br>Pec<br>PFF<br>AZE<br>FNT<br>PM<br>AZM | 220 ppm | 20 mg / 40 mL | CP 218.52<br>Pec 214.61<br>PFF 209.13<br>AZE 206.06<br>FNT 185.46<br>PM 177.15<br>AZM 151.02 | Freundlich | pseudo-2nd order | 10% HAc in MeOH | 80–117% | | 4 |
| [95] | 2022 | MSPE | $Fe_3O_4$-MIP-cellulose | ChCl:MalA | 1.5:1 | Bisphenol A | 5-140 ppm | 5 mg / 1mL | 14.1 | Langmuir | pseudo-2nd order | MeOH/HAc | 96.60% | 96.60% | 8 |

(*continued on next page*)

**Table 8** (*continued*)

| Application | | Extraction from Food | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Article info. | | Process | Material | DES | | Feed properties | | | Performance | Model | | Regeneration | | | |
| Ref | Year | Process | Composite | HBA:HBD | Ratio | Target | Conc.ppm [specified] | Adsorbent dose | Performancemg. $g^{-1}$ [specified] | Isotherm | Kinetic | Regenerant | R % | R % (last cycle) | Cycles |
| [95] | 2022 | MSPE | $Fe_3O_4$-MIP-cellulose | ChCl:MalA | 1.5:1 | Bisphenol F | 5-140 ppm | 5 mg / 1 mL | 13.7 | Langmuir | pseudo-2nd order | MeOH/HAc | 98.60% | 98.60% | 8 |
| [95] | 2022 | MSPE | $Fe_3O_4$-MIP-cellulose | ChCl:MalA | 1.5:1 | Bisphenol AF | 5-140 ppm | 5 mg / 1 mL | 15.7 | Langmuir | pseudo-2nd order | MeOH/HAc | 98.30% | 98.30% | 8 |
| [96] | 2022 | SPME | Calcium Alginate aerogel beads | ChCl:PEG | 1:1 | 5-hydroxymethylfurfural | 1 ppm | 30 mg / 3 mL | [79-102 %] | | | ACN | 78.5–102.2% | | |
| [97] | 2022 | DSPME | GO | P-ChCl:Naph | 1.5:2 | Pesticides | 1 [mg/kg] | 25 mg / 5 mL | [73-84%] | | | ACN | | | |
| [98] | 2022 | MSPE | $Fe_3O_4$ | Si-Surfactant: DodecA | 1:5 | Organophosphorus pesticides: Sulfotep Diazinon Chlorpyrifos Quinalphos Ethion Triazophos | 0.1-200 ppm | 25 mg / 10 mL | [R%] | | | hexane | 80–119 % | | 6 |
| [99] | 2023 | Ads. | MIR | ChCl:1,3-PD | 1:2 | Forchlorfenuron | 0.012-5.00 [μg/g] | 5 mg / 1 mL | 37.62 | | | water-ACN (1:1, v/v) | 89-101 % | | |
| [99] | 2023 | Ads. | MIR | ChCl:1,3-PD | 1:2 | Thidiazuron | 0.012-5.00 [μg/g] | 5 mg / 1 mL | 14.96 | | | water-ACN (1:1, v/v) | 89-101 % | | |
| [100] | 2024 | MSPE | MOF (UiO-66) | Diethanolamine: ActIM | 1:2 | Perfluoroalkyl | 2 [ug/kg] | 10 mg / 12 mL | [69-118%] | | | | | | |

ˆReported $Q_e$ value

* Reported $Q_{max}$ value

the surface of magnetic polydopamine material to enable its stable use for dye adsorption from water [25]. The surface modified $Fe_3O_4$-polydopamine had an adsorption capacity for MG of 277.78 mg.g$^{-1}$, and a controlled selectivity factor of 37.57 towards MG from an MG-SY solution. The di-selectivity of the adsorbent was enabled via the addition of $CaCl_2$ in the solution, with a recyclability of up to six cycles without change in the adsorption capacity. The adsorption of MG was also tested using a chitosan adsorbent modified via ChCl:U 1:2 DES [62]. The chitosan was functionalized to have different properties: magnetized and protonated chitosan, with an MG $Q_{max}$ of 87,72 and 78.13, respectively. A thorough investigation by Lawal *et al.* [29] considered the functionalization of CNTs using MTPPBr:Gly 1:2 DES, with a CV $Q_{max}$ of 385.27 mg.g$^{-1}$. CNTs were also functionalized with ChCl:EG 1:2 for the adsorption of MO, having a $Q_{max}$ of 310.2 mg.g$^{-1}$ [63]. Li *et al.* [64] targeted the removal of anionic dyes, including MO, CR, and indigo carmine (IC) using MgAl layered double hydroxide (LDH) synthesized from a mixture of DESs, as rapid and highly effective adsorbents. The adsorption capacities obtained in this study were 1051.87, 889.76, and 512.55 mg.g$^{-1}$ for MO, CR and IC, respectively. These remarkably high capacities were attributed to electrostatic attraction, hydrogen bonding, and ion exchange between the chloride and dye molecules. Beside these reports, several studies considered the use of DES-ADS for the extraction of other dyes such as RhB [56], ST [59], EY [65], and CaS [66].

One of the trends that was captured after reviewing the above studies on the use of DES-ADS for dye adsorption is that the constituents of the DESs comprise an alkyl ammonium/phosphonium salt as its HBA with the anions as $Cl^-$ or $Br^-$. Most of these studies reported that electrostatic interactions are a major mechanism of extraction, especially for cationic dyes [28,61,66], while others reported the extraction mechanism as a combined effect of hydrophobic, electrostatic, hydrogen bonding and π-π interactions [29,67]. Also, nearly half of the studies within dye adsorption used ChCl-based DES for the synthesis/functionalization of the DES-ADS; however, this trend seems to carry out with other fields of application as well, due to the fact that the majority of DESs used within DES-ADS studies in general are ChCl-based ones as will be discussed in *section 4*. In addition, certain DESs have been synthesized with dual functionalities of adsorbing more than one dye and heavy metal [51].

#### *4.1.2. Heavy metals*

The removal of heavy metals from water streams is of paramount importance, as exposure to such elements can have toxic manifestations on humans and aquatic ecosystems alike. DES-based adsorbents have been developed and tested for the removal of a variety of various heavy metals from water, such as arsenic, lead, chromium, nickel, and mercury, among others. With regards to Cr (VI), several studies have considered the use of DES-ADS for the adsorption of Cr(VI) of which, interestingly, four out of five of these have used a DES with urea (U) as the HBD. The ChCl:U 1:2 was used as a reaction medium to dissolve the precursor materials. The resulting CoFe oxides were evaluated for Cr(VI) adsorption, with a Q = 5.27 mg.g$^{-1}$ [51]. A similar study used the same DES to functionalize biomass material (peanut shells) having nearly the same adsorption capacity of 5.36 mg.g$^{-1}$ [68]. In a different study, Cr (VI) adsorption of 133.33 mg.g$^{-1}$ was achieved using biochar prepared from peanut shells mixed with $FeCl_3$:Urea 2:1 DES as precursors [69]. The biochar was regenerated and used for up to 5 cycles, and the removal efficiency decreased to 51 % on the last cycle. In a parallel study, biochar production using ChCl with p-toluene sulfonic acid (p-tsOH) 1:1 was presented, of which the resulting material also had Cr(VI) adsorption capability of up to Q = 270.3 mg.g$^{-1}$ [70]. Aside from using DES for the preparation of precursor materials, Chen et al.[71] used the ternary DES Fructose:Urea:Thiourea (6:1:3) as a precursor material to produce frustrated Lewis pairs (FLP) with single atom (Nitrogen) doped and heteroatom (Nitrogen, Sulfur) codoped carbon material. The N,S-codoped carbon adsorbents achieved a significant Cr(VI) adsorption capacity of 564.7 mg.g$^{-1}$ compared to N-doped carbon, pristine carbon, and other reported DES-ADS. The functional sites on the FLP material enhanced the adsorption and reduction of Cr(VI) due to the enhanced electron transfer between the adsorbent and Cr(VI) ions.

For the adsorption of Pb(II), all of the reviewed DES-ADS reported using ChCl-based DESs for adsorbent preparation. For instance, Mehrabi *et al.* [57] synthesized a magnetic $Fe_3O_4$-GO adsorbent functionalized with ChCl:Urea 1:2, of which the adsorption capacity of Pb(II) reached 120.3 mg.g$^{-1}$; The same adsorbent was used for dye removal as mentioned in the previous section. Moreover, the same DES (ChCl:Urea 1:2) was used as a reaction medium to synthesize lanthanum titanate (LTO) [72]. The developed LTO material was tested for photocatalytic degradation of reactive dyes and the adsorption of different heavy metals, including Pb, As and Cr, with removal efficiency of 96 %, 74 %, and 71 %, respectively. In a study by AlOmar *et al.* [73], a ChCl:TEG 1:3 was used as a functionalization agent on multiwall carbon nanotubes (MWCNT), of which the $q_{max}$ for Pb (II) reached 288.4 mg.g$^{-1}$.

The functionalization of MWCNTs was mostly reported from the same group (AlOmar and Alsaadi), of which they used a set of DESs with different alkyl ammonium/phosphonium salts as HBAs and glycerol (Gly) as the HBD [26,74–76]. For instance, the adsorption of $As^{+3}$ was tested using MWCNT adsorbents functionalized with N,N-diethyl ethanol ammonium chloride (NDEACl) and methyl triphenyl phosphonium bromide (MTPB) (both with Gly as HBD) of which the $Q_{max}$ was 17.085 and 23.4 mg.g$^{-1}$, respectively [74,76]. In a similar method, DES-MWCNTs with allyl triphenyl phosphonium bromide (ATPB) and tetrabutyl ammonium bromide (TBABr) were evaluated for $Hg^{+2}$ removal, where the $q_{max}$ was 177.76 and 186.97, respectively [26,76]. It can be observed that the adsorption capacity of adsorbents modified with phosphonium-based DESs seems to surpass that of ammonium-based DESs in both cases ($As^{+3}$ and $Hg^{+2}$). It is worth noting that the selectivity of such adsorbents should be evaluated more rigorously, as it is considered a crucial parameter in separation processes in which a high yield of a certain metal is required over other elements in the feed. In this context, the exact same adsorbent (MWCNT functionalized with TBABr:Gly 1:4 DES) that was tested for $Hg^{+2}$ removal [76] was later evaluated for $Ni^{+2}$ removal [77] whereby a $Q_{max}$ of 115.8 mg.g$^{-1}$ was achieved. A different study by Chen *et al.* [78] evaluated the $Hg^{+2}$ adsorption capacity of $Fe_3O_4$-GO particles functionalized with a ternary hydro sulphonyl-based DES (ChCl:Itaconic acid:3-mercaptopropionic acid 2:1:1); the inclusion of −SH groups onto the adsorbent material enhanced $Hg^{+2}$ removal where $Q_{max}$ of 215.1 mg.g$^{-1}$ was achieved and maintaining ≅ 90 % removal efficiency after the 7th regeneration cycle. Lastly, a recent study investigated the synthesis of COFs in ChCl:OA·2$H_2O$ DES for the adsorption of $La^{+3}$ and other rare earth metals (REEs) such as Ce, Eu,

**Table 9**
Applications of DES-based adsorbents within the field of treatment and extraction of valuable substances from biomass. (chronological order).

| Application | | | Extraction from biomass | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Article info. | | Process | Material | DES | Feed properties | | | Performance | | Model | | Regeneration | | | |
| Ref | Year | Process | Composite | HBA:HBD | Ratio | Target | Conc.ppm [specified] | Adsorbent dose | Performancemg. $g^{-1}$ [specified] | Isotherm | Kinetic | Regenerant | R % | R %(last cycle) | Cycles |
| [101] | 2017 | SPE | MIP | Bet:EG: Water | 1:2:1 | Levofloxacin | 50 ppm | 30 mg / 10 mL | ~1.4 [94.5%] | | | MeOH–HAc (9 : 1, v/v) | 94.5% 93.3% | | |
| [101] | 2017 | SPE | MIP | Bet:EG: Water | 1:2:1 | Tetracycline | 50 ppm | 30 mg / 10 mL | ~1.23 [93.3] | | | | | | |
| [102] | 2017 | SPE | MIP | ChCl:CafA: FA | 3:1:1.5 | Levofloxacin | 300 ppm | 30 mg / 10 mL | ~5.1 | | | | | | |
| [103] | 2018 | MSPE | $Fe_3O_4$-MIP-Chitosan | ChCl:MAA | 1:2 | (+)-Catechin | 50-150 ppm | 100 mg / 1 mL | 13.1 | | | | | | |
| [103] | 2018 | MSPE | $Fe_3O_4$-MIP-Chitosan | ChCl:MAA | 1:2 | (−)-Epicatechin | 50-150 ppm | 100 mg / 1 mL | 6.32 | | | | | | |
| [103] | 2018 | MSPE | $Fe_3O_4$-MIP-Chitosan | ChCl:MAA | 1:2 | (−)-Epigallocatechin | 50-150 ppm | 100 mg / 1 mL | 8.76 | | | | | | |
| [104] | 2019 | Ads. | $Fe_3O_4$-MIP-Boron Nitride | ChCl:EG: CA | 5:5:1 | Quercetin | 300 ppm | 30 mg / 1 mL | ~ 5.25 [96.8 %] | | $1^{st}$ order | | | | |
| [104] | 2019 | Ads. | $Fe_3O_4$-MIP-Boron Nitride | ChCl:EG: CA | 5:5:1 | Isorhamnetin | 300 ppm | 30 mg / 1 mL | [93.6%] | | $1^{st}$ order | | | | |
| [104] | 2019 | Ads. | $Fe_3O_4$-MIP-Boron Nitride | ChCl:EG: CA | 5:5:1 | Kaempferol | 300 ppm | 30 mg / 1 mL | [94.8%] | | $1^{st}$ order | | | | |
| [105] | 2020 | MSPE | $Fe_3O_4$-MIP-$MoS_2$ | VP:MlnA | 1:1 | Catechin | 50-300 ppm | 15 mg /3 mL | 70.5 | | | | | | |
| [106] | 2020 | Ads. | MIP | BTMACl: CafA:FA | 6:1:3 | Quercetin | 20-150 ppm | 10 mg / 5 mL | 23.58 21.501* | Freundlich | pseudo-$2^{nd}$ order | | | | |
| [106] | 2020 | Ads. | MIP | CTEABr: CafA:FA | 6:1:3 | Schisandrin | 20-150 ppm | 10 m g/ 5 Ml | 41.64 65.510* | Langmuir Freundlich | pseudo-$2^{nd}$ order | | | | |
| [107] | 2020 | Ads. | $Fe_3O_4$-MIP-$SiO_2$ | ChCl: OA:1,2-PD | 1:1:2 | Baicalein | 200 ppm | 10 mg / 1.5 mL | 5.36 8.78^ | | pseudo-$2^{nd}$ order | MeOH-HAc (8:2, v/v) | | | 6 |
| [108] | 2022 | Ads. - USAE | Chitosan | ChCl:OlcA | 1:2 | Flavonoids: Rutin Quercetin Isorhamnetin | 1000 ppm | 1000 mg / 24 mL | Flavonoids: 107.5 ± 0.16 30.22 ± 0.37 43.5 ± 0.22 | | | MeOH | | 100.83% ± 2.02% | 6 |
| [109] | 2022 | Ads. | MIP-Hydroxyapatite | TBACl :MA | 1:2 | Sinapic acid | 150 ppm | 10 mg / 10 mL | 121 | Langmuir | pseudo-$2^{nd}$ order | MeOH and HAc (9:1, V:V) | | | 8 |
| [109] | 2022 | Ads. | MIP-Hydroxyapatite | APTMACl: AcrIM | 1:1 | Sinapic acid | 150 ppm | 10 mg / 10 mL | 121 | Langmuir | pseudo-$2^{nd}$ order | | | | |
| [110] | 2022 | M-DSPME | $Fe_3O_4$-$TiO_2$ | MalA:Xyl: Water | 1:1:10 | Pb | 0.1 ppm | 55 mg / 50 mL | [90.3–107%] | | | 1.0M $HNO_3$ | | 86.3% | 6 |
| [110] | 2022 | M-DSPME | $Fe_3O_4$-$TiO_2$ | MalA:Xyl: Water | 1:1:10 | Cu | 0.1 ppm | 55 mg / 50 mL | [93.7–101%] | | | 1.0M $HNO_3$ | | 87.7% | 6 |

(*continued on next page*)

**Table 9** (*continued*)

| Application | | | Extraction from biomass | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Article info. | | Process | Material | DES | Feed properties | | | Performance | | Model | | Regeneration | | | |
| Ref | Year | Process | Composite | HBA:HBD | Ratio | Target | Conc.ppm [specified] | Adsorbent dose | Performancemg. $g^{-1}$ [specified] | Isotherm | Kinetic | Regenerant | R % | R %(last cycle) | Cycles |
| [111] | 2022 | MSPE | $Fe_3O_4$-Chitosan | L-pro:MAA | 3:1 | Flavonoids: icariin epimedin A epimedin B epimedin C baohuoside I | 180 ppm | 8 mg / 4 mL | icariin 47.87 [μg/mg] | Freundlich | pseudo-2nd order | HAc:MeOH 8:2 | 80-110% | 70% | 5 |
| [112] | 2022 | Ads. | $Fe_3O_4$-MIP | VBTMACl: VBenA | 1:1 | Laminarin | 2000 ppm | 5 mg / 2 mL | 322.58 | Langmuir | pseudo-2nd order | MeOH/HAc (9:1, v/v) | 94.55-97.39%. | 88.24% | 5 |
| [113] | 2022 | Ads. | MIP | ChCl:MAA | 1:2 | Gallic Acid | 10.0 [mM] | 20 mg / 1 mL | [0.7110 mmol/g] | multilayer Ads. | pseudo-2nd order | MeOH-HAc (9/1, v/v) | 87.85–96.75% | 90% | 12 |

* Reported $Q_{max}$ value
^ Reported $Q_e$ value

Er, Pr, Nd, Tm, Yb, and Sc [79]. The maximum adsorption capacity for $La^{+3}$ reached 84.67 $mg.g^{-1}$, and the study included a detailed taxonomy of the different separation factors of the adsorbed REEs.

Overall, the adsorption of heavy metals through DES-ADS has notable potential. Nevertheless, more focus should be spent on studying the selectivity of the tested adsorbents to distinguish their true capability for recovery/removal of certain metal ions in water. That said, further efforts must be spent studying the fundamental adsorption routes of the target metal ions with the designed adsorbent. The extraction mechanism in such processes should be studied using proper analytical techniques to have a deeper understanding of such reactions.

#### *4.1.3. Pharmaceuticals*

Pharmaceuticals and personal care products (PPCPs) comprise a wide range of chemicals that are always in demand by the public. With the prominent use of such chemicals and the inefficiency of conventional wastewater treatment technologies to completely remove the pollutants released to water bodies from these products, more selective water treatment and advanced remediation techniques are required. The use of DES-ADS to remove certain bioactive and pharmaceutical products from wastewater streams was recently studied, of which around one-tenth (11 %) of all DES-ADS reported in the literature are concerned with the removal of different PPCPs from wastewater, including Ofloxacin (OFL), Naproxen, Salbutamol, Salicylic acid, and others. For instance, Ofloxacin, a fluoroquinolone antibacterial compound used as an antibiotic for the treatment of different infections, was extracted from an aqueous stream using molecularly imprinted resins (MIR) synthesized in ChCl:EG 1:2 DES, achieving a $Q_{max} = 32.92$ $mg.g^{-1}$ [80]. In a similar approach, Row *et al.* [81] synthesized molecularly imprinted polymers (MIPs) via a ChCl:MAA 1:2 DES to target levofloxacin in environmental wastewater samples with a removal efficiency of 98.3 %. Salicylic acid, a compound used to treat many skin problems was also extracted via molecularly imprinted chitosan hydrogels (MIH) synthesized by the same DES (ChCl:EG 1:2) [82], with adsorption capacity of 106.5 $mg.g^{-1}$, suggestion that electrostatic static interactions facilitated the adsorption between MIH and salicylic acid. Additionally, all these studies depended on the molecular recognition of the imprinted adsorbent materials (with template analyte) to tailor their selectivity towards the target analyte, be it OFL, LOFL or salicylic acid. Other DES-ADS were also used to remove fluoroquinolone-based compounds from water, such as Norfloxacin [83], Sparfloxacin [84] as detailed in Table 5. Several other compounds were targeted in addition to fluoroquinolone compounds. For instance, a study by Selkala *et al.* [85] reported the succinylation of cellulose nanofibrils (CNF) in LiCl:U 1:5 DES for the adsorption of Salbutamol from wastewater. The anionic CNF had an adsorption capacity for Salbutamol of 196 $mg.g^{-1}$. Another group reported the adsorption of paracetamol using calix[4]pyrrole (C[4]P) adsorbents synthesized using a DES of tartaric acid and dimethylurea (3:7). The uptake of paracetamol by the C[4]P adsorbents was mainly driven via hydrogen bonding, π-π, n-π, anion-π, and cation-π interactions, with a maximum adsorption of 479.3 $mg.g^{-1}$. Other pharmaceutical products were adsorbed via DES-ADS (especially ChCl-based DESs), including Acetaminophen [28], Naproxen [86], Diclofenac [87], and Quercetagetin [88], as shown in Table 5

#### *4.1.4. Phenols & other applications*

Phenolic compounds are present in the effluent of several manufacturing industries, including oil refining, pharmaceuticals, paper, paints, and plastics. Once discharged to surface water without proper treatment, phenolic compounds might pose a risk to animal and aquatic systems, and human life.; Consequently, phenol has been designated by US Environmental Protection Agency (EPA) as a priority pollutant, stressing the requirements for proper phenol remediation in water bodies. Few studies in the DES-ADS field were concerned with the removal of phenol and its other derivatives. The adsorption of phenol from an aqueous medium was attempted using CNTs functionalized with various DESs. For instance, Lawal *et al.* [29] used a MTPPBr:Gly 1:2 DES to functionalize CNTs for phenol adsorption, achieving a Qmax of 274.51 $mg.g^{-1}$; the DES-functionalized CNTs was also used for CV dye adsorption. A more detailed mechanistic approach for evaluating the extraction mechanism [29] showed that π-π interactions between phenol and the functionalized CNTs are the main adsorption route. Ibrahim et al.[89] used the conventional ChCl:EG 1:2 DES to functionalize CNT to remove 2,4-dichlorophenol. The maximum adsorption capacity reached was 390.53 $mg.g^{-1}$. In a similar approach, CNTs were functionalized using a ternary mixture of Amphiprotic surfactant (BS-12), 1,3-propanediol and Glycerol (1:1:1) for the adsorption of different bromophenols [90], with high adsorption capacities for 4-bromophenol (155.82 $mg.g^{-1}$), 2,4-dibromophenol (276.42 $mg.g^{-1}$), 2,6-dibromophenol (761.19 $mg.g^{-1}$) and 2,4,6-tribromophenol (1719.68 $mg.g^{-1}$). Notably, the strong withdrawing property of the three Br atoms in 2,4,6-tribromophenol enhanced the π-π interactions between the target molecule and the functionalized MWCNTs. In a different approach by Xiong *et al.* [60], adsorption of 4-nitrophenol using N-doped porous carbon adsorbents prepared from Glucose:Urea 1:5 DES; A $Q_{max}$ of 487 $mg.g^{-1}$ was achieved.

In addition to the major categories of interest, DES-ADS were also evaluated for the adsorption of other substances from water, such as polycyclic aromatic hydrocarbons (PAHs) [91], thidiazuron [92], flavonoids [93] and other colloidal substances.

### *4.2. Applications in protein isolation*

Separation and purification of proteins is one of the major research fields in biotechnology and proteomics. It is challenged, however, by the sensitivity of proteins towards extreme conditions, which increases their tendency to be denatured during the separation process. Nearly one-eighth of the DES-ADS studies (12.7 %) were targeting certain types of proteins for isolation and purification (Table 7). Among the various technologies investigated for protein isolation, magnetic nano-adsorbents – within the scope of MSPE process – showed significant potential for researchers to study them in depth [20]. It is worth noting that the prevalent materials used in the preparation of DES-based adsorbents for protein isolation were mainly MIPs, $Fe_3O_4$ or a hybrid of both. Various adsorbents were tested for the isolation and detection of proteins such as BSA, BHb, OVA, transferrin, lysozyme and other peptides. For instance,

**Table 10**
Applications of DES-based adsorbents in other 'uncategorized' fields. (chronological order).

| Application | | Other applications | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Article info. | | Process | Material | DES | | Feed properties | | | Performance | Model | | Regeneration | | | |
| Ref | Year | Process | Composite | HBA:HBD | Ratio | Target | Conc.ppm [specified] | Adsorbent dose | Performancemg.g$^{-1}$ [specified] | Isotherm | Kinetic | Regenerant | R % | R %(last cycle) | Cycles |
| [114] | 2010 | Ads. | Cotton fibers | C-ChCl:U | 1:2 | Hyaluronic acid | 2500 ppm | 5 mg / 5 mL | 351.3* | Langmuir | | 1N NaCl, glycine–HCl buffer | 36.50% | | |
| [115] | 2020 | Ads. | β-cyclodextrin polymers | BTBACl: CitA | 1:1-2 | Methylene blue | 5 ppm | 10 mg / 10 mL | [17.4±0.4 %] | | | | | | |
| [115] | | | | BTMACl: CitA | 1:1-2 | Methyl orange | 5 ppm | 10 mg / 10 mL | [82.7±0.2 %] | | | | | | |
| [115] | | | | CTEABr: CitA | 1:1-2 | Caffeine | 5 ppm | 10 mg / 10 mL | [50.7±3.4 %] | | | | | | |
| [116] | 2021 | Ads. | HsGY | ChCl:EG | 1:2 | Thiabendazole | 25 ppm | 10 mg / 2 mL | 0.85 | | | | | | |
| [117] | 2021 | Ads. | MIP | ChCl:EG: MalA | 6:6:2 | Metronidazole | | 40 mg / 5 mL | 11.53* | Freundlich | pseudo-2$^{nd}$ order | ACN | | | |
| [118] | 2022 | Ads. | HsGY-CNT | ChCl: Catecol | 1:2 | Myricetin | 200 ppm | 5 mg / 0.5 mL | 19.9-25.72 | N/A | N/A | N/A | N/A | N/A | N/A |
| [119] | 2022 | M-DSPME | $Fe_3O_4$-MIP-$SiO_2$ | ChCl: CafA:FA | 6:1:3 | Hydrocortisone | 50 ppm | 35.2 mg / 10 mL | 13.21 | Langmuir | pseudo-2$^{nd}$ order | MeOH/HAc (9:1, v/ v) | 81.2 – 96.7 % | decreased 10% | 6 |
| [119] | | | | | | Cortisone | 50 ppm | 35.2 mg / 10 mL | 14.5138 | Langmuir | pseudo-2$^{nd}$ order | MeOH/HAc (9:1, v/ v) | 81.2 – 96.7 % | decreased 10% | 6 |
| [119] | | | | | | Dexamethasone | 50 ppm | 35.2 mg / 10 mL | 24.3902 | Langmuir | pseudo-2$^{nd}$ order | MeOH/HAc (9:1, v/ v) | 81.2 – 96.7 % | decreased 10% | 6 |
| [120] | 2023 | Ads. | MIP | Men:Thy | 1:1 | Sertraline | 0.35 ppm | 0.9 mg / 1 mL | 1.15 [89-100%] | Langmuir | pseudo-2$^{nd}$ order | | | | |

ˆReported $Q_e$ value
* Reported $Q_{max}$ value

several studies reported the development and use of DES-based MIP and MIP-$Fe_3O_4$ adsorbents for the extraction of BHb from blood samples, achieving an adsorption capacity ranging from 151.28 to 229.54 mg/g [94–98]. Likewise, the DES-based $Fe_3O_4$–MIP hybrid was tested for the extraction of transferrin ($Q_{max}$ 37.5 mg/g) and lysozyme ($Q_{max}$ 108 mg/g). Moreover, three different MIPs synthesized with different ChCl-based DESs were used for the recognition/enrichment of peptides such as lysine-acetylated peptides [99] Glutarylated peptides [100], or benzoylation peptides [101].

As for BSA and OVA extraction, different DES-ADS were explored including $TiO_2$ nanotubes [102], $Fe_3O_4$–GO [27], and $Fe_3O_4$–Cyclodextrin [103] adsorbents. It was noticed that all the DESs used for the preparation of these adsorbents were with ChCl as HBA, except a study that used another alkyl ammonium salt [103]. Notably, a prominent use of ChCl: MAA 1:2 DES can be observed in recent studies for the preparation of MIPs. The use of MIPs for protein extraction primarily utilizes tailor-made templating, which provides specific sites for interacting with target analytes [22]. It was also observed that most of the chosen DES components for synthesizing such hybrid adsorbents comprised MAA (HBD) as a functional monomer in the synthesis of MIPs. However, this is not specific for protein isolation; rather, it is the norm for DES-based MIPs. Further information about DES-based MIPs is detailed in *section 5.1*. The use of $Fe_3O_4$ was merely to serve the magnetic functionality to facilitate adsorbent separation within the MSPE process. Nevertheless, as an unbiased justification for this trend, it should be noted that a significant proportion of these studies were conducted by the same research group, of which different DESs were explored within the preparation of $Fe_3O_4$-MIP hybrid adsorbents for protein isolation.

### 4.3. Extraction from Food

The extraction of different chemical substances from food and agri-food products is done by different entities for multiple purposes. On one hand, value-added biomolecules can be extracted from certain food products before or after food processing. On the other hand, different analyses and measures are taken to detect harmful substances in food sources or products. Hence, most of the adsorption studies within this field, particularly using DES-ADS, utilize SPE approaches for method development to detect/quantify different chemical compounds in food products, whether for productive or protective measures. Accordingly, it should be noted that the metrics reported by these studies usually include process-specific ones such as limit of detection (LOD), and limit of quantification (LOQ), in addition to extraction rate (E%). These stats are systematic and comparable across different processes and other developed quantification techniques.

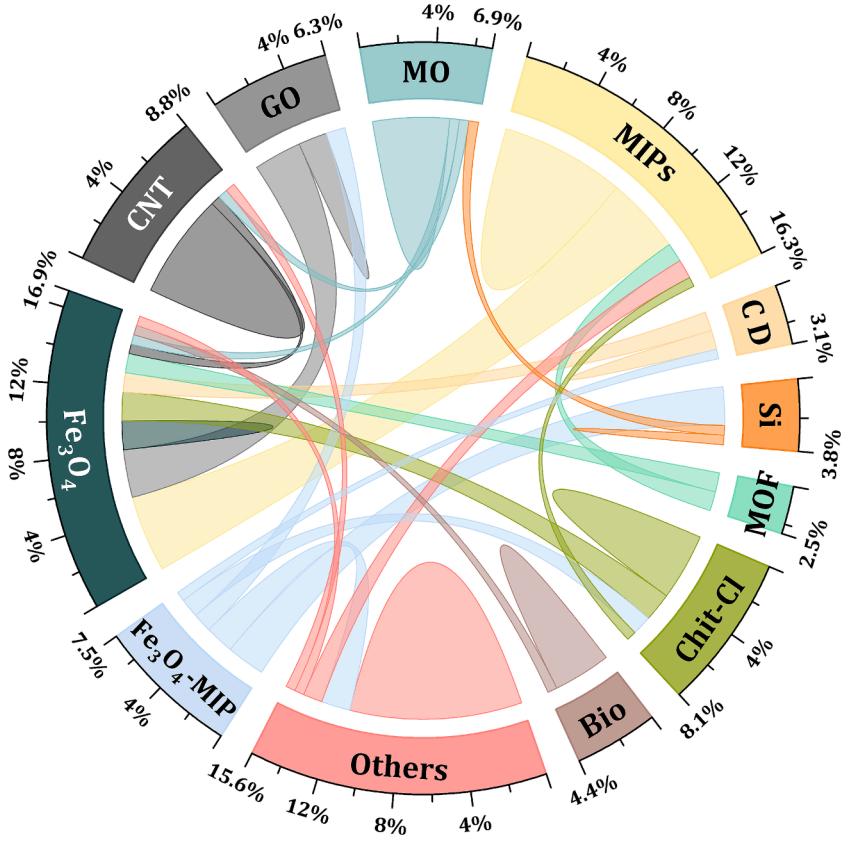


**Fig. 5.** Chord diagram mapping the different base materials used in the development of DES-ADS in literature (from 2010 to 2024). The percentage of each base-material used is segmented according to hybridization with other base materials (i.e., as composites or functionalization agents).

**Table 11**
DES-based adsorbents prepared via the hybridization of MIPs with different materials. (chronological order).

| Material classification | | | Molecularly Imprinted Polymers (MIP) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Article info. | | Field | Material | | | Deep Eutectic Solvent | | | | | | Synthesis route |
| Ref | Year | Process | Application | Target | Composite | HBA | HBD | HBD II | Ratio | Role | Function | Method |
| [73] | 2016 | Ads. | Proteins | BHb | $Fe_3O_4$-MIP | ChCl | MAA | | 1:2 | Functionalization | Functional monomer | I |
| [101] | 2017 | SPE | Biomass | LevofloxacinTetracycline | MIP | Bet | EG | Water | 1:2:1 | Synthesis | Modifier | I |
| [102] | 2017 | SPE | Biomass | Levofloxacin | MIP | ChCl | CafA | FA | 3:1:1.5 | Functionalization | Functional monomer | I |
| [74] | 2018 | Ads. | Proteins | Transferrin | $Fe_3O_4$-MIP | ChCl | AA | | 1:2 | Functionalization | Functional monomer | I |
| [75] | 2018 | MSPE | Proteins | Lysozyme | $Fe_3O_4$-MIP | ATECl | Gly | | 1:1 | Functionalization | Functional monomer | I |
| [76] | 2019 | Ads. | Proteins | BHb | $Fe_3O_4$-MIP | APTMACl | U | | 1:2 | Functionalization | Functional monomer | I |
| [46] | 2019 | Ads. | Water | Ofloxacin | MIR | ChCl | EG | | 1:2 | Synthesis | Reaction medium/Solvent | II |
| [47] | 2020 | Ads. | Water | Levofloxacin | MIP | ChCl | MAA | | 1:2 | Functionalization | Functional monomer | I |
| [87] | 2020 | SPME | Food | Phthalate esters | MIP-MOF | BTBACl | Gly | | 2:1 | Synthesis | | I |
| [106] | 2020 | Ads. | Biomass | Quercetin | MIP | BTMACl | CafA | FA | 6:1:3 | Functionalization | Functional monomer | I |
| [106] | 2020 | Ads. | Biomass | Schisandrin | MIP | CTEABr | CafA | FA | 6:1:3 | Functionalization | Functional monomer | I |
| [124] | 2021 | SPE | Medical | Paclitaxel (PTX) | MIP | ChCl | CafA | FA | 6:1:3 | Functionalization | Functional monomer | I |
| [49] | 2021 | Ads. | Water | Naproxen | $Fe_3O_4$-MIP | ChCl | BuIM | | 1:1 | Synthesis | Co-solvent / Functional monomer | I |
| [116] | 2021 | Ads. | Proteins | BHb | MIP-MOF | ChCl | MAA | | 1:2 | Functionalization | Functional monomer | I |
| [67] | 2021 | Ads. | Water | ThidiazuronForchlorfenuron | MIP | ChCl | 1,4-BD | | 1:2 | Synthesis | Porogen - Co-solvent | I |
| [117] | 2021 | Ads. | Other | Metronidazole | MIP | ChCl | EG | MalA | 6:6:2 | Functionalization | Functional monomer | I |
| [82] | 2022 | SPE | Proteins | lysine acetylation peptides | MIP | ChCl | MAA | | 1:2 | Functionalization | Functional monomer | I |
| [83] | 2022 | Ads. | Proteins | Glularylated peptide | MIP-molecular sieve | ChCl | EG | | 1:16.725 | Synthesis | Porogen | II |
| [91] | 2022 | Ads. | Food | oxalic acid | $Fe_3O_4$-MIP | Bet | CitA | Gly | 1:1:1 | Functionalization | Functional monomer | I |
| [93] | 2022 | Ads. | Food | Vanillin | $Fe_3O_4$-MIP-$SiO_2$ | ChCl | MAA | | 1:2 | Functionalization | Functional monomer | I |
| [84] | 2022 | SPE | Proteins | benzoylation peptides | MIP | ChCl | AA | | 1:2 | Functionalization | Functional monomer | I |
| [109] | 2022 | Ads. | Biomass | Sinapic acid | MIP-Hydroxyapatite | TBACl | MA | | 1:2 | Functionalization | Functional monomer | I |
| [109] | | | | | | APTMACl | AcrIM | | 1:1 | Synthesis | Cross-linker | I |
| [94] | 2022 | MSPE | Food | Organophosphorus pesticides | Fe-MIP | ChCl | CafA | FA | 3:1:1.5 | Functionalization | Functional monomer | I |
| [112] | 2022 | Ads. | Biomass | Laminarin | $Fe_3O_4$-MIP | VBTMACl | VBenA | | 1:1 | Functionalization | Functional monomer | I |
| [113] | 2022 | Ads. | Biomass | Gallic Acid | MIP | ChCl | MAA | | 1:2 | Functionalization | Functional monomer | I |
| [120] | 2023 | Ads. | Other | Sertraline | MIP | Men | Thy | | 1:1 | Synthesis | Reaction medium/Solvent | II |
| [99] | 2023 | Ads. | Food | ForchlorfenuronThidiazuron | MIR | ChCl | 1,3-PD | | 1:2 | Synthesis | | I |
| [58] | 2023 | Ads | Water | Salicylic acid | Chitosan-MI (hydrogel) | ChCl | EG | | 1:4 | Synthesis | Reaction medium/Solvent | I |

**Table 12**
DES-based adsorbents prepared via the hybridization of $Fe_3O_4$ and MIPs with different materials. (chronological order).

| Material classification | | | $Fe_3O_4$-Molecularly Imprinted Polymers (MIP) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Article info. | | Field | | | Material | Material | Deep Eutectic Solvent | | | | | | Synthesis route |
| Ref | Year | Process | Application | Composite I | Composite I-II | Composite III | HBA | HBD | HBD II | Ratio | Role | Function | Method |
| [103] | 2018 | MSPE | Biomass | Catechins | $Fe_3O_4$-MIP | Chitosan | ChCl | MAA | | 1:2 | Functionalization | Functional monomer | I |
| [123] | 2019 | Ads. | Medical | L-asparaginase | $Fe_3O_4$-MIP | GO | Poly(VP) | MlnA | | 1:1 | Functionalization | Functional monomer | I |
| [104] | 2019 | Ads. | Biomass | QuercetinIsorhamnetinKaempferol | $Fe_3O_4$-MIP | Boron Nitride | ChCl | EG | CA | 5:5:1 | Functionalization | Functional monomer | I |
| [105] | 2020 | MSPE | Biomass | Catechin | $Fe_3O_4$-MIP | $MoS_2$ | VP | MlnA | | 1:1 | Functionalization | Functional monomer | I |
| [64] | 2020 | MSPE | Water | Cholorphenol | $Fe_3O_4$-MIP | GO | CTEABr | 2,4,6-TCP | | 1:1 | Functionalization | Functional monomer - Template | I |
| [77] | 2020 | Ads. | Proteins | BHb | $Fe_3O_4$-MIP | $SiO_2$ | BTBACl | OHMA | | 1:2 | Functionalization | Functional monomer | I |
| [77] | | | | BHb | $Fe_3O_4$-MIP | $SiO_2$ | BTMACl | AcrTMA | | 1:1 | Synthesis | Cross-linker | I |
| [107] | 2020 | Ads. | Biomass | Baicalein | $Fe_3O_4$-MIP | $SiO_2$ | ChCl | OA | 1,2-PD | 1:1:2 | Functionalization | Functional monomer | I |
| [88] | 2021 | Ads. | Food | Aspartame | $Fe_3O_4$-MIP | Zein | ChCl | CafA | FA | 1:6:3 | Functionalization | Functional monomer | I |
| [80] | 2021 | Ads. | Proteins | BHb | $Fe_3O_4$-MIP | β-cyclodextrin | MATACl | ItA | | 2:1 | Functionalization | Functional monomer | I |
| [93] | 2022 | Ads. | Food | Vanillin | $Fe_3O_4$-MIP | $SiO_2$ | ChCl | MAA | | 1:2 | Functionalization | Functional monomer | I |
| [95] | 2022 | MSPE | Food | Bisphenol A, F, AF | $Fe_3O_4$-MIP | cellulose | ChCl | MalA | | 1.5:1 | Synthesis | Reaction solvent | I |
| [119] | 2022 | M-DSPME | Other | HydrocortisoneCortisoneDexamethasone | $Fe_3O_4$-MIP | $SiO_2$ | ChCl | CafA | FA | 6:1:3 | Functionalization | Functional monomer | I |
| [65] | 2024 | Ads. | Water | Bisphenol AF | $Fe_3O_4$ | MIP-COF | ChCl | HFIP | | 1:4 | Synthesis | Solvent | II & III |

**Table 13**
DES-based adsorbents prepared via the hybridization of $Fe_3O_4$ with different materials. (chronological order).

| Material classification | | | $Fe_3O_4$ | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Article info. | | Field | | | Material | Material | Deep Eutectic Solvent | | | | | | Synthesis route |
| Ref | Year | Process | Application | Target | Composite I | Composite II | HBA | HBD | HBD II | Ratio | Role | Function | Method |
| [72] | 2016 | MSPE | Protein | BSA | $Fe_3O_4$ | GO | ChCl | Gly | | 1:1 | Functionalization | | I |
| [72] | | | | | | | ChCl | EG | | 1:2 | Functionalization | | I |
| [72] | | | | | | | ChCl | Glu | | 2:1 | Functionalization | | I |
| [72] | | | | | | | ChCl | Sor | | 1:1 | Functionalization | | I |
| [73] | 2016 | Ads. | Protein | BHb | $Fe_3O_4$ | MIP | ChCl | MAA | | 1:2 | Functionalization | Functional monomer | I |
| [74] | 2018 | Ads. | Protein | Transferrin | $Fe_3O_4$ | MIP | ChCl | AA | | 1:2 | Functionalization | Functional monomer | I |
| [34] | 2018 | SPE | Water | Hg2+ | $Fe_3O_4$ | GO | ChCl | ItA | MPrA | 2:1:1 | Functionalization | | I |
| [75] | 2018 | MSPE | Protein | Lysozyme | $Fe_3O_4$ | MIP | ATECl | Gly | | 1:1 | Functionalization | Functional monomer | I |
| [4] | 2019 | SPE | Water | Malachite GreenCrystal Violet | $Fe_3O_4$ | MOF (HKUST-1) | APTMACl | Sor | | 1:1<br>2:1 | Functionalization | Functional monomer | I |
| [76] | 2019 | Ads. | Protein | BHb | $Fe_3O_4$ | MIP | APTMACl | U | | 1:2 | Functionalization | Functional monomer | I |
| [13] | 2020 | Ads. | Water | Methylene Blue | $\Upsilon$-$Fe_2O_3$ | Polyacrylamide | BTMACl | ActA | | 1:1 | Synthesis | Internal phase (HIPE) | I |
| [48] | 2020 | Ads. | Water | OfloxacinMefenamic acid | $Fe_3O_4$ | MOF | CTEABr | LacA | | 1:2 | Functionalization | | I |
| [14] | 2020 | Ads. | Water | Methylene Blue | $Fe_3O_4$ | GO | CTEABr | U | | 1:2 | Functionalization | | II |
| [14] | | | | Pb (II) | $Fe_3O_4$ | GO | BTBACl | U | | 1:2 | Functionalization | | II |
| [121] | 2020 | SPE | Medical | Trypsin | $Fe_3O_4$ | β-cyclodextrin | BTMACl | TFAI | | 1:2 | Functionalization | | II |
| [49] | 2021 | Ads. | Water | Naproxen | $Fe_3O_4$ | MIP | ChCl | BuIM | | 1:1 | Synthesis | Co-solvent/ Functional monomer | I |
| [79] | 2021 | Ads. | Protein | OVA | $Fe_3O_4$ | β-cyclodextrin | BTMACl | MAA | | 1:2 | Functionalization | Functional monomer | I |
| [51] | 2021 | Ads. | Water | Diclofenac | $Fe_3O_4$ | $Fe_3O_4$ | ChCl | BuIM | | 1:1 | Functionalization | | I |
| [19] | 2021 | Ads. | Water | Malachite GreenSunset Yellow | $Fe_3O_4$ | Polydopamine | TBACl | MAA | | 1:2 | Functionalization | Functional monomer | I |
| [89] | 2021 | Ads. | Food | Indigotin Blue | $Fe_3O_4$ | GO | TMACl | U | | 1:1 (mass) | Functionalization | | II |
| [20] | 2021 | Ads. | Water | Malachite green | $Fe_3O_4$ | Chitosan | ChCl | U | | 1:2 | Functionalization | | II |
| [91] | 2022 | Ads. | Food | oxalic acid | $Fe_3O_4$ | MIP | Bet | CitA | Gly | 1:1:1 | Functionalization | Functional monomer | I |
| [93] | 2022 | Ads. | Food | Vanillin | $Fe_3O_4$ | MIP-$SiO_2$ | ChCl | MAA | | 1:2 | Functionalization | Functional monomer | I |
| [110] | 2022 | M-DSPME | Biomass | PbCu | $Fe_3O_4$ | $Fe_3O_4$-TiO2 | MalA | Xyl | Water | 1:1:10 | Functionalization | | II |
| [94] | 2022 | MSPE | Food | Organophosphorus pesticides | Fe | MIP | ChCl | CafA | FA | 3:1:1.5 | Functionalization | Functional monomer | I |

(*continued on next page*)

**Table 13** (*continued*)

| **Material classification** | | | **$Fe_3O_4$** | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Article info.** | | **Field** | | | **Material** | **Material** | **Deep Eutectic Solvent** | | | | | | **Synthesis route** |
| **Ref** | **Year** | **Process** | **Application** | **Target** | **Composite I** | **Composite II** | **HBA** | **HBD** | **HBD II** | **Ratio** | **Role** | **Function** | **Method** |
| [111] | 2022 | MSPE | Biomass | Flavonoids | $Fe_3O_4$ | Chitosan | L-pro | MAA | | 3:1 | Functionalization | Functional monomer | I |
| [112] | 2022 | Ads. | Biomass | Laminarin | $Fe_3O_4$ | MIP | VBTMACl | VBenA | | 1:1 | Functionalization | Functional monomer | I |
| [55] | 2022 | MSPE | Water | Methcathinone | $Fe_3O_4$ | biochar | ChCl | Gly | | 1:2 | Functionalization | | I |
| [56] | 2022 | LPME | Water | OfloxacinSparfloxacin | $Fe_3O_4$ | GO | ChCl | EG | | 1:2 | Synthesis | Carrier solvent | II |
| [122] | 2022 | MSPE | Medical | Trypsin | $Fe_2O_4$ | $MnFe_2O_4$-CNT | Bet | U | Glu | 1:1:1 | Functionalization | | I |
| [98] | 2022 | MSPE | Food | Organophosphorus pesticides | $Fe_3O_4$ | | Si-Surfactant | DodecA | | 1:5 | Functionalization | | I |
| [26] | 2023 | Ads. | Water | Acid Blue 80 | FeO | Chitosan | ChCl | U | | 1:2 | Functionalization | | II |

**Table 14**
DES-based adsorbents prepared via the hybridization of CNTs with different materials. (chronological order).

| Material classification | | | Carbon nanotubes (CNT) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Article info. | | Field | Material | | | Deep Eutectic Solvent | | | | | | Synthesis route |
| Ref | Year | Process | Application | Target | Composite | HBA | HBD | HBD II | Ratio | Role | Function | Method |
| [29] | 2016 | Ads. | Water | Pb (II) | CNT | ChCl | TEG | | 1:3 | Functionalization | | II |
| [30] | 2016 | Ads. | Water | $As^{3+}$ | CNT | MTPPB | Gly | | 1:3 | Functionalization | | II |
| [30] | 2016 | Ads. | Water | $As^{3+}$ | CNT | BTPCl | Gly | | 1:16 | Functionalization | | II |
| [31] | 2017 | Ads. | Water | $As^{3+}$ | CNT | DEthACl | Gly | | 1:2 | Functionalization | | II |
| [32] | 2017 | Ads. | Water | $Hg^{2+}$ | CNT | ATPPBr | Gly | | 1:14 | Functionalization | | II |
| [33] | 2017 | Ads. | Water | $Hg^{2+}$ | CNT | TBABr | Gly | | 1:4 | Functionalization | | II |
| [62] | 2018 | Ads. | Water | 2,4-dichlorophenol | CNT | ChCl | EG | | 1:2 | Functionalization | | II |
| [3] | 2019 | Ads. | Water | Methyle orange | CNT | ChCl | EG | | 1:2 | Functionalization | | II |
| [3] | | | | | | DEACl | EG | | 1:3 | Functionalization | | II |
| [63] | 2019 | Ads. | Water | Bromophenols | CNT | (BS-12) | 1,3-PD | Gly | 1:1:1 | Functionalization | | II |
| [7] | 2019 | Ads. | Water | Eosin Y | CNT-$ZnCo_2O_4$ | CTEABr | Gly | | 1:2 | Functionalization | | I |
| [10] | 2019 | Ads. | Water | Phenol | CNT | BTMACl | Gly | | 1:2 | Functionalization | | I |
| [10] | 2019 | Ads. | Water | Crystal violet | CNT | CTEABr | Gly | | 1:2 | Functionalization | | I |
| [37] | 2021 | Ads. | Water | $Ni^{2+}$ | CNT | TBABr | Gly | | 1:4 | Functionalization | | II |
| [90] | 2022 | In-situ DLPME | Food | Triazoles | CNT (nanofluid) | ChCl | EG | | 1:2 | Synthesis | Solvent | II |
| [122] | 2022 | MSPE | Medical | Trypsin | $MnFe_2O_4$-CNT | Bet | U | Glu | 1:1:1 | Functionalization | | I |
| [118] | 2022 | Ads. | Other | Myricetin | HsGY-CNT | ChCl | Catecol | | 1:2 | Functionalization | | II |

**Table 15**
DES-based adsorbents prepared via the hybridization of GO with different materials. (chronological order).

| **Material classification** | | | **Graphene Oxide (GO)** | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Article info.** | | **Field** | **Material** | | | **Deep Eutectic Solvent** | | | | | | **Synthesis route** |
| Ref | Year | **Process** | **Application** | **Target** | **Composite** | **HBA** | **HBD** | **HBD II** | **Ratio** | **Role** | **Function** | **Method** |
| [72] | 2016 | MSPE | Proteins | BSA | $Fe_3O_4$-GO | ChCl | Gly | | 1:1 | Functionalization | | I |
| [72] | | | | | | ChCl | EG | | 1:2 | Functionalization | | I |
| [72] | | | | | | ChCl | Glu | | 2:1 | Functionalization | | I |
| [72] | | | | | | ChCl | Sor | | 1:1 | Functionalization | | I |
| [34] | 2018 | SPE | Water | $Hg^{2+}$ | $Fe_3O_4$-GO | ChCl | ItA | MPrA | 2:1:1 | Functionalization | | I |
| [123] | 2019 | Ads. | Medical | L-asparaginase | $Fe_3O_4$-GO-MIP | Poly(VP) | MlnA | | 1:1 | Functionalization | Functional monomer | I |
| [64] | 2020 | MSPE | Water | Cholorphenol | $Fe_3O_4$-MIP-GO | CTEABr | 2,4,6-TCP | | 1:1 | Functionalization | Functional monomer - Template | I |
| [66] | 2020 | SPE | Water | PAHs | GO | ChCl | EG | | 1:3 | Synthesis | Porogen | Other |
| [14] | 2020 | Ads. | Water | Methylene Blue | $Fe_3O_4$-GO | CTEABr | U | | 1:2 | Functionalization | | II |
| [14] | 2020 | Ads. | Water | Pb (II) | $Fe_3O_4$-GO | BTBACl | U | | 1:2 | Functionalization | | II |
| [89] | 2021 | Ads. | Food | Indigotin Blue | $Fe_3O_4$-GO | TMACl | U | | 1:1 (mass) | Functionalization | | II |
| [92] | 2022 | SPE | Food | indole-3-carbinol | GO-Poly(DES) | ChCl | MAA | | 1:2 | Functionalization | | I |
| [56] | 2022 | LPME | Water | OfloxacinSparfloxacin | $Fe_3O_4$-GO | ChCl | EG | | 1:2 | Synthesis | Carrier solvent | II |
| [97] | 2022 | DSPME | Food | Pesticides | GO | P-ChCl | Naph | | 1.5:2 | Functionalization | | I |

**Table 16**
DES-based adsorbents prepared via the hybridization of (a) Chitin/Cellulose, (b) β-cyclodextrin and (c) biomass with different materials. (chronological order).

| **(a) Material classification** | | | **Chitin / Cellulose** | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Article info.** | | **Field** | **Material** | | | **Deep Eutectic Solvent** | | | | | | **Synthesis route** |
| **Ref** | **Year** | **Process** | **Application** | **Target** | **Composite** | **HBA** | **HBD** | **HBD II** | **Ratio** | **Role** | **Function** | **Method** |
| [103] | 2018 | MSPE | Biomass | Catechins | $Fe_3O_4$-MIP-Chitosan | ChCl | MAA | | 1:2 | Functionalization | Functional monomer | I |
| [45] | 2018 | Ads. | Water | Salbutamol | Cellulose nanofibrils (anionic) | LiCl | U | | 1:5 | Synthesis | Reaction solvent: Succinylation | II |
| [2] | 2019 | SPE | Water | Red 70 | Cellulose monolith | ChCl | U | | 1:2 | Synthesis | Reaction medium/ cationization reagent | I |
| [6] | 2019 | Ads. | Water | Chrome azurol S | CNF-halloysite | Amino GA-HCl | Gly | | 1:2 | Synthesis | Reaction medium/ reagent | II |
| [15] | 2020 | Ads. | Water | Malachite Green | Chitosan beads | CTEABr | U | | 1:2 | Functionalization | Reaction medium/ reagent | II |
| [15] | | | | | Chitosan beads | BTBACl | Gly | | 1:2 | Functionalization | Reaction medium/ reagent | II |
| [20] | 2021 | Ads. | Water | Malachite green | $Fe_3O_4$-Chitosan | ChCl | U | | 1:2 | Functionalization | | II |
| [108] | 2022 | Ads. - USAE | Biomass | Flavonoids | Chitosan | ChCl | OlcA | | 1:2 | Synthesis | Reaction medium | II |
| [69] | 2022 | Ads. | Water | Polygalacturonic acid | lignocellulose nanofibers (CNF) | TEAOH (35 wt% in water) | dmU | | 1:2 | Synthesis | Reaction solvent | II |
| [111] | 2022 | MSPE | Biomass | Flavonoids | $Fe_3O_4$-Chitosan | L-pro | MAA | | 3:1 | Functionalization | Functional monomer | I |
| [95] | 2022 | MSPE | Food | Bisphenol A, F, AF | $Fe_3O_4$-MIP-Cellulose | ChCl | MalA | | 1.5:1 | Synthesis | Reaction solvent | I |
| [25] | 2022 | Ads. | Water | Methylene Blue | Carboxylated Cellulose | ChCl | OA | H2O (10 wt. %) | 1:5 | Synthesis | Reaction medium | II |
| [58] | 2023 | Ads. | Water | Salicylic acid | Chitosan-MI (hydrogel) | ChCl | EG | | 1:4 | Synthesis | Reaction medium/ Solvent | I |
| [26] | 2023 | Ads. | Water | Acid Blue 80 | FeO-Chitosan | ChCl | U | | 1:2 | Functionalization | | II |
| **(b) Material classification** | | | **β-cyclodextrin** | | | | | | | | | |
| [115] | 2020 | Ads. | Other | Methylene blue | β-cyclodextrin polymers | BTBACl | CitA | | 1:1, 1:1.5, and 1:2 | Synthesis | Reaction medium | II |
| [115] | | | | Methyl orange | β-cyclodextrin polymers | BTMACl | CitA | | 1:1, 1:1.5, and 1:2 | Synthesis | Reaction medium | II |
| [115] | | | | Caffeine | β-cyclodextrin polymers | CTEABr | CitA | | 1:1, 1:1.5, and 1:2 | Synthesis | Reaction medium | II |
| [121] | 2020 | SPE | Medical | Trypsin | β-cyclodextrin-Magnetic beads | BTMACl | TFAI | | 1:2 | Functionalization | | II |
| [79] | 2021 | Ads. | Proteins | OVA | $Fe_3O_4$-β-cyclodextrin | BTMACl | MAA | | 1:2 | Functionalization | Functional monomer | I |

(*continued on next page*)

**Table 16** (*continued*)

| (a) Material classification | | | Chitin / Cellulose | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Article info.** | | **Field** | **Material** | | | **Deep Eutectic Solvent** | | | | | | **Synthesis route** |
| **Ref** | **Year** | **Process** | **Application** | **Target** | **Composite** | **HBA** | **HBD** | **HBD II** | **Ratio** | **Role** | **Function** | **Method** |
| [80] | 2021 | Ads. | Proteins | BHb | $Fe_3O_4$-MIP-β-cyclodextrin | MATACl | ItA | | 2:1 | Functionalization | Functional monomer | I |
| [70] | 2022 | Ads. | Water | Atenolol | β-cyclodextrin | ChCl | CitA | | 1:2 | Synthesis | Reaction medium | II |
| **(c) Material classification** | | | **Biomass-based material** | | | | | | | | | |
| [5] | 2019 | Ads. | Water | Acid Blue 74AcetaminophenCiprofloxacin | Biochar–clay | HTMABr | Gly | | 2:1 | Functionalization | | I |
| [125] | 2021 | Ads. | Medical | DNA-toxic compounds (DNA-T-Cs), | Sorghum powder-biomass | VP | MlnA | | 1:1 | Functionalization | Functional monomer | II |
| [52] | 2021 | Ads. | Water | Ofloxacin | Rice Husk Ash | ChCl | GlyA | | 1:3 | Functionalization | | II |
| [38] | 2021 | Ads. | Water | Cr (VI) | Biomass | ChCl | p-tsOH | | 1:1 | Synthesis | Reaction medium | II |
| [39] | 2022 | Ads. | Water | Cr (VI) | Biochar | $FeCl_3$ | U | | 2:1 | Synthesis | Precursor material | II |
| [55] | 2022 | MSPE | Water | Methcathinone | $Fe_3O_4$-biochar | ChCl | Gly | | 1:2 | Functionalization | | I |
| [42] | 2022 | Ads. | Water | Cr (VI) | Peanut shell | ChCl | U | | 1:2 | Functionalization | | II |

**Table 17**
DES-based adsorbents prepared via the hybridization of (a) MO and MOH, (b) MOFs and (c) Si with different materials. (chronological order).

| **(a) Material classification** | | **Metal oxides and metal hydroxides (MO/OH)** | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Article info.** | | **Field** | **Material** | | | **Deep Eutectic Solvent** | | | | | | **Synthesis route** |
| **Ref** | **Year** | **Process** | **Application** | **Target** | **Composite** | **HBA** | **HBD** | **HBD II** | **Ratio** | **Role** | **Function** | **Method** |
| [1] | 2015 | Ads. | Water | Congo red | CoFe oxide | ChCl | U | | 1:2 | Synthesis | Reaction medium | I |
| [1] | 2015 | Ads. | Water | Cr(VI) | CoFe oxide | ChCl | U | | 1:2 | Synthesis | Reaction medium | I |
| [7] | 2019 | Ads. | Water | Eosin Y | CNT-ZnCo2O4 | CTEABr | Gly | | 1:2 | Functionalization | | I |
| [126] | 2019 | Ads. | Water | Congo red | MnO2 | BTBACl | ActIM | | 1:7 | Synthesis | Solvent/ reducing agent | II |
| [9] | 2019 | Ads. | Water | Congo redAmaranthIndigo carmine | MgO | $MgCl_2 \bullet 6H_2O$ | U | | 1:2 | Synthesis | Precursor material | III |
| [11] | 2020 | Ads./Mem | Water | Methylene Blue | $MnO_2$ | ChCl | EG | | 1:2 | Synthesis | Reaction medium - reducing agent | I |
| [78] | 2020 | SPE | Proteins | BSA | $TiO_2$ nanotubes | BTBACl | MAA | | 1:2 | Functionalization | Functional monomer | I |
| [78] | 2020 | SPE | Proteins | OVA | $TiO_2$ nanotubes | BTMACl | MAA | | 1:2 | Functionalization | Functional monomer | I |
| [17] | 2020 | Ads. | Water | Methyle OrangeCongo redIndigo carmine | MgAl LDH | MgCl2·6H2O | U | | 1:2 | Synthesis | Precursor material | III |
| [21] | 2021 | Ads. | Water | Congo red | $Ni_2CO_3(OH)_2$-$SiO_2$ | NiCl2·6H2O | EG | | 1:2 | Synthesis | Precursor material | III |
| [110] | 2022 | M-DSPME | Biomass | PbCu | $Fe_3O_4$-$TiO_2$ | MalA | Xyl | Water | 1:1:10 | Functionalization | | II |
| [23] | 2022 | Ads. | Water | Methylene Blue | $NiSO_4$ | ChCl | EG | | 1:2 | Synthesis | Reaction medium | II |
| [41] | 2022 | Ads. | Water | $Pb^{2+}As^{3+}Cr$ | LTO | ChCl | U | | 1:2 | Synthesis | Reaction medium | III |
| **(b) Material classification** | **Metal Organic Frameworks (MOF)** | | | | | | | | | | | |
| [4] | 2019 | SPE | Water | Malachite Green | $Fe_3O_4$-MOF (HKUST-1) | APTMACl | Sor | | 1:1<br>2:1 | Functionalization | Functional monomer | I |
| [4] | 2019 | SPE | Water | Crystal Violet | | | | | | Functionalization | Functional monomer | I |
| [87] | 2020 | SPME | Food | Phthalate esters | MIP-MOF | BTBACl | Gly | | 2:1 | Synthesis | | I |
| [48] | 2020 | Ads. | Water | OfloxacinMefenamic acid | $Fe_3O_4$-MOF | CTEABr | LacA | | 1:2 | Functionalization | | I |
| [81] | 2021 | Ads. | Proteins | BHb | MIP-MOF | ChCl | MAA | | 1:2 | Functionalization | Functional monomer | I |
| **(c) Material classification** | **Silicon-based material** | | | | | | | | | | | |

(*continued on next page*)

**Table 17** (*continued*)

| (a) Material classification | | Metal oxides and metal hydroxides (MO/OH) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Article info.** | | **Field** | **Material** | | | **Deep Eutectic Solvent** | | | | | | **Synthesis route** |
| **Ref** | **Year** | **Process** | **Application** | **Target** | **Composite** | **HBA** | **HBD** | **HBD II** | **Ratio** | **Role** | **Function** | **Method** |
| [86] | 2016 | Ads. / SPE | Food | Organic acids | Silica-tris (indolyl) methane | ChCl | U | | 1:2 | Synthesis | Reaction medium | II |
| [77] | 2020 | Ads. | Proteins | BHb | $Fe_3O_4$-MIP-$SiO_2$ | BTBACl | OHMA | | 1:2 | Functionalization | Functional monomer | I |
| [77] | | | | | | BTMACl | AcrTMA | | 1:1 | Synthesis | Cross-linker | I |
| [107] | 2020 | Ads. | Biomass | Baicalein | $Fe_3O_4$-MIP-$SiO_2$ | ChCl | OA | 1,2-PD | 1:1:2 | Functionalization | Functional monomer | I |
| [21] | 2021 | Ads. | Water | Congo red | $Ni_2CO_3(OH)_2$-$SiO_2$ | NiCl2·6H2O | EG | | 1:2 | Synthesis | Precursor material | III |
| [93] | 2022 | Ads. | Food | Vanillin | $Fe_3O_4$-MIP-$SiO_2$ | ChCl | MAA | | 1:2 | Functionalization | Functional monomer | I |
| [119] | 2022 | M-DSPME | Other | HydrocortisoneCortisoneDexamethasone | $SiO_2$ | ChCl | CafA | FA | 6:1:3 | Functionalization | Functional monomer | I |

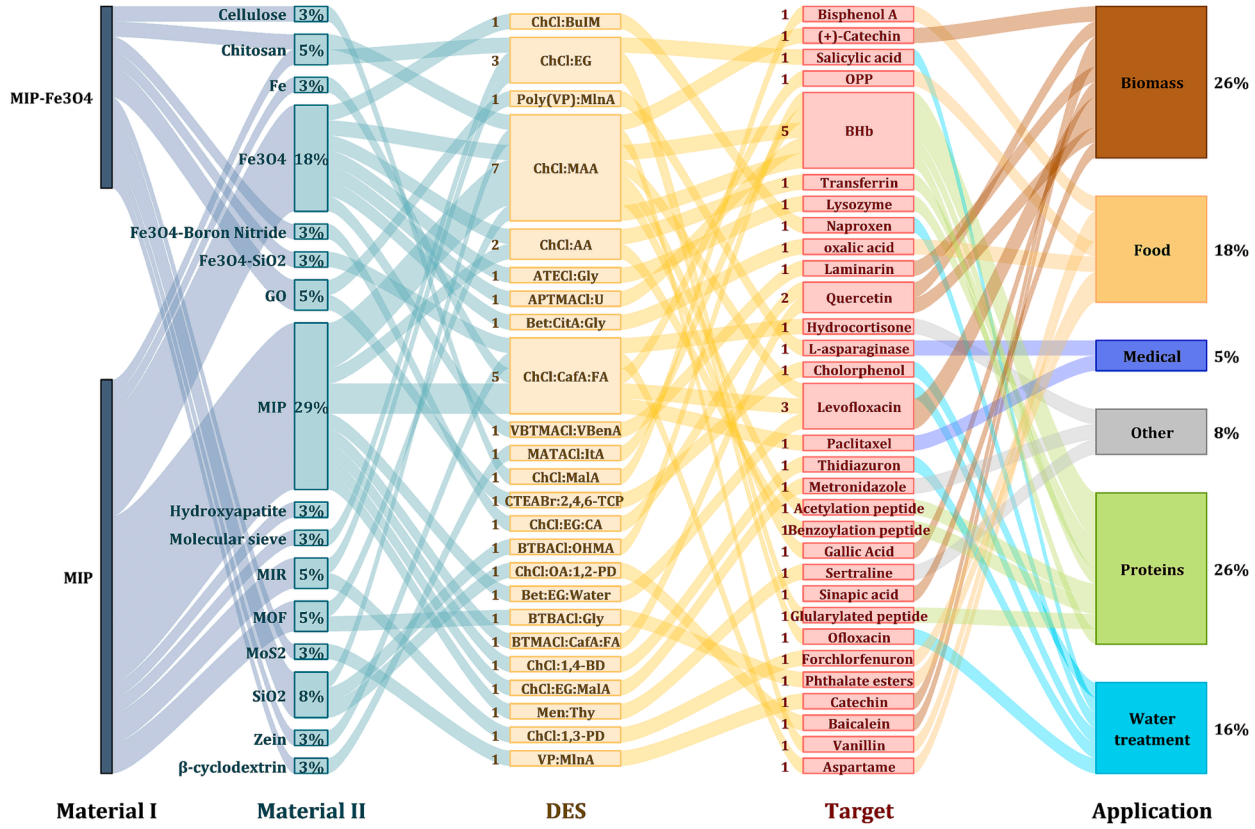


**Fig. 6.** Mapping of DES-based Adsorbents incorporating MIPs. The alluvial chart illustrates the type of MIP-composite developed using a particular DES for a specific target within a field of application.

Among the DES-ADS studies in the literature, 12.7 % were applied for the adsorption of different substances from food extracts (Table 8) including but not limited to organic acids [104,105], pesticides [106,107], dyes [108], and phenolic compounds [109]. It should be noted here that the number of research articles within this field is actually higher, yet only the papers fitting the scope and criteria (detailed in methodology section) were included. Moreover, nearly two-thirds of the DES-ADS were synthesized/functionalized with ChCl-based DESs. For instance, a silica-based adsorbent with tris(indolyl)methane was prepared using ChCl:U 1:2 for the determination of different organic acids (Benzoic, p-anisic, salicylic and cinnamic acid) from grape juice and mineralized drinking water [27]. A study by Lin *et al.* [110] evaluated the dispersion of CNTs in ChCl:EG 1:2 to use them as nanofluid in the detection of

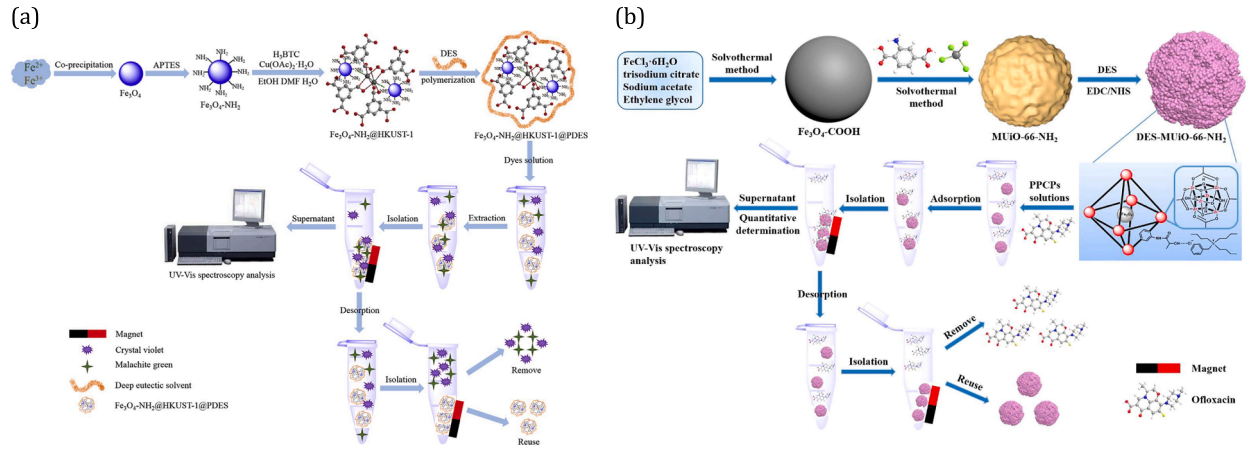


**Fig. 7.** (a) Synthesis of amino magnetic functionalized, DES polymerized HKUST-1 composites and its application in MSPE of different dyes (MG and CV) [61]; Copyright 2019 Elsevier B.V. (b) Synthesis of amino magnetic fictionalized. DES regulated MUiO-66 composites and its application in the MSPE of PPCPs [153]; Copyright 2020 Elsevier B.V.

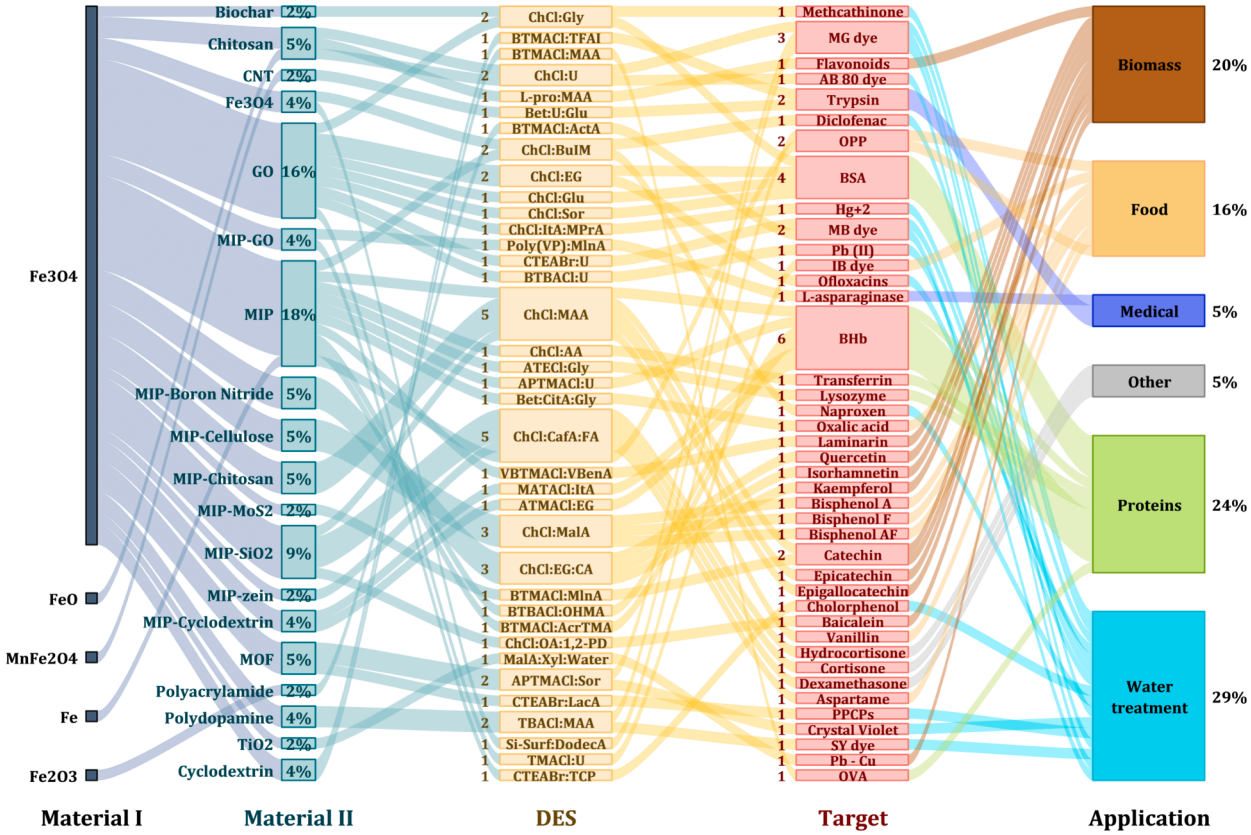


**Fig. 8.** Mapping of DES-based Adsorbents incorporating magnetic-based composites (i.e., $Fe_3O_4$). The alluvial chart illustrates the type of MIP-composite developed using a particular DES for a specific target within a field of application.

triazoles in fruit juices and tea, in a process of DLPME. Another interesting observation is the use of different organic acids as HBDs within the DES such as malic acid (MalA), Methacrylic acid (MAA), and caffeic acid; Such DESs were predominantly used for the synthesis of MIPs. In fact, most of DES-ADS applied for adsorption of compounds from food products were actually MIPs. Similar to the DES-ADS applied for pharmaceutical compounds and protein isolation, MIPs were used herein for the specific recognition of target substances in food sources and products, which is a functionality provided by templating the target substance during MIP preparation. It was also noted that these MIPs are functionalized with $Fe_3O_4$ to induce magnetic separation i.e., MSPE process. For example, MIPs of

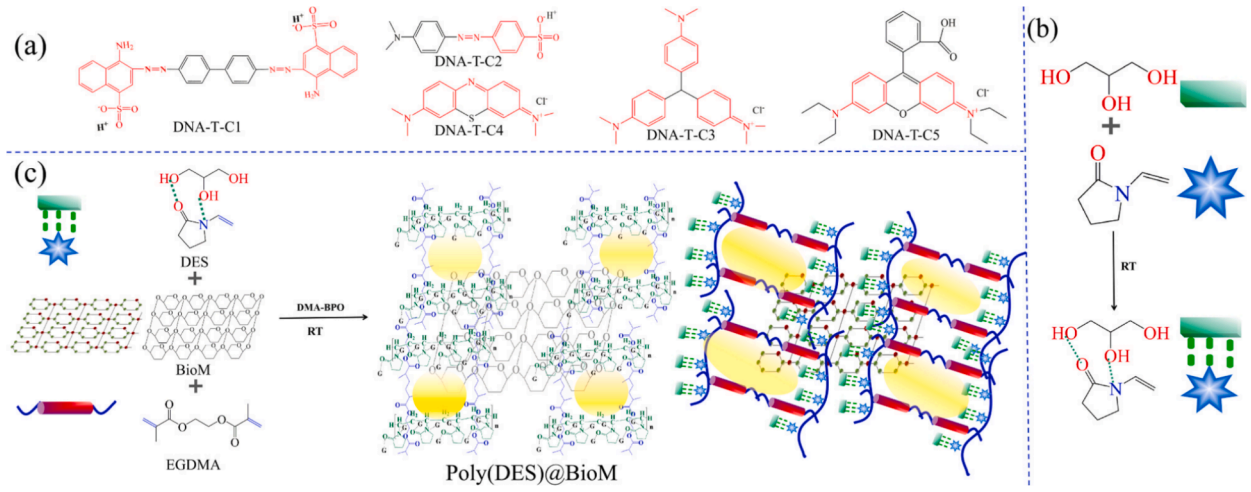


**Fig. 9.** Chemical structures of (a) the target analytes (DNA toxic compounds; DNA-T-Cs), (b) components of the used DES, (c) and schematics of the preparation of Poly(DES)-Biomass. Copyright 2019 Elsevier B.V.[130].

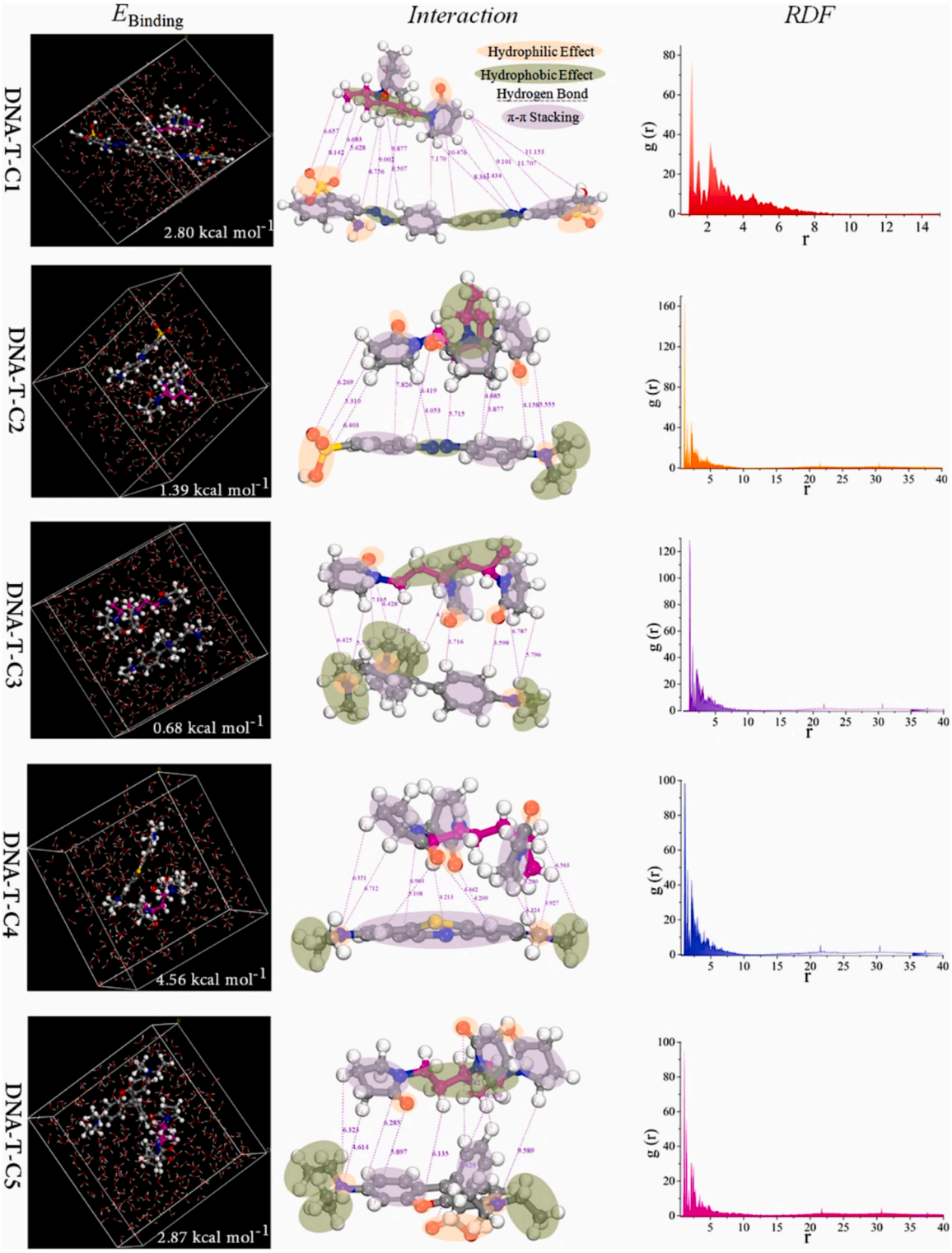


**Fig. 10.** $E_{Binding}$ values, interactions, and the radial distribution function (RDFs) of DNA toxic compounds (DNA-T-Cs) and Poly(DES)@BioMs. (RDF: the probability of finding a target analyte within the adsorbent range). Copyright 2019 Elsevier B.V. [130].

**Table 18**
Listing of DES-based adsorbents prepared via the hybridization of different 'uncategorized' materials. (chronological order).

| Material classification | | | Others | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Article info. | | Field | Material | | | Deep Eutectic Solvent | | | | | | Synthesis route |
| Ref | Year | Process | Application | Target | Composite | HBA | HBD | HBD II | Ratio | Role | Function | Method |
| [114] | 2010 | Ads. | Other | Hyaluronic acid | Cotton fibres | C-ChCl | U | | 1:2 | Functionalization | | II |
| [35] | 2019 | Ads. | Water | Pb (II)Cd (II) | Chondroitin sulphate | ChCl | EG | | 1:2 | Synthesis | Reaction medium - mesoporosity agents | I |
| [35] | 2019 | Ads. | Water | Pb (II)Cd (II) | Fucoidan | ChCl | EG | | 1:2 | Synthesis | Reaction medium - mesoporosity agents | I |
| [104] | 2019 | Ads. | Biomass | QuercetinIsorhamnetinKaempferol | $Fe_3O_4$-MIP-Boron Nitride | ChCl | EG | CA | 5:5:1 | Functionalization | Functional monomer | I |
| [105] | 2020 | MSPE | Biomass | Catechin | $Fe_3O_4$-MIP-$MoS_2$ | VP | MlnA | | 1:1 | Functionalization | Functional monomer | I |
| [12] | 2020 | Ads. - LLE | Water | Rhodamine B | L-amino acid gel | BTBACl | PhActA | | 1:2 | Synthesis | Solvent | II |
| [16] | 2020 | Ads. | Water | Methylene Blue4-nitrophenol | N-doped porous carbon | Glucose | U | | 1:5 | Synthesis | Precursor material | III |
| [18] | 2021 | Ads. | Water | Methylene BlueSafranine T | COF | TBABr | IM | | 3:7 | Synthesis | Reaction medium | III |
| [50] | 2021 | Ads. | Water | Norfloxacin | Keratin | ChCl | EG | | 1:2 | Synthesis | Solvent | II |
| [88] | 2021 | Ads. | Food | aspartame | $Fe_3O_4$-MIP-Zein | ChCl | CafA | FA | 1:6:3 | Functionalization | Functional monomer | I |
| [116] | 2021 | Ads. | Other | Thiabendazole | HsGY | ChCl | EG | | 1:2 | Functionalization | | I |
| [19] | 2021 | Ads. | Water | Malachite GreenSunset Yellow | $Fe_3O_4$-polydopamine | TBACl | MAA | | 1:2 | Functionalization | | I |
| [68] | 2021 | Ads. | Water | Flavonoids | COF | ChCl | HFP | | 1:2 | Synthesis | Reaction medium | III |
| [22] | 2022 | Ads. | Water | Methylene Blue | Lignin | ChCl | EthN | | 1:6 | Synthesis | Reaction medium | II |
| [83] | 2022 | Ads. | Proteins | Glularylated peptide | MIP-molecular sieve (SBA15) | ChCl | EG | | 1:16.725 | Synthesis | Porogen | II |
| [53] | 2022 | Ads. | Water | Chrysophanol acid | HsGY | ChCl | m-Cresol | | 1:4 | Functionalization | | I |
| [53] | | | | | | ChCl | p-Cresol | | 1:2 | Synthesis | Reaction medium | I |
| [54] | 2022 | In-situ SPE | Water | Arbidol | Chloromethyl polystyrene resin | DMEA | Arbidol | | | Functionalization | In-Situ Extraction | I |
| [109] | 2022 | Ads. | Biomass | Sinapic acid | MIP-Hydroxyapatite | TBACl | MA | | 1:2 | Functionalization | Functional monomer | I |
| [109] | | | | | | APTMACl | AcrIM | | 1:1 | Synthesis | Cross-linker | I |
| [85] | 2022 | Ads. | Proteins | BSAOVACyt cAvidin | Monomer-Monolith | ChCl | MAA | | 1:2 | Synthesis | Extraction | I |
| [24] | 2022 | Ads. | Water | Crystal violetMBRhB | halogenated dibenzylidene-D-sorbitol-Euteectogel | ChCl | EG | | NA | Synthesis | Reaction solvent | II |

(*continued on next page*)

**Table 18** (*continued*)

| Material classification | | | Others | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Article info. | | Field | Material | | | Deep Eutectic Solvent | | | | | | Synthesis route |
| Ref | Year | Process | Application | Target | Composite | HBA | HBD | HBD II | Ratio | Role | Function | Method |
| [96] | 2022 | SPME | Water | 5-hydroxymethylfurfural | Calcium Alginate aerogel beads | ChCl | PEG | | 1:1 | Synthesis | Reaction solvent | I |
| [40] | 2022 | Ads. | Water | $La^{+3}$ Other REEs | COF | ChCl | $OA.2H_2O$ | | 1:1 | Synthesis | Reaction medium | II |
| [118] | 2022 | Ads. | Other | Myricetin | HsGY-CNT | ChCl | Catecol | | 1:2 | Functionalization | | II |
| [57] | 2022 | Ads. | Water | Paracetamol | Calix[4]pyrrole | L-(+)-TarA | dmU | | 3:7 | Synthesis | Reaction medium | II |
| [43] | 2022 | Ads. | Water | $Sr^{2+}$ | Chalcogenidometalates | TEACl | Thio urea | | 1:2 | Synthesis | Reaction media and structure-directing agents | III |

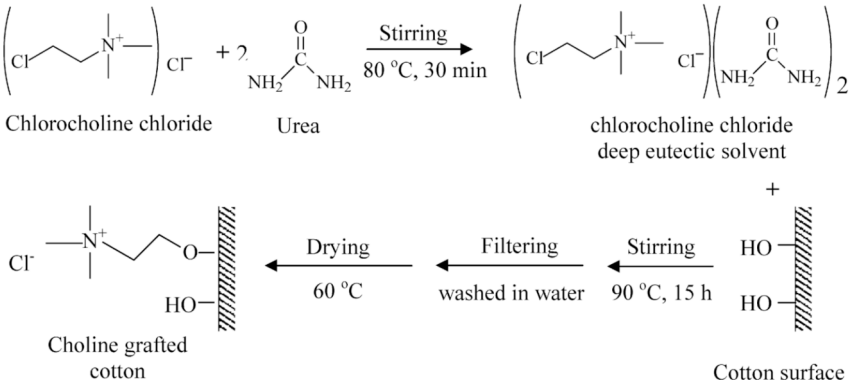


**Fig. 11.** Synthesis of antimicrobial cotton fibers via grafting of choline molecules of Chloro ChCl:U 1:2 DES. Copyright 2010 Elsevier B.V. [131].

magnetic porous cellulose were prepared by Wen *et al.* [109] for the specific recognition of different bisphenols, such as bisphenol A, F, and AF from food samples. ChCl:MalA 1:2 was used initially to dissolve cellulose and later in the preparation of MIPs. The resulting MIPs had adsorption capacities of 14.1, 13.7, and 15.7 mg.g$^{-1}$ for bisphenol A, F, and AF, respectively, with high performance up to 8 regeneration cycles. In a different study, magnetic $SiO_2$-based MIPs were prepared via ChCl:MAA 1:2 as a carrier and a functional monomer (MAA) [111]. The resulting $Fe_3O_4$-$SiO_2$-MIPs were used for the quantification of vanillin in infant complementary food, yielding an adsorption capacity of 6.31 mg.g$^{-1}$. The same DES (ChCl:MAA 1:2) was used to functionalize GO for the isolation of indole-3-carbinol, an anticancer compound found in broccoli and other cruciferous plants, where the adsorption of indole-3-carbinol reached 83.8 mg.g$^{-1}$ [112]. Magnetic-based MIPs were also prepared with ChCl:CA:FA at 3:1:1.5 for the concentration of organophosphorus pesticides from fruits and vegetable samples [113], with adsorption capacities ranging from 151.02 – 218.82 mg.g$^{-1}$ for different types of organophosphorus pesticides. Likewise, using the same DES (at a different molar ratio = 1:6:3), zein-based $Fe_3O_4$-MIPs were prepared for the detection of aspartame in soft drinks [114]. A DES composed of betaine:CA:Gly (1:1:1) was used similarly to provide the needed functional monomers for $Fe_3O_4$-MIPs preparation [105], which in turn were used for the removal of oxalic acid (OA) from vegetable and human blood samples. The adsorption capacity for OA reached 18.73 mg.g$^{-1}$ with a sustained performance for up to 5 adsorption–desorption cycles. Other DES-ADS targeting phthalate esters [115], indigotin blue [108], and other substances were also investigated.

### 4.4. *Extraction from Biomass*

Processing of organic matter from different sources has been conducted through different means for the extraction of useful substances and chemical compounds such as flavonoids, carbohydrates, or antimicrobial agents. Such compounds can be extracted from plant-based matter for medicinal use. It should also be noted that these studies are also primarily conducted to develop methods for the quantification/detection of certain chemical compounds in biomass. Hence, the procedure follows an SPE/MSPE process, and the reported metrics are mainly the LOD, LOQ, and recovery %. The use of different adsorbents to isolate these compounds is preceded by several processing steps to release such compounds from the organic matter into an enriched liquid solution. Most of the 7.8 % of DES-ADS studies in this work focused on the adsorption of flavonoids (e.g., catechin, quercetin, isorhamnetin) from different plant leaves (Table 9). The DES-ADS in nearly all these studies were basically composed of MIPs synthesized/functionalized with different DESs (mostly ChCl-based). For instance, the adsorption of catechins from tea powder was evaluated using chitosan-based $Fe_3O_4$-MIPs synthesized with ChCl:MAA 1:2 DES [116]. The adsorption capacity of (+)-catechin, (−)-epicatechin and −(−)epigallocatechin was 13.1, 6.32, and 8.76 mg.g$^{-1}$, respectively. The same group later investigated the adsorption of catechins using DES-ADS of $MoS_2$-based $Fe_3O_4$-MIPs [117], as well as the adsorption of quercetin, isorhamnetin, and kaempferol from *Ginkgo Biloba* tea leaves using $Fe_3O_4$-MIPs synthesized on 2D boron nitride [118]. The use of $Fe_3O_4$-MIPs with $SiO_2$ was also tested for the separation of baicalein from *Scutellaria baicalensis* Georgi, with tested reusability of up to six adsorption–desorption cycles [119]. In a study by Zhang *et al.* [120], MIPs were synthesized with ChCl:CafA:FA DES as a functional monomer and quercetin and schisandrin b as template molecules. The MIPs were utilized for the enrichment of both templates from mixed crude extracts of *penthorum* and *schisandra*, yielding adsorption

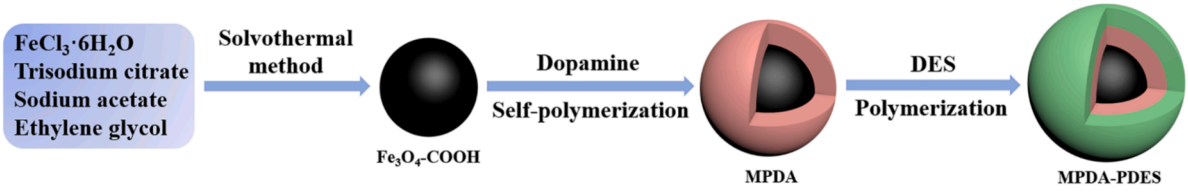


**Fig. 12.** Preparation of DES-functionalized magnetic-polydopamine adsorbents. Copyright 2020 Elsevier B.V.[25].

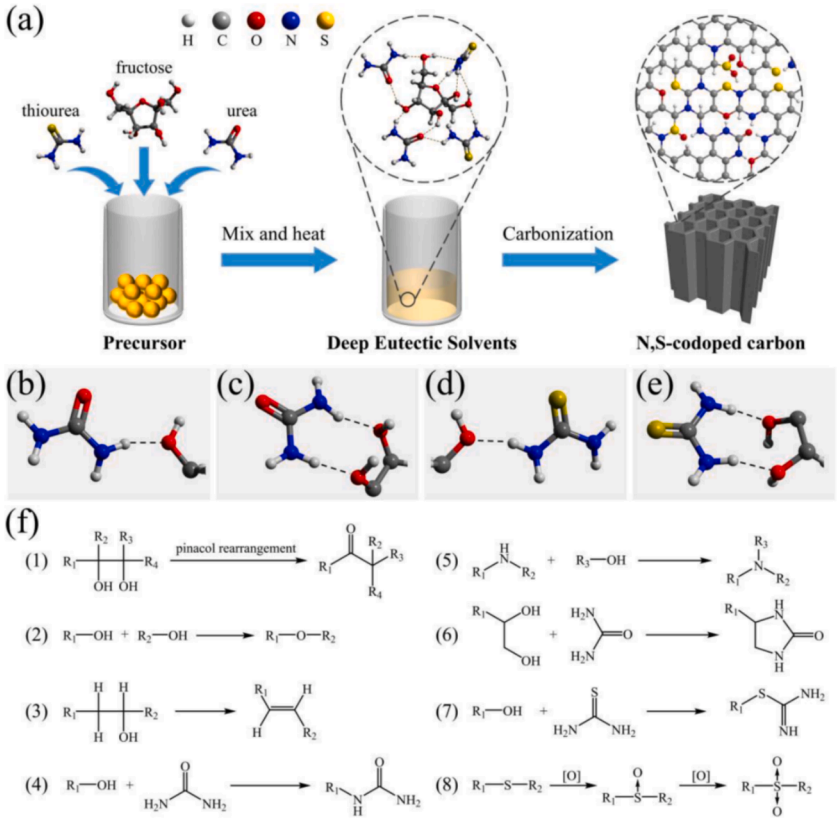


**Fig. 13.** (a) Schematic illustration of the synthesis process for N,S-codoped carbon. (b–e) Four types of hydrogen bonds in the DESs. (f) Possible chemical reactions during the carbonization process by using concentrated sulfuric acid. Copyright 2021 Elsevier B.V. [71].

capacities of 23.58 $mg.g^{-1}$and 41.64 $mg.g^{-1}$ for quercetin and schisandrin b, respectively. The same DES-ADS was used to purify an antibiotic, levofloxacin, from millet extract [121]. A parallel study (by the same group)[122] also investigated the purification of levofloxacin (and tetracycline) from millet extract; however, the DES used during the synthesis of the MIPs was based on a ternary mixture of Bet:EG:$H_2O$ (1:2:1) and yielded similar results. Consequently, a more thorough discussion about the specific effect of DES and its components on the synthesized adsorbents is required in order to contrast the effectiveness of each DES towards the final DES-ADS performance.

Moreover, DES-based MIPs were also used for the adsorption of other substances including laminarin, an anti-bacterial compound [123], and organic acids (synaptic acid [124]; Gallic acid [125]). A recent study by Zhang *et al.* reported the use of $Fe_3O_4$-$TiO_2$ composite functionalized with NADES (MalA:Xyl:$H_2O$ 1:1:10) in a method for the determination of heavy metals (Pb, Cu) in *Polygonatum kingianum* [126]. High recoveries of both metals were attained (Pb: 90.3–107 % and Cu: 93.7–101 %), and the regenerated adsorbents yielded recoveries for pb and Cu of 86.3 % and 87.7 %, respectively, at the sixth cycle.

### 4.5. Medical applications

A few studies reported the adsorption of chemical compounds for medicinal uses. A couple of papers have investigated the solid-phase extraction of trypsin, an enzyme that supports food digestion and has several other uses. For instance, Xu *et al.* [127], used β-cyclodextrin-magnetic beads functionalized with DES to extract trypsin, with an adsorption capacity of 549.87 $mg.g^{-1}$. The adsorbents were applied to extract trypsin from bovine pancreas crude extract solution, and its stability was tested over multiple regeneration cycles. A later study from the same group by Chen et al. [128] used MWCNTs functionalized with an $MnFe_2O_4$ composite and a Bet:U:Gly 1:1:1 DES for trypsin adsorption. The addition of the $MnFe_2O_4$ composite provided magnetic functionality (MSPE process), and the developed adsorbent yielded a maximum adsorption capacity of 1020.1 $mg.g^{-1}$ for trypsin, maintaining an adsorption capacity of more than 90 % after seven regeneration cycles. The DES-ADS in both studies were also evaluated for the adsorption of several biomolecules, such as BSA, BHb, Lyz, and Chymotrypsin.

Tan et al. [129] reported using MIPs with the ChCl:CafA:FA 6:1:3 DES as functional monomers for the separation and purification of Paclitaxel (PTX), a strong anticancer natural drug. This study adopted an SPE process using MIPs to separate PTX from its structural analogs. The results yielded an adsorption capacity of 87.08 $mg.g^{-1}$. Lastly, a study by Li et al. [130] evaluated the removal of trace DNA toxic compounds (DNA-T-C) of the azo and aromatic groups using biomass from sorghum powder functionalized with DES (VP:

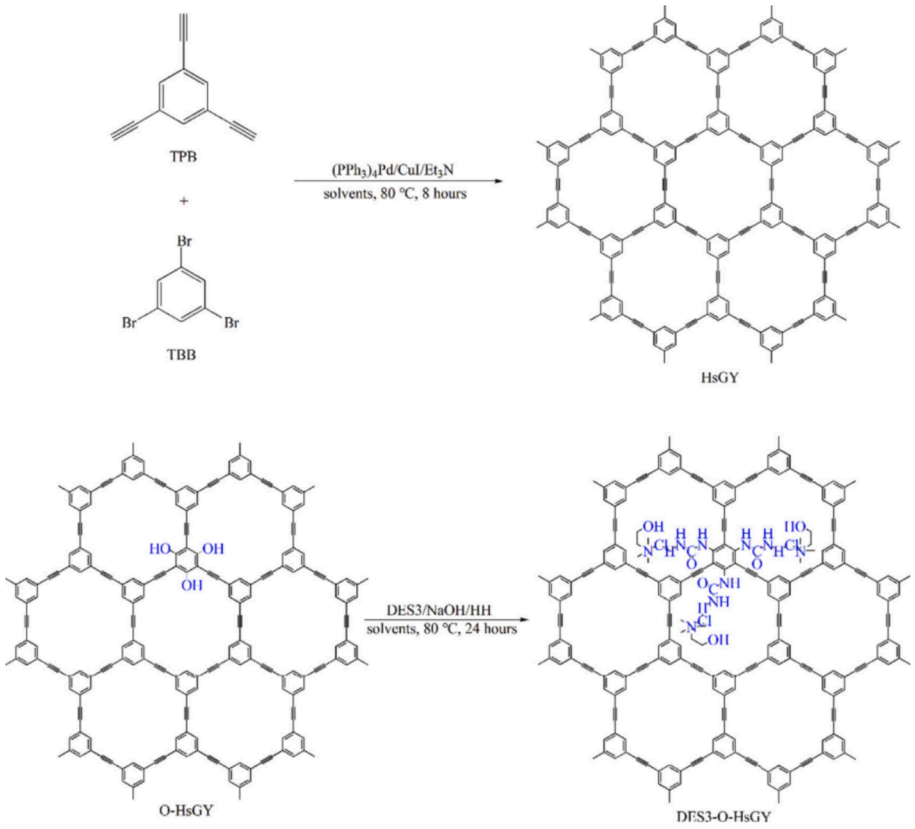


**Fig. 14.** Synthesis of HsGYs and structure of the DES functionalized HsGY (eximplified using ChCl:m-cresol DES). Copyright 2021 Elsevier B. V. [135].

MlnA 1:1) as a functional monomer. The adsorption efficiency of the five different azo and aromatic groups was in the range of 92.4 – 96.0 %. The study was complemented with further theoretical investigations regarding the DES-ADS/Analyte interactions, and the obtained adsorbents were also tested on a spiked industrial waste sample.

### *4.6. Other applications*

In addition to the previous applications of DES-ADS in numerous fields, some studies applied DES-ADS in the adsorption of

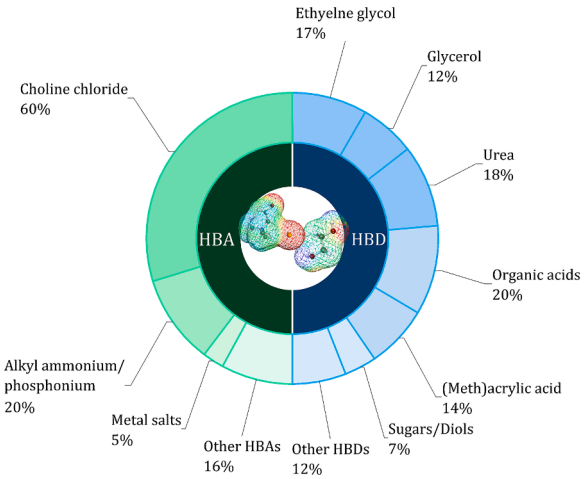


**Fig. 15.** Different genres of HBAs and HBDs used for DES formation in the development of DES-based adsorbents (from 2010 to 2024).

**Table 19**
Use cases of ChCl-based DESs with urea (HBD) across different applications.

| DES | | Ratio | Role | Function | Adsorbent material | Target analyte | Performance | Ref |
|---|---|---|---|---|---|---|---|---|
| HBA | HBD | HBA:HBD | | | | | (mg/g) [E%] | |
| C-ChCl | U | 1:2 | Functionalization | | Cotton fibers | Hyaluronic acid | 351.3* | [114] |
| | | | Synthesis | Reaction medium / cationization agent | Cellulose | Red 70 | 29.2^ [83.3%] | [2] |
| ChCl | U | 1:2 | Functionalization | | $Fe_3O_4$-GO | MB | [~100%] | [14] |
| | | | Functionalization | | Peanut shell | Cr (VI) | 5.36 | [42] |
| | | | Functionalization | | FeO-Chitosan | AB 80 | 61.64 | [26] |
| | | | Functionalization | | Chitosan | MG | 78.13* | [20] |
| | | | Functionalization | Reaction medium / reagent | Chitosan | MG | 6.54 | [15] |
| | | | Synthesis | Reaction medium | Silica-tris(indolyl)methane | Benzoic acid | 0.418 | [86] |
| | | | Synthesis | Reaction medium | CoFeO | CR | 305 [95%] | [1] |
| | | | Synthesis | Reaction medium | LTO | $Pb^{2+}$ | [96%] | [41] |

* Reported $Q_{max}$ value
^ Reported $Q_e$ value

**Table 20**
Use cases of ChCl-based DESs with ethylene glycol (HBD) across different applications.

| DES | | Ratio | Role | Function | Adsorbent material | Target analyte | Performance | Ref |
|---|---|---|---|---|---|---|---|---|
| HBA | HBD | HBA: HBD | | | | | (mg/g) [E%] | |
| ChCl | TEG | 1:3 | Functionalization | | CNT | $Pb^{2+}$ | 288.4* | [29] |
| ChCl | EG:CA | 5:5:1 | Functionalization | Functional monomer | $Fe_3O_4$-MIP-BN | Quercetin | ~5.25 [96.8 %] | [104] |
| ChCl | EG: MalA | 6:6:2 | Functionalization | Functional monomer | MIP | Metronidazole | 11.53* | [117] |
| ChCl | EG | 1:2 | Functionalization | | CNT | 2,4-dichlorophenol | 390.53* | [62] |
| | | | Functionalization | | CNT | MO | 310.2* | [3] |
| | | | Functionalization | | $Fe_3O_4$-GO | BSA | ~44 | [127] |
| | | | Functionalization | | HsGY | Thiabendazole | 0.85 | [116] |
| ChCl | EG | 1:16.725 | Synthesis | Porogen | MIP-molecular sieve (SBA15) | Glularylated peptide | 8.35* | [83] |
| ChCl | EG | 1:4 | Synthesis | Reaction medium/Solvent | Chitosan-MI (hydrogel) | Salicylic acid | 106.5 | [58] |
| ChCl | EG | 1:2 | Synthesis | Solvent | CNT (nanofluid) | Triazolein juice(in Tea) | 4.55-17.98 (3.24-11.63) | [90] |
| | | | Synthesis | Solvent | Keratin | Norfloxacin | 79.36* | [50] |
| | | | Synthesis | Reaction medium/Solvent | MIR | Ofloxacin | 32.92* | [46] |
| | | | Synthesis | Carrier solvent | $Fe_3O_4$-GO | Ofloxacin | [>70.3%] | [56] |
| | | | Synthesis | Carrier solvent | $Fe_3O_4$-GO | Sparfloxacin | [>70.3%] | [56] |
| | | | Synthesis | Reaction medium - mesoporosity agents | Chondroitin sulfate | $Pb^{2+}$ | 55* | [35] |
| | | | Synthesis | Reaction medium - mesoporosity agents | Fucoidan | $Pb^{2+}$ | 79* | [35] |
| | | | Synthesis | Reaction medium | $NiSO_4$ | MB | 19.56-24.38 | [23] |
| | | | Synthesis | Reaction medium - reducing agent | $MnO_2$ | MB | 253 | [11] |
| ChCl | EG | - | Synthesis | Reaction solvent | Eutectogel | CV | [>90%] | [24] |

^Reported $Q_e$ value
* Reported $Q_{max}$ value

compounds (Table 10) that are not strictly categorized within the fields of Fig. 4. For instance, the isolation of hyaluronic acid from a bacterial culture (*B. subtilis*) solution was tested using DES-functionalized cotton fibers [131]. The quaternary ammonium-based DES (Chloro ChCl:Urea 1:2) was used to functionalize cotton fibers leading to a maximum adsorption capacity of 351.3 $mg.g^{-1}$. A study by Cecone et al. [132] evaluated the synthesis of β-cyclodextrin polymers in ChCl:CA DES. The main function of the DES was to serve as a reaction medium to replace conventional toxic solutions, but the process enabled the fine-tuning of β-cyclodextrin to form positively charged water-soluble hyperbranched polymer structures. The polymers were ultimately tested for different target analytes, such as MB, MO dyes and caffeine. The use of ChCl with other organic acids, such as MalA [133] or a CafA:FA [134] combination was also used for the preparation of MIPs; the later DES was used to prepare a magnetic ($Fe_3O_4$-based) MIP-$SiO_2$ adsorbents for the detection of different glucocorticoids in commercial lotion samples. Moreover, hydrogen-substituted graphyne (HsGY) was synthesized in a ChCl:EG 1:2 as a reaction medium [135], and, in a later study by the same group, a ChCl:Catecol 1:2 DES was used to modify the properties of HsGY [136]. The resulting material was tested for electrochemical and adsorption applications in both studies. Lastly, and perhaps distinctively, the non-ionic DES Menthol:Thymol 1;1, which is a classical type-V hydrophobic DES, was used as a swelling agent in the synthesis of a fluorescent-based MIP probe for the detection of sertraline in human urine samples [137]. The presence of the hydrophobic DES positively affected the adsorption capacity in the developed sensor.

The aforementioned applications are promising with regard to detection limits and adsorption performance. Nevertheless, more studies on functional moieties are required to understand and improve the functionalization/synthesis procedure and introduce specific properties in accordance with the role of the DES. Further in-depth analyses are also required to identify the newly formed DES-ADS and the location and function of the DES (or its components) in the final structure.

## 5. Base materials for DES-based adsorbents preparation

The selection of the adsorbent material for a given application represents perhaps one of the most essential tasks in the adsorption process, where critical factors such as adsorption capacity, selectivity, recyclability, and cost must be considered. In general, selecting an adsorbent is usually done on a case-by-case basis, dictated by the type of application, technical considerations, and past experience [23]. Additionally, an adsorbent material can be synthesized from a combination of different base materials or substrates to add one or more functionalities (e.g., using $Fe_3O_4$ for magnetic characteristics). The chord diagram in Fig. 5 details the different types of adsorbent materials prepared with DESs (DES-ADS). The graph displays information on the (i) type (base material) of the adsorbent, (ii) the percentage (%) of uses of this adsorbent in the DES-Adsorption literature, and (iii) a mapping of occurrences (%) of the adsorbents

prepared in a combination/composite of one or more different base materials.

From this broad perspective (Fig. 5), the major categories of base materials used in DES-ADS are $Fe_3O_4$ (24.4 %), molecularly imprinted polymers (MIPs, 23.8 %), carbon nanotubes (CNTs, 8.8 %), Chitosan/Cellulosic material (Chit/Cl, 8.1 %), metal oxides & hydroxides (MO, 6.9 %), and graphene oxide (GO, 6.3 %). A few other reports considered the use of Biochar (Bio, 4.4 %) silica particles (Si, 3.8 %), cyclodextrin (3.1 %), and metal organic frameworks (MOFs, 2.5 %). A detailed listing of the studies in each category, the composite material, the DES used and its role in the preparation of the DES-ADS are available in Tables 11-17. The category labeled "*Others*" (15.6 %) constitutes a significant portion of adsorbents. However, these adsorbents were investigated once or twice within the literature and thus were not classified within a separate category. Table 18 separately lists the different base materials within this category. The composite DES-ADS are mostly prepared from a binary combination of the base materials in Fig. 5. Adsorbents prepared combining three base materials have also been reported, specifically with $Fe_3O_4$–MIPs (7.5 %). The subsections below highlight the major materials utilized in the preparation of DES-based adsorbents, along with their distinctive characteristics as adsorbents.

### 5.1. *Molecularly imprinted polymers*

Molecular imprinting (MI) is an advanced technology that creates template-shaped voids within a polymer matrix by stimulating molecular recognition properties in synthetic polymers towards targeted molecules [138,139]. This technique is commonly applied in analytical chemistry in processes such as solid-phase extraction (SPE), the development of chemical sensors, and $CO_2$ capture technologies [96]. Generally, several reagents acting as template molecules, functional monomers, crosslinking monomers, porogenic solvents, and radical initiators are used in the synthesis of molecularly imprinted polymers (MIPs) [140]. In essence, the template molecule and the functional monomers are copolymerized in the presence of the crosslinker and initiator through covalent, non-covalent, or semi-covalent imprinting schemes. Later, the imprinted template molecules are removed from the template-polymer complex using a solvent, leaving specific binding sites or cavities suitable for rebinding with the target analyte.

The target compound to be extracted is usually added to the imprinted polymer to create such specific binding sites. The functional

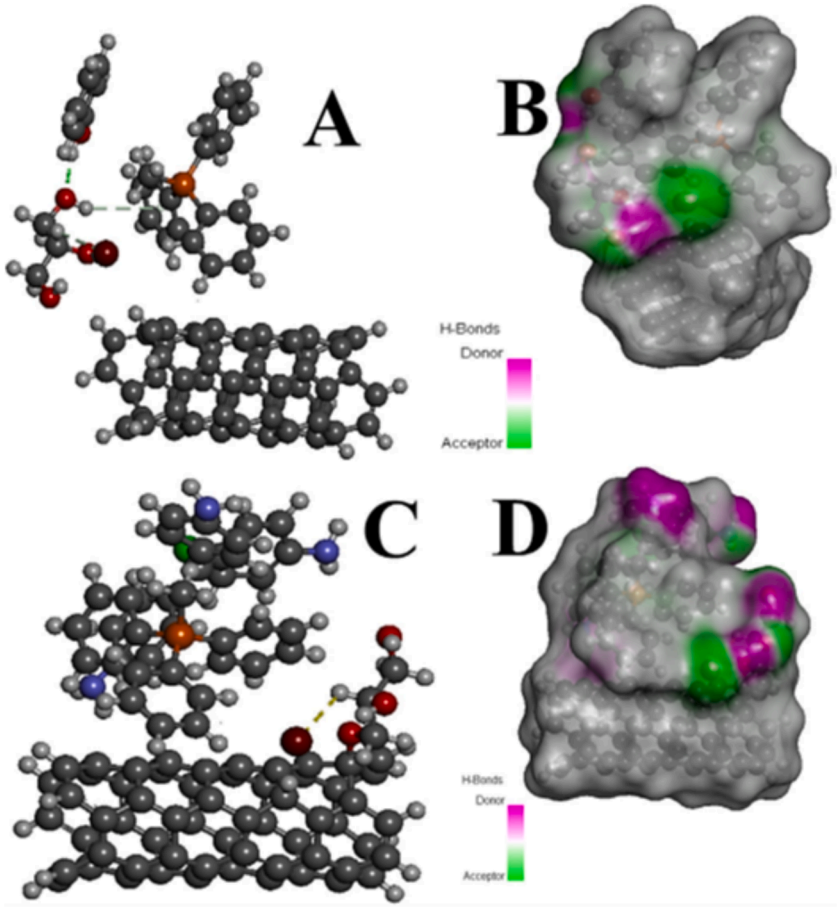


**Fig. 16.** Hydrogen bonds in CNT–DES adsorption of PHE (A & B) and CV (C & D) using; black = carbon, white = hydrogen, red = oxygen, brown = bromine, orange = phosphorous. Analysis from Lawal et al. [29]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

monomer should contain polymerizable and polar functional groups that enable it to connect to crosslinkers with similar functional groups. Porogenic agents (or porogens) are required to create the macroporous structure of MIPs, in addition to their role as reaction solvents. Porogens can affect the internal pore size and particle homogeneity of the polymer by increasing its surface area and the available number of imprinting sites. Different solvents are used as porogenic agents, including ethylene glycol dimethacrylate (EGDMA), toluene, acetonitrile, and chloroform.

Recently, DESs have been extensively explored in the synthesis of MIPs to improve the greenness of the synthesis procedure. DESs can be involved in the synthesis of MIPs as functional monomers, crosslinkers, porogens, or modifiers. It can be noted from Fig. 5 that DES-based MIPs can be synthesized with magnetite/iron (II, III) oxide ($Fe_3O_4$) to enable their use in MSPE processes. DES-MIP adsorbents comprise a total of 23.8 % of all DES-based adsorbents in the literature; 16.3 % as single/binary substrate material and 7.5 % as ternary substrate material. It can be noted as well (Tables 11-12) that most of the DESs used in the preparation of MIPs were used as functional monomers, which means that the HBAs and HBDs in such DESs contain polymerizable substances (e.g., MAA) as will be discussed in the following sections. The addition of DESs in the synthesis procedure of MIPs contributed to enhancing their selectivity and adsorption capacity.[21] Moreover, one of the primary objectives of using DESs in the synthesis of MIPs is to utilize environmentally friendly and cheap components such as those present in some DESs. MIPs are conventionally prepared in toxic organic solvents, which reduces the compatibility and molecular recognition of the target analytes in aqueous environments and to the associated environmental implications [92]. For this, certain DESs can be used as co-solvents or as a reaction medium to limit the use of hazardous organic solvents and to synthesize water-compatible MIPs [82,92]. A couple of studies targeting the removal of pharmaceutical products from wastewater considered the synthesis of chitosan-based molecularly imprinted hydrogel and MIRs in ChCl:EG DES as a reaction solvent. Other studies tested the use of ChCl-based DESs as porogens [100], while many studies mainly used DESs with HBDs of MAA, CafA:FA among other organic acids to be used as functional monomers for the synthesis of MIPs [22,113,129].

Here, the study considering DES-MIP composites are quantitively mapped (Fig. 6) in terms of DES used, target molecule, and field of application. The prevalent use of this type of DES-ADS in targeting organic molecules is notable, given the specificity of such molecules, which requires the construction of customized cavities or binding sites for their adsorption, as discussed previously (*sections 4.2 and 4.3*). Moreover, among these studies, nearly one third have considered using MIPs along without an addition base material or composite. A recent report provided a critique on the topic, with a detailed listing of the DES used within the field of MIPs [22]. Noteworthy, it was pointed out that properties of DESs were not considered during the utilization of DESs within MIP synthesis, calling out for a deeper understanding of the thermal behavior of DESs at the molecular level, as it is necessary for effective utilization in molecular imprinting. Such understanding is also required to evaluate the stability of DESs and prevent any hindering side reactions, such as decomposition and volatilization, during polymerization mixtures.

### 5.2. Carbon nanotubes (CNTs)

CNTs are tube-like materials consisting of a rolled sheet of carbon atoms to form hollow cylindrical tubes with a diameter of less than 1 nm and a thickness of one atom approximately [141]. The unique properties of CNTs with regard to their structural and functional properties attracted scientific and industrial interest. Moreover, CNTs exhibit exceptional electrical properties as they are capable of electrical conduction along with their nano-scale size and high aspect ratio [142]. Such properties rendered CNTs as potential candidates in different applications such as polymer composite reinforcement, microelectronics, and biotechnology [143]. Lately, DESs have been explored in the synthesis of CNT adsorbents as functionalization agents or for surface modification purposes.

In essence, DES-based CNTs were mostly used without hybridization with other materials, except for a few reports on the synthesis of DES-based CNTs with metal oxide hybrids. This could be attributed to the unique properties of CNTs which are further enhanced by the functionalities of added DESs, making such materials stand as viable and efficient adsorbents without needing a hybrid or composite additive. Nevertheless, regarding the analyzed papers within the scope of this review, it was found that the majority of functionalized CNTs with DESs were reported by the same group of AlOmar *et al.* [74,76] following the same protocol and using multiwalled CNT solely with different DESs as functionalization agents. These studies reported the preparation of an oxidized form of MWCNTs (using $KMnO_4$), then functionalized with different alkylammonium-based DESs to enhance the adsorption capacity toward heavy metals among other target analytes. Lawal et al. [65] followed the same synthesis procedure to prepare DES-functionalized CNTs, supported by an in-depth theoretical investigation of the adsorbent-adsorbate interactions. As for the other studies, coupling CNTs with other metal oxides, CNT-$ZnCo_2O_4$ [65] and MWCNT-$MnFe_2O_4$ [128] were reported for the adsorption of Eosin Y and Trypsin, respectively. In a more recent study, an oxidized form of hydrogen-substituted graphyne was functionalized with different DESs and later composited with MWCNTs [136]. It was reported that the modification with DES (ChCl:Cathecol 1:2) affected the pi-pi conjugation of graphyne to enhance its adsorption capacity towards myricetin, while the CNTs contributed to enhancing the porosity of the composite adsorbents.

### 5.3. Graphene oxide

Graphene is a two-dimensional (2D) nanomaterial of $sp^2$ carbon atoms arranged into a honeycomb (hexagonal) lattice [144]. Graphene is generally available in its original pristine form as graphene oxide (GO), or as reduced graphene oxide (rGO). GO simply results from the oxidation of graphite in protonated solvents, in which the stacking of GO into multiple layers forms graphite oxide [145]. Graphene-based nanomaterials have been the focus of researchers in many fields due to their attractive features, such as electrical conductivity, high mechanical strength, and high surface area [146]. As a result, graphene materials were also investigated for their potential application in water treatment and purification.

Regarding incorporating DESs in GO-based adsorbent materials, most of the examined studies reported the use of magnetic GO adsorbents ($Fe_3O_4$-GO). The extensive use of $Fe_3O_4$ in combination with GO could be due to the magnetic properties endowed by $Fe_3O_4$, leading to an enhanced and easier separation of the GO from the feed after adsorption takes place. The role of the DES herein is mainly for the functionalization of the adsorbents to enhance the adsorption capacity through the introduction of different moieties. For instance, functionalizing $Fe_3O_4$-GO with the ternary DES ChCl:ItA:MPrA (2:1:1) introduced S-H groups on the surface of the magnetic adsorbent, yielding better adsorption capacity toward $Hg^{+2}$ [78]. Furthermore, a couple of studies synthesized a ternary adsorbent with $Fe_3O_4$-MIP-GO to harness the magnetic properties of $Fe_3O_4$, the high surface area of GO, and the selective binding sites of MIPs [147,148]. The role of the DES in this case is to introduce the functional monomers [147], or even the template, for the MIPs [148]. In other cases, similar DES components to that used in MIP synthesis can be used for preparing poly(DES)s [61]. An example is the synthesis of GO-based adsorbents functionalized with a ChCl:MAA 1:2 DES for the solid phase extraction of Indole-3-carbinol [112].

Another important role of the DESs during the synthesis of GO-based adsorbents is the excellent dispersibility it provides. For instance, GO-based monolithic chips with good homogeneity and permeability were synthesized in ChCl:EG 1:2 DES as porogens [91]. Additionally, one study simply investigated the dispersion and ultrasonication of $Fe_3O_4$-GO in the same DES (ChCl:EG 1:2) to produce ferrofluid. The GO-based ferrofluid was used in a liquid phase microextraction setting, but given its gel-like form, the same adsorption experiments were applicable. In another study, CNT nanofluids were prepared in a similar method [110].

### 5.4. *Metal organic frameworks*

Another heavily researched emerging class of nanomaterials is metal organic frameworks (MOFs), which are significantly characterized by their unique geometric and highly porous structures [149]. MOFs are characterize by their crystalline structure, ease of synthesis, and have high specific surface area and tunable functionalities [150]. They consist of metal ions or clusters and organic ligands; Hence, with various pairs of different metal ions/clusters and different organic ligands, the number of MOF variations is vast [151]. The metal ions/clusters are coordination centers that form a crystalline structure connected by fixed bonds [149]. Due to the promising characteristics of such materials, there has been a notably rapid increase in MOFs development and usage in the past few decades in different fields such as catalysis, energy storage, photoreduction, electrochemical applications and adsorption technology [149,152]. The high surface area of MOFs allows such materials to specifically adsorb certain contaminants efficiently. While few studies reported the utilization of DESs in the synthesis and functionalization of MOFs, it is noted that MOFs with DESs were not used without hybridization with other materials such as $Fe_3O_4$ and MIPs. Furthermore, within the framework of this review (i.e., adsorption-related), the reports on MOFs functionalized with DESs seem to be carried out by just certain research groups [97,115,153]. One study by Wei et al. [61] investigated the synthesis of an amino magnetic ($Fe_3O_4$-$NH_2$) HKUST MOFs functionalized via DES with polymeric constituents 3-acrylamidopropyl trimethylammonium chloride as HBA and D-sorbitol as HBD (Fig. 7**a**). The resulting adsorbent exhibited specific and selective extraction for several cationic dyes. Another study by the same group used quaternary ammonium-based DESs to regulate magnetic MUiO-66-$NH_2$ MOFs during synthesis (Fig. 7**b**) [153]. It was concluded that the structure of the DES affected the selectivity of the MUiO-66-$NH_2$ towards different types of PPCPs, elucidating the strength and importance of selecting adequate designer's solvents for the desired target analyte. A couple of studies reported the syntheses of MOF-MIP composites

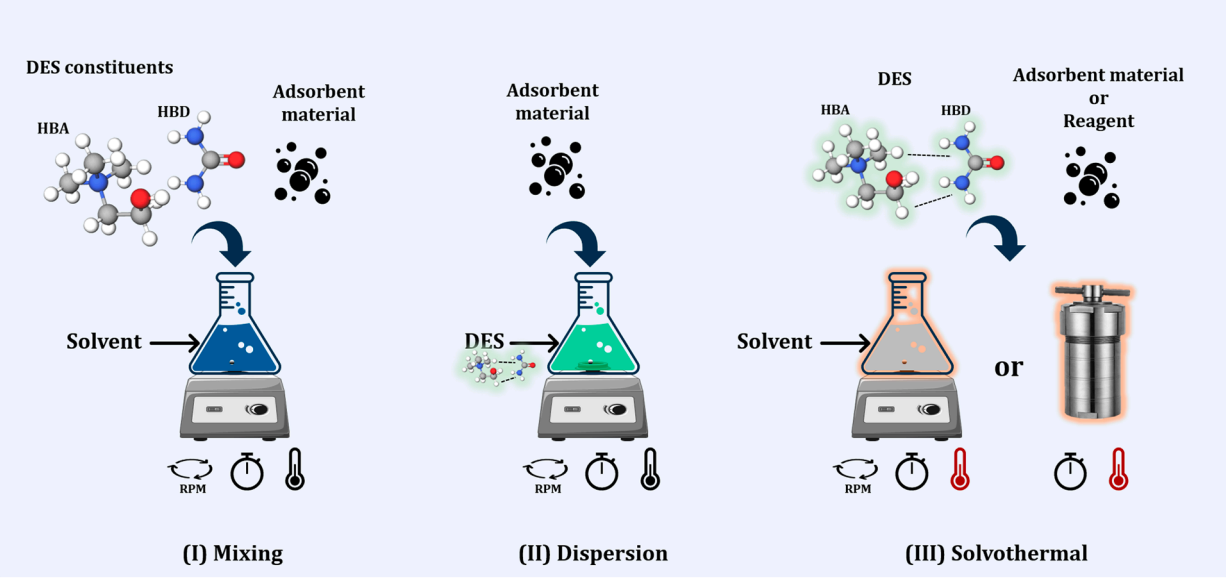


**Fig. 17.** The major synthesis routes used for incorporating DESs with adsorbents in the literature.

using MOF UMCM-1 [115] and MOF-199 [97] to enhance the stability and selectivity of such MOFs.

### 5.5. Metal oxides/hydroxides

Metal oxides (MO) and hydroxides (MOH) stands out as an important class of adsorbents due to their promising adsorption performance, availability and low-cost, as well as ease of modification and adsorbent regeneration [154]. Some common examples of metal oxides include chromium oxide ($Cr_2O_3$), zinc oxide, and most importantly, iron (II, III) oxide ($Fe_3O_4$), which will be discussed separately given its ubiquitous magnetic properties and its inclusion with different adsorbent composites. Examples of common metal hydroxides include lithium hydroxide (LiOH), and potassium hydroxide (KOH) and others. From Fig. 5, it can be noted that MO and MOH were mostly used as standalone adsorbents. For instance, Li et al. [52] reported the synthesis of MgO adsorbents synthesized from Mg-based DES ($MgCl_2{\cdot}6H_2O$:Urea 1:2) as a precursor via solvothermal method for the adsorption of different anionic dyes. A later study by the same group reported the synthesis of MgAl layered double hydroxide (LDH) following a similar protocol and DES [64], with the latter using an additional DES ($AlCl_3{\cdot}6H_2O$:PEG 200) to introduce Al into the LDH composite. Similarly, LDH from CoFe oxide were prepared in a ChCl:EG 1:2 as a reaction medium, which was later converted into CoFe spinel oxides [51]. In a different study, using $KMnO_4$ as precursor and DES as reducing agent, $MnO_2$ were synthesized and tested for a couple of applications including, adsorption of MB dye [54]. An earlier study reported the synthesis of the same adsorbent for the adsorption of CR dye, however, with a slightly different synthesis procedure [155].

The use of DES as the precursor material was also applied for the synthesis of Ni-based adsorbents. Shi et al. [53] synthesized a composite adsorbent of $Ni_2CO_3(OH)_2$-$SiO_2$ using $NiCl_2{\cdot}6H_2O$:EG 1:2 as a precursor. The adsorbents were then modified with Si, yielding $Ni_2CO_3(OH)_2$-$SiO_2$ composite tested for the adsorption of CR dye. Different Mesoporous nickel sulfides were also prepared and tested for MB dye adsorption.

Several other MO-based DES-ADS were also synthesized using $TiO_2$ and other derivates. For example, a polymer monolith incorporating $TiO_2$ nanotubes was used for the solid phase separation of BSA [102]; a quaternary ammonium and MAA were used as components for the functional DES to prepare the $TiO_2$-based polymer monolith. More recently, Ti-based composites functionalized with a natural-based DES were synthesized and evaluated for the extraction of heavy metals. On that front, Zhang et al. [126] prepared $Fe_3O_4$-$TiO_2$ adsorbents functionalized with a ternary DES (MalA:Xyl:$H_2O$ 1:1:10) for the determination of Pb and Cu in plants (*Polygonatum kingianum*). The adsorption of other heavy metals was also evaluated using lanthanum titanate (LTO) synthesized with ChCl:EG 1:2 DES [72]. The adsorbent was also tested for other applications, including photocatalytic degrading of reactive dyes.

### 5.6. Iron (II, III) oxide ($Fe_3O_4$)

Iron (II, III) oxide ($Fe_3O_4$) is among the most important metal oxides discussed in the previous section. This section further expands on the use of $Fe_3O_4$ in adsorbent preparation since this type of metal oxides is prevalent in DES-ADS literature. The significant and intensive use of $Fe_3O_4$ is mainly attributed to its unique magnetic properties, which eases the separation and recovery process. In

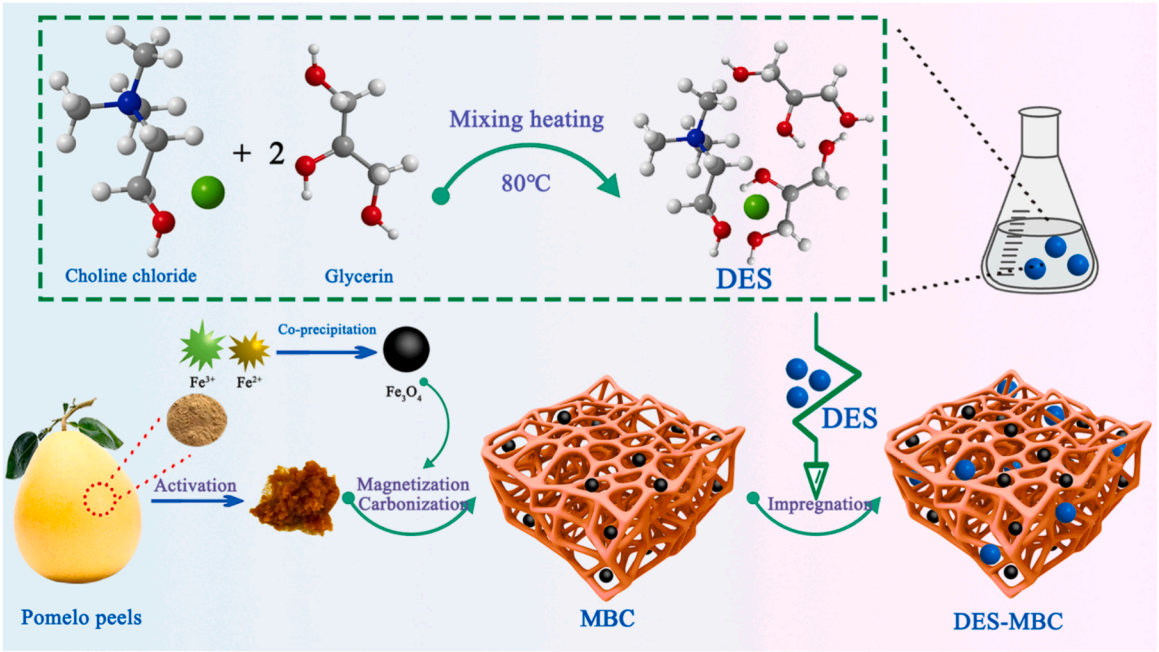


**Fig. 18.** Illustration of the fabrication process of DES impregnated Fe3O4-biochar adsorbents.[170] Copyright 2022 Elsevier B.V.

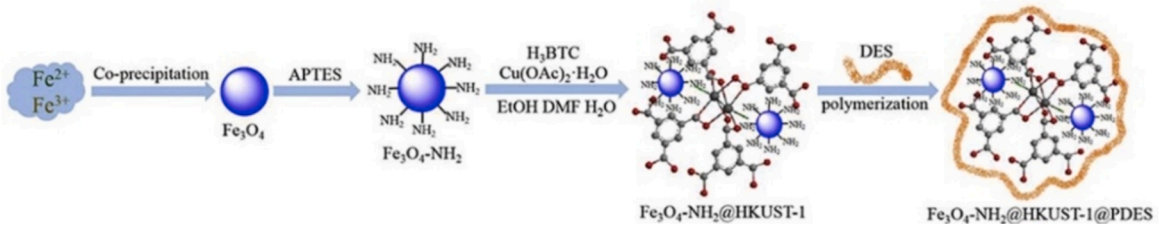


**Fig. 19.** Fabrication of Fe3O4eNH2@HKUST-1@PDES composites [61]. Copyright 2019 Elsevier B.V.

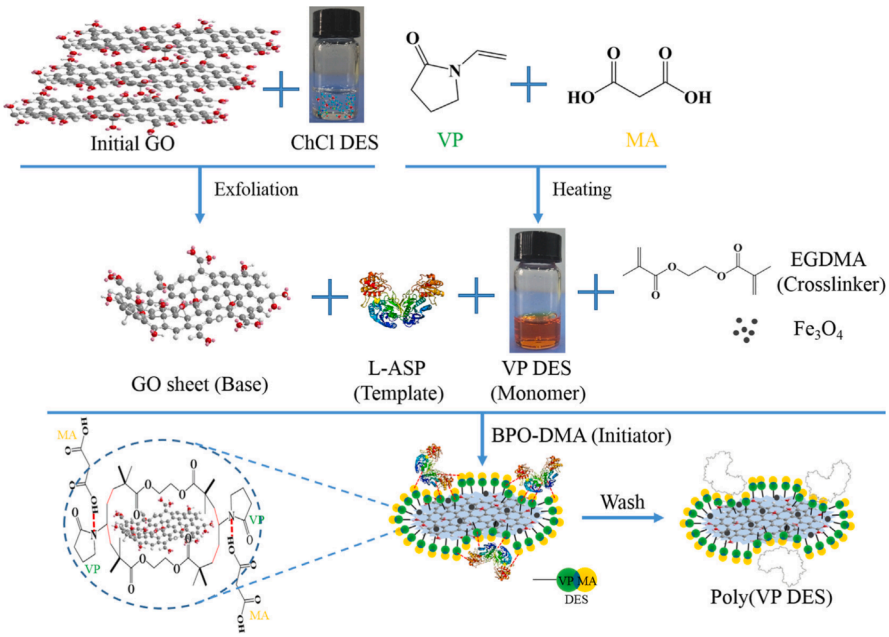


**Fig. 20.** Synthesis of poly(DES)-functionalized GO-MIP composites [147]. Copyright 2019 Elsevier B.V.

addition, the wide availability of this metal oxide also promotes its application, since it occurs naturally in the form of mineral magnetite [156]. In recent years, the application of iron oxide nanomaterials has been intensively explored due to their high versatility, nano-sized particles, ease of synthesis, applicability of coating or surface modification, high surface area to volume ratios, and, most importantly, superparamagnetism [156]. In essence, the incorporation of $Fe_3O_4$ as a base material with other materials for the preparation of DES-ADS amounts to 24.4 % of all the DES-ADS reviewed in this literature (16.9 % as binary composites of $Fe_3O_4$ + adsorbent material and 7.5 % as ternary composites of $Fe_3O_4$-MIP + adsorbent material) as shown in Table 12-13. $Fe_3O_4$-based adsorbents were mostly synthesized in combination with MIPs, followed by GO, MOFs, cyclodextrin, and other materials, respectively. In general, $Fe_3O_4$ can be considered as a complementary base material for the synthesis of efficient adsorbents with magnetic properties for enhanced isolation and separation from the feed solution. Fig. 8. quantitively maps the different DES-ADS incorporating $Fe_3O_4$ and used for various applications. Although there is a prevalent use of $Fe_3O_4$ with MIPs (as base materials) and ChCl (as HBA in DESs), this observation is universal for the whole material database, given the trending application of MIPs and ChCl-based DESs in general. Therefore, given the diverse use of $Fe_3O_4$ with multiple materials, DESs, and applications, the discussion on using $Fe_3O_4$ with each of the materials was allocated in the relevant subsections.

### 5.7. *β-Cyclodextrin*

β-cyclodextrin (β-CD) is a cyclic oligosaccharide that consists of seven α-1,4-linked D-glucopyranoside units, forming a toroidal structure with a hydrophilic exterior and a hydrophobic cavity. The distinctive structure of β-CD facilitates the formation of inclusion complexes with diverse hydrophobic guest molecules, enhancing their solubility, stability, and bioavailability. Moreover, the use of β-CD is manifested in the development of polymeric adsorbent materials, promoted by the hydroxyl functionalities in their structures [157]. Due to their valuable properties such as availability, biocompatibility and biodegradability [158], β-CD were heavily tested in different applications including food, agriculture, pharmaceuticals, and for treating different contaminants from wastewater [159]. It should be noted that incorporating CD with different adsorbents, membranes and other composites has been and still a heavily studied

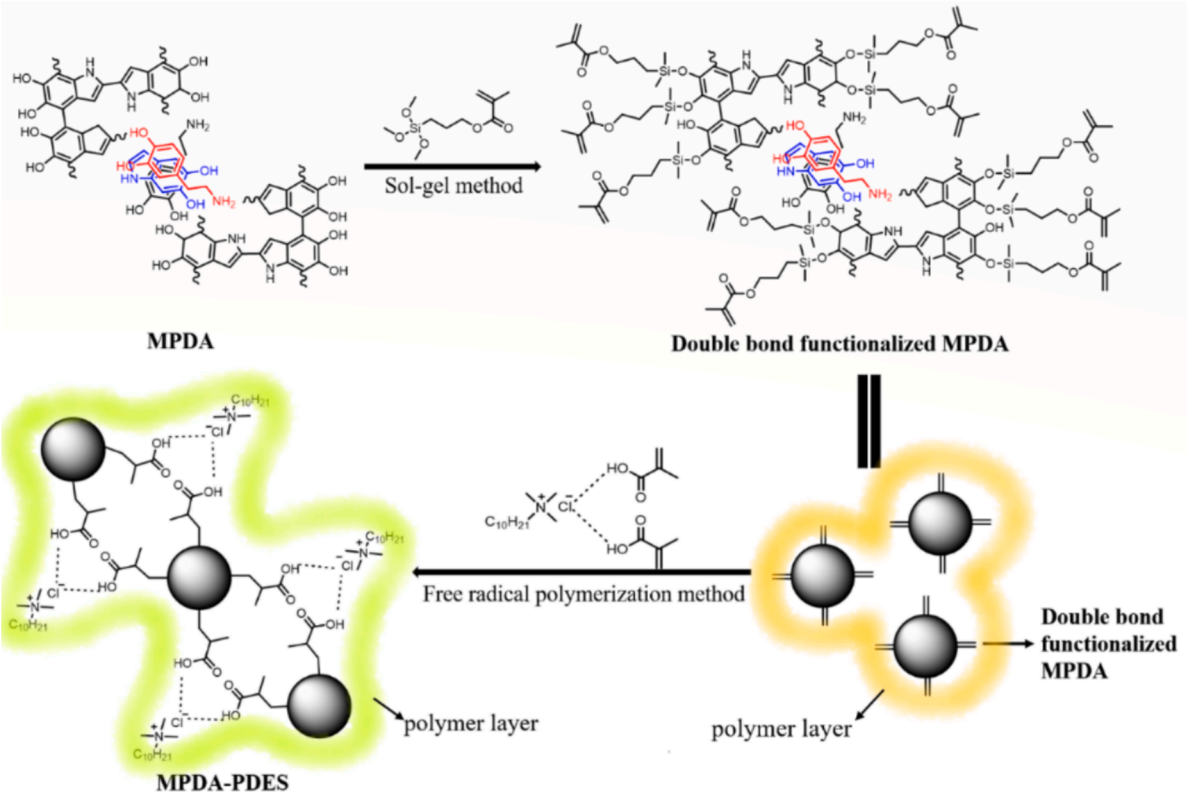


**Fig. 21.** Synthetic routes of double bond functionalized magnetic-polydopamine adsorbents. Copyright 2020 Elsevier B.V. [25].

research field, with thousands of reports published on the topic. The context of this review only reflects upon those reports that considered the use of DESs in the synthesis/functionalization of CD-based adsorbents.

The development of DES-based β-CD adsorbents was primarily via quaternary ammonium-based DESs (Table 16). For instance, magnetic ($Fe_3O_4$) beads of β-CD were prepared using BTMACl:TFAI 1:2 DES for the extraction of trypsin [127]. In another report, combining the same HBA with the functional monomer MAA, a functionalized $Fe_3O_4$-β-CD composite was prepared for the isolation of OVA [103]. Likewise, the separation of another protein (BSA) was also attempted using MIPs of $Fe_3O_4$ β-CD primarily synthesized with MATACl as a functional monomer within the MATACl:ItA 2:1 DES [96]. β-CD adsorbents were also synthesized in DES as a reaction medium containing quaternary ammonium salt (HBA) and citric acid (HBD) [132,157].

### 5.8. *Silica-based materials*

Silicon, one of Earth's most abundant elements, is frequently found in nature in its bonded form with oxygen as silicon oxide ($SiO_2$), also known as silica [160,161]. Silica exhibits a three-dimensional network structure characterized by a central Si atom surrounded by four oxygen atoms, ultimately forming a tetrahedral coordination, constructed through packing [$SiO_4$] units. The maturity, abundance, and ability to use this type of material on the nanoscale enables its use in multiple applications including catalysis, separation,

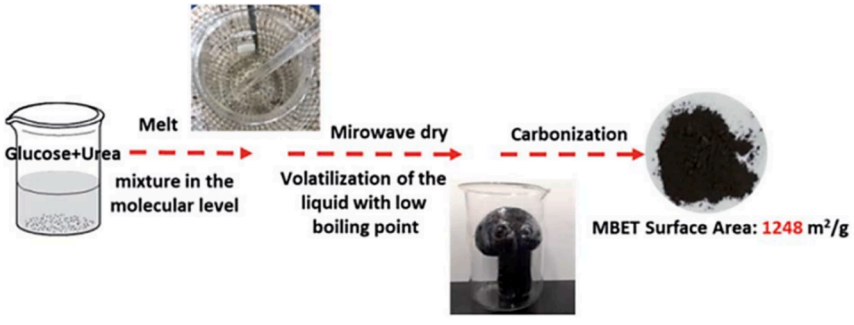


**Fig. 22.** Synthesis of N-doped carbon from Glu:U DES [60]. Copyright 2020 The Royal Society of Chemistry.

and sensors, among others [161]. Moreover, the use of silica nanomaterials also proliferated due to their favorable surface chemistry, chemical inertness, and biocompatibility. Silica material also serves as a suitable platform for functionalization with other materials [119]. The majority of the DES-ADS developed with silica as a base material was in conjunction with other metal oxides and MIPs. For instance, composites of $Fe_3O_4$-MIP-$SiO_2$ were synthesized as DES-ADS using different DESs and for different applications including the adsorption of BHb [95], vanillin [111], Baicalein [119], and Hydrocortisone [134]. The reasoning for using Si-coating was justified for its ability to prevent the aggregation and oxidation of $Fe_3O_4$ particles, thus enhancing its water dispersibility and chemical stability throughout [95,119]. The complementary influence of $SiO_2$ was also evaluated for enhancing the surface properties of $Ni_2CO_3(OH)_2$ nanosheets synthesized in DES; The $Ni_2CO_3(OH)_2$-$SiO_2$ DES-ADS was efficient for the removal of anionic dye (CR) due to the enhanced surface area, porous structure, and strong electrostatic interactions [53]. A more direct use of silica as a DES-ADS was with Wang et al. [104] where the DES was used as a reaction medium for the immobilization of tris(indolyl)methane on silica particles for the SPE of benzoic acid as well as other organic acids. Table 17 shows the studies that incorporated $SiO_2$ within the DES-ADS base material.

### 5.9. Chitosan (Chit) and cellulose nanofibrils (CNF)

Chitosan and Cellulose both are polysaccharides attained from natural biodegradable sources. Chitosan is derived from chitin, a material typically found in the exoskeleton of crustaceans and the cell walls of fungi, whereas cellulose is a natural polymer available in the cell walls of plants. Chitosan, a partially deacetylated product of chitin which mostly consists of β-(1 → 4)-2-amino-2-deoxy-D-glucose units (deacetylated) and a smaller percentage of β-(1 → 4)-2-acetamido-D-glucose (acetylated) [162]. Cellulose, on the other hand is composed of long chains of β-D-glucopyranose joined by β-(1 → 4) glycosidic bonds [163]. CNFs are usually produced via mechanical disintegration and/or chemical/enzymatic breakdown of plant matter. Cellulose-derived materials, particularly CNFs, have been extensively studied. CNFs and chitosan-based adsorbents were evaluated for the removal of a number of pollutants from water, including heavy metals, dyes [162,163], and pharmaceuticals [162].

About 8.1 % of the reviewed DES-ADS have used an adsorbent based on chitosan or CNFs material (Table 16), half of which targeted dye removal. In general, the insolubility of cellulose in water and in many organic solvents presents a challenge in its processing and chemical treatment. Hence, using DESs provided an alternative green media for cellulose dissolution, processing and treatment [164]. On that front, a cellulose monolith was synthesized in and functionalized with a chloro ChCl:U 1:2 DES; The cationic functionalized cellulose adsorbent was used for the removal of anionic dye (red 70) [165]. Similarly, the synthesis of cationized dialdehyde cellulose was carried out in an amino GA-HCL:Gly 1:2 DES for the adsorption of anionic dye chrome azurol S [66]. Likewise, the use of DES as a reaction solvent was also tested for the carboxylation of cellulose for the adsorption of MB dye [166]. In a different study, Selkälä et al. [85] used LiCl:U 1:5 DES as a reaction medium for the sacculation of CNFs. The resulting anionic CNFs were used for the removal of salbutamol from aqueous streams. Cellulose was also used in conjunction with other base materials, including a trio of cellulose-functionalized $Fe_3O_4$-MIP [109]. The DES herein was also used for dissolving cellulose and as a reaction medium for the subsequent synthesis phases, where the final DES-ADS was used for the adsorption of bisphenols.

With regards to chitosan-based DES-ADS, some studies used Chit DES-ADS either as stand alone, or as a composite with other base materials for different applications, including the adsorption of dyes, pharmaceuticals, and bioactive compounds from biomass. The major role of the DES in most cases was also as a reaction medium. For instance, Sadiq et al. [167] dissolved chitosan material in a CTEABr:U 1:2 DES, then later suspended in a basic 0.5 M NaOH solution to form chitosan beads. The beads were subsequently used to remove MG dye. In a later study [168], the same group used a similar approach for the removal of MG, however using a ChCl:U 1:2 DES this time. The synthesis of a composite $Fe_3O_4$-MIP-chitosan was also attempted for the adsorption of different catechins [116], where a DES incorporating MAA as the HBD was used to provide the needed functional monomers for the MIP synthesis, $Fe_3O_4$ used for the magnetic phase separation process, and chitosan as the DES-ADS base material. Similarly, an $Fe_3O_4$-Chit composite was used for the MSPE of several flavonoids from *Epimedium folium* [169]. The studies that used both cellulosic and chit materials within the framework of DES-ADS applications are listed in Table 16.

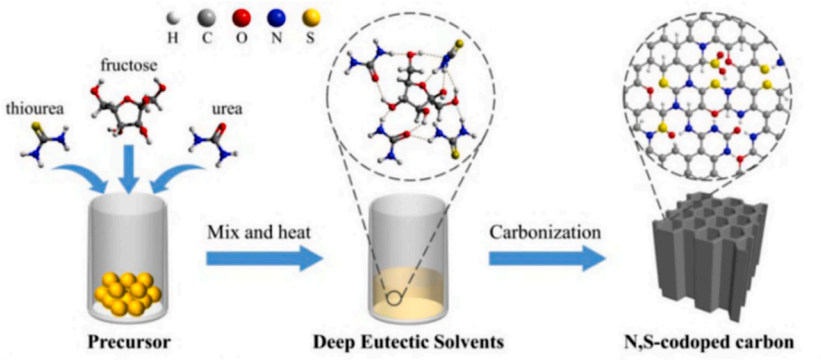


**Fig. 23.** Synthesis process for N,S-codoped carbon [71]. Copyright 2021 Elsevier B.V.

### 5.10. Biomass-based materials

Biochar and biomass-based adsorbents are a class of adsorbents usually derived from biomass residue or, in the case of biochar, the carbonization or thermal decomposition of such residue. The resulting material functions as a viable adsorbent for extracting organic and inorganic contaminants. Such adsorbents are usually cost effective to produce, making them a viable option for several applications in $CO_2$ absorption as well as water and wastewater treatment. The development of biomass-derived adsorbents with the aid of DESs is mainly to add different functionalities for enhancing the adsorption process. For instance, Li et al. [130] developed an adsorbent from sorghum powder in DES (VP:MlnA 1:1) (Fig. 9); The resulting poly(DES)-biomass adsorbent was used for the removal of different azo/aromatic toxic compounds, leveraging the physical and chemical interactions promoted by the additional functional groups. MD simulations were performed to further understand the interactions between the poly(DES)-functionalized biomass adsorbents and the target DNA-T-Cs, of which it was concluded (based on the bonds' length) that adsorption was facilitated by the collective effects of physical interactions as shown in Fig. 10.

Several research groups also used different biomass-based adsorbents synthesized/functionalized with DES for the adsorption of Cr (VI). For example, the use of the conventional ChCl:U 1:2 DES for functionalization of peanut shells was investigated for Cr(VI) removal [68]. Moreover, a ChCl:p-tsOH 1:1 DES was used as a precursor for biochar synthesis by Zhang et al. [70] targeting the same Cr(VI) analyte. Likewise, nitrogen-doped magnetic biochar was prepared by Ke et. [69] from $FeCl_3$:U 2:1 as a precursor material. The inclusion of $FeCl_3$ within the DES constituents forged the magnetic properties of the final DES-ADS which in turn removed Cr(VI) via different mechanisms.

In a different study by Huang et al. [170], ChCl:Gly 1:2 DES was impregnated in magnetic-biochar adsorbents from pomelo peels; the DES-ADS was then used for the removal of methcathinone from water, taking advantage of the reaction sites presumably provided by the DES functionalization; Further in-depth DFT simulations elaborated the role of such constituents during the adsorption process,

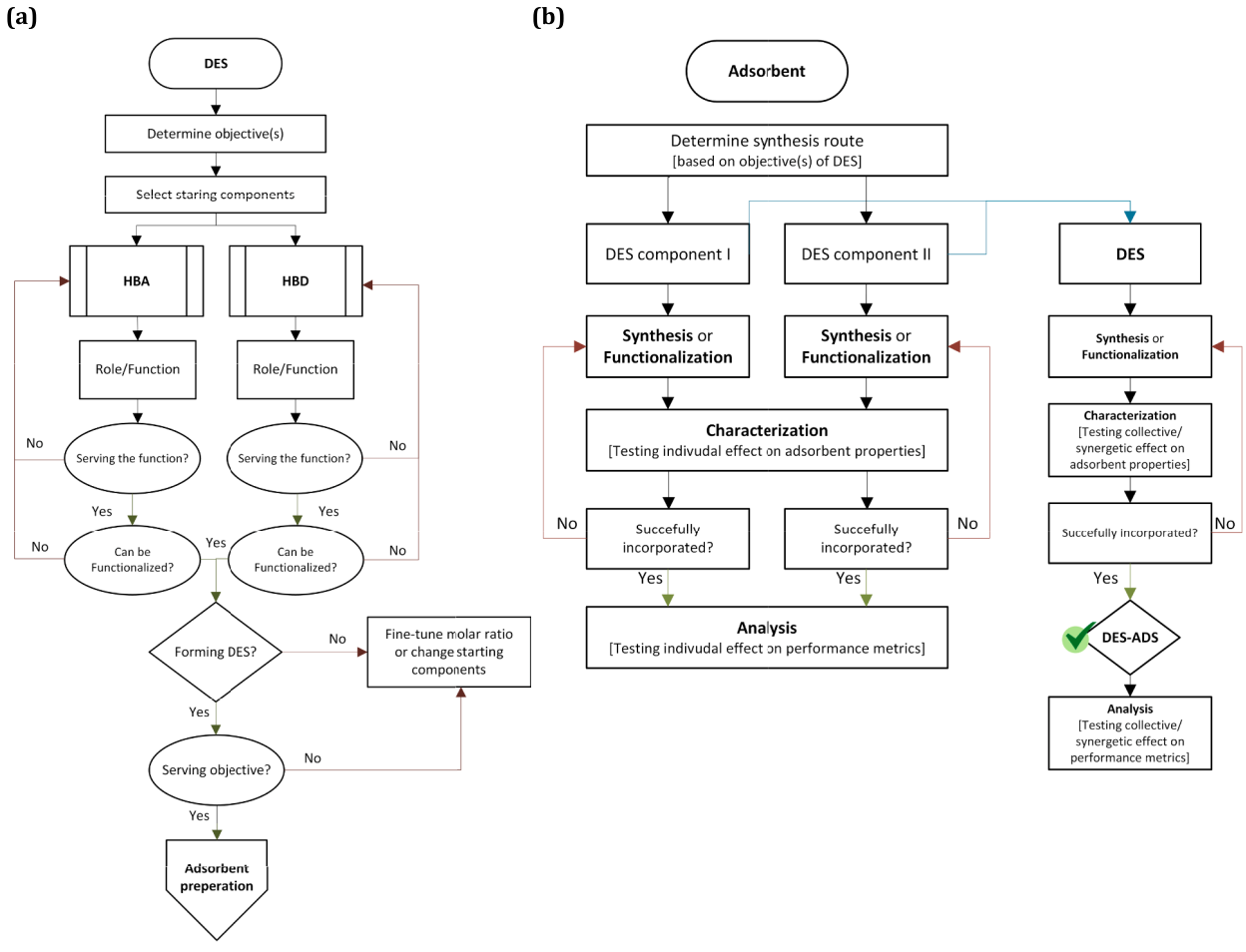


**Fig. 24.** Flow chart for (a) the selection and preparation of DES based on function and compatibility with adsorbent; (b) the development of DES-ADS through sequential investigation of the influence of DES' components. Notes: these flow charts have been generalized to encompass the different DES objectives, functions and adsorbent synthesis routes. This does not mean that all steps are strictly required for successful DES-ADS development for any particular application, but rather it varies based on objective(s) and synthesis routes.

including the provision of electrostatic interactions, π-π interactions, and hydrogen bonding. Other studies also considered the functionalization of biochar using ChCl-based DESs as detailed in Table 16.

### 5.11. Other DES-ADS

Aside from the above-mentioned categories, there are DES-ADS derived from other base materials that – within the context of this review – have been reported once or twice, and therefore, were unclassified into a specific category. Such adsorbents include different carbon materials such as polydopamine, N-doped porous carbon, covalent organic frameworks (COV), 2D materials (e.g., boron nitride and molybdenum disulfide), and other plant- and carbon-based materials. Table 18 lists all such materials with their respective target analytes. Several studies have considered the use of different plant-based materials for the preparation of DES-ADS. For instance, Wibowo et al. [131] used cotton fibers functionalized with Chloro ChCl:U 1:2 DES for the adsorption of hyaluronic acid. The final adsorbent is to include a choline molecule (Fig. 11), promoting antimicrobial effect, which ultimately can be used for medical applications. The authors also evaluated the antimicrobial effect of other quaternary ammonium moieties grafted onto the same adsorbent. Likewise, a ChCl-based DES was also tested for the synthesis of lignin-based adsorbents for dye adsorption [171]; The ChCl:EthN 1:6 DES was used to dissolve lignin, of which the final solution was dialyzed and evaporated to obtain lignin nanoparticles, ultimately used to adsorb MB dye.

The use of $Fe_3O_4$ and/or MIPs in conjunction with other base materials have also been reported. On that front, different 2D composite materials have been developed with $Fe_3O_4$-MIP using quaternary ammonium DESs. For instance, Tan et al. [114], synthesized a magnetic ($Fe_3O_4$) zein MIP for the detection of aspartame, where the ternary DES (ChCl:CafA:FA 1:6:1) was used as a functional monomer. Another example is the synthesis of magnetic ($Fe_3O_4$) boron nitride (BN) MIPs, of which a different ternary DES (ChCl:EG:CA 5:5:1) was used to provide the functional monomers for the DES-ADS [172] for the recognition and extraction of different flavonoids. The same research group later investigated a similar DES-ADS, using $MoS_2$ instead of BN, to extract catechins from green tea [173]. The DES used for the $Fe_3O_4$-MIP-$MoS_2$ preparation was also composed of polymerizable constituents (VP:MlnA 1:1) to provide the needed functional monomers for the MIPs. Since VP is mainly used for the monomers, it might be unnecessary to go through the DES preparation step, which will incur more material (MlnA) and energy to synthesize. Therefore, a thorough investigation of each DES constituent's role is required.

In a study by Wei et al. [25], different quaternary ammonium DESs were polymerized on the surface of magnetic polydopamine adsorbents (Fig. 12). The DES coating provided stability and functionality to the polydopamine for the adsorption of different dyes from water. The functionalization method in this work was discussed in *section 8* as an example of the use of polymerizable DES for the preparation of DES-ADS. Different research groups tested carbon-based DES-ADS. For instance, Nitogen-doped porous carbon was synthesized from DES precursors, namely Glucose:U 1:5 [60], of which the amide group (from urea) introduced nitrogen (N-element) within the synthesized carbon material. The constituents of the DES and the molar ratio presumably aided the pore formation during the carbonization process. The attained DES-ADS was used for the adsorption of different pollutants from water, including nitrophenol and MB dye. Another study by Chen et al. [71] investigated the synthesis of N,S-codoped carbon material inducing frustrated Lewis pairs (FLP). The precursors were also composed of a sugar (fructose) and an amide group (urea), however with the inclusion of a ternary constituent (thiourea), which in effect introduced the sulfur atoms within the synthesized carbon material (Fig. 13). The N,S-codoped carbon showed high performance for Cr(VI) adsorption due to the induced FLP from $–NH^{3+}$ and $–SO_2$ groups. The positive and negative electrostatic potential from these groups can act as electrophilic and nucleophilic sites, attracting O and H atoms on $HCrO_4^-$, respectively. The methodology in this work covered the individual effect of doping a single element (N) and the synergetic effect of co-coping both elements (N,S) on the performance of Cr(VI) adsorption.

Among the reviewed works, three relatively recent studies have used different DESs as a reaction medium for the synthesis of COVs, which are a type of crystalline porous materials fabricated via the combination of organic building blocks through covalent bonds. In all three studies, quaternary ammonium DESs were used as a reaction medium for the synthesis of DES-based COVs. Where Gao et al. [93] and Dong et al. [59] both used the solvothermal method in their synthesis procedure, while Xiao et al. [79] maintained the synthesis for an extended duration at room temperature, which can be more favorable to the overall reaction footprint and to the integrity of the DES' structure.

Graphyne, a family of 2D materials composed of carbon allotropes similar to graphene, however with slight variations in atomic arrangement and bonding, has been also investigated for applications in electronics, catalysis, energy storage. A derivative of graphyne, hydrogen-substituted graphyne (HsGY), was also evaluated for its improved ion transport properties and active sites. HsGY has been modified via three ChCl-based DESs in different studies by the same research groups [88,135,136]. The DESs were introduced within the reaction medium used for the functionalization/modification of HsGY (Fig. 14) [135], and ultimately, the DES-modified HsGY were evaluated for their electrochemical properties and the adsorption of different contaminants. Many other base materials were also reported, of which further information can be found in Table 18.

## 6. HBAs and HBDs for DES-based adsorbents

As the selection of an appropriate adsorbent material is essential for the target application, the selection of the right DES used in the synthesis, modification or functionalization of the adsorbent is equally important. One of the features that makes DESs standout from other classical organic solvents is their versatile tunability. DESs can be composed of a wide range of HBAs and HBDs in various molar combinations, enabling the fine-tuning of the DESs' physical, chemical, and thermal properties for a specific task. Regarding adsorption processes, different DESs were utilized (Fig. 15), with the majority composed of HBAs such as ChCl (60 %) or other alkyl

ammonium/phosphonium salts (20 %) along with HBDs such as urea (18 %), EG (17 %) and Gly (12 %). Organic acids were widely used (20 %), especially methacrylic acids and its derivatives (MAA, 14 %). Other types of HBDs, sometimes composed of natural components (e.g., sugars) and diols (7 %) were also used. The following sections discuss each type of HBAs and HBDs and their potential use as DES' constituents within the DES-ADS framework.

### 6.1. Hydrogen bond acceptors (HBAs)

#### 6.1.1. Choline chloride (ChCl)

ChCl was widely adopted for the preparation of DESs, given its low cost and biodegradability. The early generation of novel DESs were actually prepared from a multitude of mixtures of ChCl with other components, especially urea and its derivatives [174]. As for DESs used within adsorption processes, it can be noticed that one-third of the studies used ChCl-based DESs via the specific combinations of ChCl:EG or ChCl:U – at the molar ratio 1:2. Indeed, these particular combinations are from the well-established, thoroughly studied DESs in the literature[32,175]. Nevertheless, most of the studies reviewed herein seems to dismiss the reasoning behind selecting these DESs, while others mention the environmental friendliness as a metric for using them; Although this could be a valid reason for using this particular combination of ChCl-based DES, especially in the case where the DESs are used as an alternate reaction medium in the preparation of the adsorbents [93], yet it requires further investigations to justify using such DES as a functionalization agent for studies with dis-similar applications and target analytes. This is because the mere fact that a DES can be environmentally friendly does not entail its adequacy for the selected application. Table 19 lists the different use cases of the specific combination of ChCl (or C-ChCl) and urea. The ChCl:U 1:2 DES was used as a reaction medium for the synthesis of adsorbents based on different materials including chitosan, cellulose and silica particles, in addition to metal oxides such as CoFeO and LTO. The ChCl:U 1:2 Des was also used for the functionalization agent for various similar materials. The majority of the DES-ADS prepared with ChCl:U 1:2 were used for the extraction of different dyes from water. This is also the case for other DESs with urea as an HBD (***Section 6.2.1***).

As for ChCl:EG, Table 20 lists the various use cases of this DES, with the majority of DESs at the 1:2 HBA:HBD ratio. This particular combination was mostly used for during the synthesis of different adsorbents including magnetic based GO, metal oxides (i.e. $NiSO_4$ and $MnO_2$), eutectogels and other materials. Interestingly, the same DES was used for the functionalization of CNTs which in turn was used in a variety of applications such as the extraction of heavy metals, dyes, phenols and triazoles.

The generic use of ChCl-DESs was recurring in literature, even for other fields other than water and wastewater treatment such as gas separation [179] or electrochemical applications [180]. Nevertheless, certain studies used specific DES constituents for the targeted analyte. For instance, Chen et al. [78] used a ternary DES of ChCl: Itaconic acid: 3-mercaptopropionic acid (2:1:1) to prepare functionalized magnetic GO adsorbents for the extraction of $Hg^{2+}$. ChCl and itaconic acid were used as constituents for DES formation, whereas the hydro sulphonyl group of 3-mercaptopropionic acid provided stronger interactions with $Hg^{2+}$, thereby enhancing its removal. Moreover, Chloro-ChCl:U 1:2 DES was used for the functionalization of cotton fibers as a mean to incorporate quaternary ammonium groups onto the base material, thereby enhancing the adsorption capacity towards hyaluronic acid, which was achieved through electrostatic interactions [131]. In another study chloro-ChCl:U 1:2 DES was utilized to remove acidic red 70 dye. The same DES was used for the cationization of cellulose with trimethylammonium groups through nucleophilic addition [165].

#### 6.1.2. Ammonium/Phosphonium salts

Apart from ChCl, other alkyl ammonium salts were used to prepare DES-based adsorbent. In most cases, the charge within the HBA facilitated the extraction of several compounds through electrostatic attractions. For instance, tetrabutylammonium bromide (TBAB) and N,N-diethylethanol ammonium chloride were used in a DES for the modification, and ultimately, the extraction of As and Hg, respectively [75,76]. The extraction mechanism was proposed to be governed by the interaction of cationic molecules with the HBA's counterion. Only a couple of studies – from the same group – considered using alkyl phosphonium groups as HBAs; with Gly as the HBD. The bromide salts of methyl triphenyl phosphonium (MTPP) and allyl triphenyl phosphonium were used to functionalize MWCNTs for the extraction of As and Hg, respectively [26,74]. In a different study, the same DES (MTPPBr:Gly) was used to functionalize CNTs for phenol and crystal violet dye adsorption [29]. The extraction mechanism for these molecules with the developed adsorbent was governed by physical adsorption through hydrophobic interactions and π-π interactions. Moreover, bond orbital analysis was further conducted on this type of functionalized adsorbents, suggesting that the DES increased the reactivity performance of CNTs towards the adsorption of phenol and crystal violet.

The use of TBAB as HBA with imidazole as HBD was considered for the synthesis of COVs [59]. The TBAB:Imidazole 3:7 DES was used as a reaction solvent, utilizing the DES's low vapor pressure to synthesize the COVs under atmospheric pressure, hence eliminating the use of intricate procedures if conventional organic solvents were to be used. However, a recycling procedure for the DES was not considered in this study.

#### 6.1.3. Other HBAs

In addition to alkylammonium/phosphonium salts, different types of hydrated metal salts, sugars and functional monomers were used as HBAs. For example, a DES based on $MgCl_2{\cdot}6H_2O$:Urea 1:2 was used for the synthesis of MgO microcubes and MgAl layered double hydroxide (LDH) via a solvothermal method [52,64]; both materials had the DES as a precursor. A similar approach was used for the synthesis of $Ni_2CO_3(OH)_2$ nanosheets using NiCl2·6H2O:EG 1:2 as a precursor [53]. The DES $MnCl_2{\cdot}4H_2O$:Acetamide 1:7 was also used to prepare mesoporous α-$MnO_2$ with $KMnO_4$ as a reducing agent [155]. Interestingly, all of these materials – synthesized with DES based on hydrated metal salts – were used for the adsorption of anionic dyes with high efficacy reported for Congo Red (CR). Apparently, the strong electrostatic interactions coupled with hydrogen bonding across the $–NH_2$ group in CR molecules facilitated the

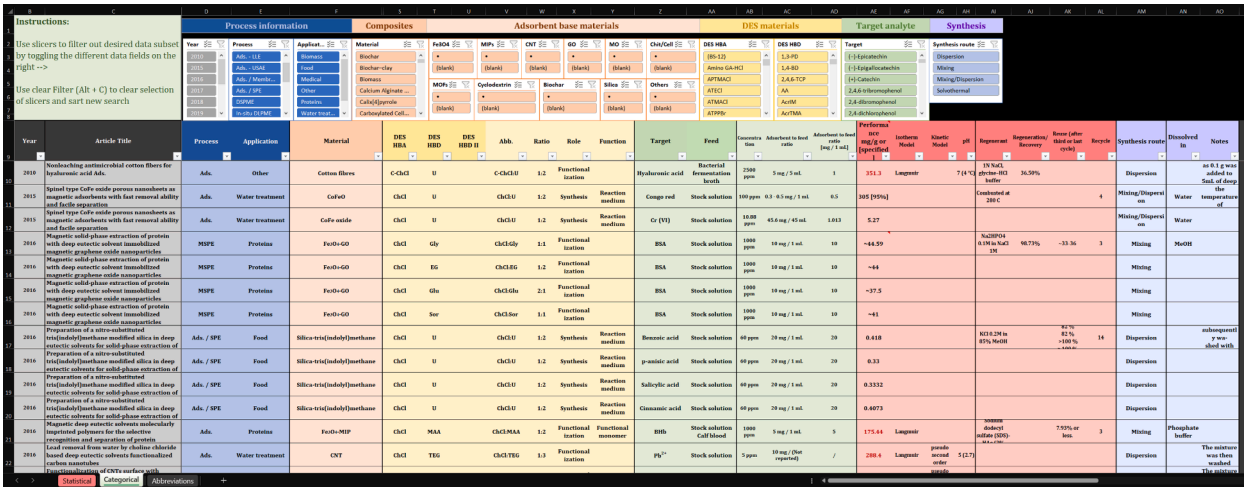


**Fig. 25.** User-friendly Database comprising all the references reviewed on the topic within this work. The database includes other parameters that were not necessarily discussed in this review given the scope of this work such as Adsorption isotherms, Regeneration, and Feed conditions.

adsorption of this dye. Other mechanisms were also suggested such as anion exchange with $Cl^-$ (in the case of MgAl LDH).

DESs derived from natural materials (e.g., sugars, amino acids, organic acids, choline derivative…etc.) received great attention in the literature, leading to sub-treating this class as natural DESs (NADESs) [181]. This genre of DESs fully represents the criteria of a green solvent, justifying the notable traction in this field of research. In the DES-adsorption literature, a couple of studies discussed the use of sugar-based DESs for the development of N-doped [60] and N,S-co-doped [71] carbon material. Using sugars (carbon source) and urea (nitrogen source) the former study considered a mixture of glucose with urea (1:3) to develop the N-doped carbon adsorbents with a strong Lewis basicity. In contrast, the latter study used Fructose:Urea:Thiourea (6:1:3) to construct frustrated Lewis pairs within the N,S-codoped carbon adsorbents.

Lastly, a couple of studies also depended on using DES as a base material for the development of the adsorbents, however, using DESs derived from functional monomers. It is worth mentioning that DESs prepared from polymerizable constituents have been introduced to carry out different polymerization reactions whereby the HBA or the HBD can provide the building blocks (monomers) for the synthesis or modification of a certain material. For instance, the DES comprising vinyl pyrrolidone (VP) as the HBA and malonic acid as the HBD (ratio 1:1) was used in the synthesis of MIPs [117,130,147]. The lone electron pair in the tertiary amine (VP) allows it to act as an HBA; simultaneously, the unsaturated bond of VP can be polymerized into polyvinyl pyrrolidone (PVP). This particular combination VP:MlnA 1:1 was successfully used for the synthesis of MIPs onto the surface of magnetic GO, for the specific adsorption of L-asparaginase. Another study by the former group featured different VP-based DES used to functionalize sorghum powder for the removal of different trace DNA toxic compounds and methyl violet solution. Additionally, the earlier mentioned DES (VP:MlnA 1:1) and procedure were followed to synthesize magnetic $MoS_2$-based MIPs for the removal of several bioactive compounds (i.e., catechins). However, the combination of VP:MlnA 1:1 – or other VP-based DESs for that matter – has not been thoroughly characterized as DESs. Hence, it would be necessary to provide a full analysis of the phase behavior and physicochemical properties of such mixtures as *a priori*.

## 6.2. *Hydrogen bond donors (HBDs)*

### 6.2.1. *Ethylene Glycol, glycerol and urea*

With respect to the hydrogen bond donating group(s), 54 % of the HBDs used for the preparation of DES-based adsorbents include either EG, Gly, or U, of which nearly half were mixed with ChCl as the HBA. In contrast, the remaining were mixed with other quaternary ammonium/phosphonium salts and other HBAs. Most of these DESs were used as functionalization agents for different adsorbents and applications. For instance, the ChCl:EG (1:2) and ChCl:Gly (1:1) were used to functionalize $Fe_3O_4$-GO adsorbents used in the SPE of proteins (e.g., OVA, BSA, Lys, BHb) [27]. The ChCl:EG (1:2) was similarly used to functionalize CNTs for the removal of dichlorophenols, and, in a different study methyl orange, from water [63,89]. The functionalization presumably enhanced the capability of the adsorbents through the introduction of various –OH and –COOH groups from the DES, as well as increasing the surface area of CNT. It was also noticed that the use of these particular HBDs (i.e., EG, Gly or U) is mostly investigated for the adsorption of different cationic and anionic dyes; In fact, two-thirds of the studies concerned with dye removal from aqueous media using DES-based adsorbents used DESs with HBDs as EG, Gly or, mostly, U. However, as mentioned earlier, these model DESs have been used for their promoted characteristic properties without reflection on their role within the context of each adsorption study. An example of this is the use of alkyl ammonium/phosphonium salts (***section 6.1.2***) as HBAs in combinations with EG, Gly and U, for the functionalization of MWCNTs. Several studies by AlOmar & Alsaadi et al. [26,73,74,76] targeted the adsorption of different heavy metals using adsorbents based on such DESs, however, with limited information on the extraction mechanism underpinning the process.

A more detailed analysis of MWCNT functionalization with phosphonium-based DESs was conducted by Lawal et. al, of which the DES characteristics and their effect on the extraction of phenol (PHE) and Crystal Violet (CV) dye was theoretically and experimentally evaluated [29]. A mapping of the hydrogen bonding network among MTTPS:Gly 1:2 DES and the analytes (PHE and CV) are depicted in Fig. 16 for both CNT, and DES-CNT systems. The results suggest a strong hydrogen bonding between the glycerol of the DES with phenol (analyte), and an apparent reaction of glycerol with CNT when CV is adsorbed onto CNT-DES. Although unfunctionalized CNT has more surface area and pore volume than CNT-DES, the adsorption capacity was higher for the latter, indicating that pore trapping is not the main mechanism for the adsorption, but rather it is more driven by electrostatic, hydrophobic, hydrogen bonding and π-π interactions.

#### 6.2.2. Organic acids

DESs prepared from organic acids, especially polymerizable ones (e.g., MAA) have been used for the synthesis of numerous materials aside from DES-based adsorbents. It is important to highlight here, that a stand-alone field of polymer science (free-radical polymerization) has been progressively finding uses for the discoveries made in the field of green solvents, starting by utilizing ionic liquids to introduce various functionalities in the polymer structure (i.e., poly(ILs)), and, recently, the synthesis of different polymer materials and eutectogels using the DES itself as a green reaction medium and/or the DES constituents as functional monomers [182]. On the premise of mixing one of the polymer ingredients as the HBA or HBD of the DES, the resulting mixture can be used for the synthesis of polymeric materials due to the presence of functional monomers, in addition to its role as a reaction solvent. In the first case, HBDs such as acrylic acid, methacrylic acid and acrylamide are used for the formation of DES, where the polymerization yields a homogeneous polymer composite while preserving the HBA for further reuse. On the other hand, HBAs comprising polymerizable ammonium salts, among other materials, can be used as building blocks for the polymerization reaction, along with other HBDs for DES formation. Both processes have been scrutinized in a different review, of which the formation of poly(DESs) is applied within the scope of various applications in polymer science, catalysis, biocatalysis and nanomaterials [182].

In adsorption, organic acids including malonic, acetic, citric, lactic and caffeic acid, as well as monomers such as (meth)acrylic acid and its derivatives, were used to prepare DESs for the synthesis/modification of different adsorbents including, mainly, MIPs, as well as GO, MOF, cyclodextrin and biomass-based materials. For example, VP – as a polymerizable HBA – was mixed with different organic acids as HBDs to provide functional groups such as cycloalkyl, hetero-atom, carbonyl, carboxyl, and hydroxyl groups [130]. Similarly, the ternary DES ChCl:CafA:FA was used as a functional monomer, by a couple of research groups, in the preparation of MIPs. Although the parametric investigations conducted were rigorous, the adsorption mechanism and the role of caffeic acid in the formation of MIPs or the extraction of the target analytes was not clearly identified. More importantly, to our knowledge, the DES ChCl:CafA:FA is not validated through thermophysical characterization or studying of its phase behavior, which is another flag to be attentive to when it comes to the fundamental behavior of the used DES, irrespective of the apparent performance exhibited by using such combinations [114,120,129,172,183].

Other cases of using carboxylic acids, such as acetic acid (AA), for the preparation of DESs used in adsorption include the formation of high internal phase emulsions (HIPEs) [58]; however, this application found more appeal within polymerization studies rather than adsorption applications [182]. Other interesting use cases of DES-ADS from carboxylic acids – citric, lactic, oxalic and glycolic – were also explored, including tailoring of MOFs and synthesis of β-cyclodextrin [132] as well as other base materials.

#### 6.2.3. (Meth)acrylic acid and its derivatives

Different studies used methacrylic acid (MAA) and its derivatives, such as 2-hydroxyethyl methacrylate (HMA) and acrylamide (AAM), in the synthesis and functionalization of DES-based adsorbents. Notably, all of these studies used MAA with either ChCl or alkylammonium chloride as the HBA, at the specific ratio of 1:2. Moreover, the general theme of these studies was concerned with the development of MIPs – mostly magnetic – for the adsorption of proteins, which as discussed earlier, a suitable fit for customized adsorbent sites for different protein molecules. MAA and its derivatives are commonly used as monomers during MIP synthesis and, when combined with a proper HBA, DESs from MAA were reportedly prepared and used to enhance MIP synthesis and functionality. For instance, the DES ChCl:MAA (1:2) was used as a functional monomer for developing MIPs by different researchers for the adsorption of BHb, BSA, OVA and levofloxacin [81,94,97]. Moreover, the same DES (ChCl:MAA 1:2) was also used in the modification of $TiO_2$ nanotubes for the recognition of BSA and OVA [102]. Few reports considered MAA-based DESs for functionalizing of adsorbents other than MIPs, including magnetic β-cyclodextrin [103] and magnetic polydopamine [25]. With the exception of the modified magnetic dopamine, these DES-based adsorbents were also applied for protein extraction.

The DESs used for the synthesis of MIPs assumed different roles including (i) functional monomers, (ii) porogenic solvents, (iii) cross-linkers, and (iv) modifiers [22]. By liquifying the components typically used for any of the four mentioned functions into a stable DES – when combined with the proper HBA/HBD, the resulting DES can be used for each particular role (or multiple roles simultaneously). Most of these studies justified using DES due to its green merit as a stable, less toxic solvent. Yet, the need for using the cross-linkers or functional monomer in a DES system for the synthesis of MIPs still requires further analysis in order to identify the role of HBA and its behavior under the synthesis conditions, as mentioned in ***section 5.1***.

#### 6.2.4. Other HBDs

In addition to the above categories of HBDs, several other compounds that are known to form DESs were utilized such as sorbitol [61], imidazole [59,86], and butanediol [92], synthesized with ChCl or other alkylammonium salts as the HBA, and used mainly for protein isolation or dye removal among other applications. Further details about such HBDs are listed in the ***Supplementary Information*** file.

## 7. Methodologies, functional roles, and shortcomings in the preparation of DES-ADS

The DESs in the studied adsorption literature assume many roles during the development of the adsorbents' material. Most of the DESs were used as functionalization agents to modify and introduce new functional groups onto the surface of the adsorbents, thereby enhancing their selectivity towards a particular analyte, or enhancing their adsorption capacity. Moreover, DESs were also utilized as reducing agents, reaction media, functional monomers and porogens. As pointed out earlier, the same DES can have single or multiple functionalities during adsorbent synthesis. Noteworthy, the various functional roles assumed by DESs in the development of different advanced functionalized materials are mostly documented in the bodies of other reviews [21,22,184,185]. On that front, the specific roles of DESs in the synthesis of MIPs were well elucidated by Madikizela et al. [22] In a broader and more comprehensive tutorial study by Ma et al. [184], Zhu group discussed the different trends in the usage of DESs for the synthesis and modification of various composites including nanomaterials, gels and MXenes. Even beyond the scope of this work, DESs assumed multiple roles as structural directing agents for controlling nanoscale material synthesis, electrodeposits, colloidal assemblies and other carbon materials [186]. These systematic reviews provide a good listing of the different roles of DESs as well in a broader context. Nevertheless, the development and validation of DES-based adsorbents considered synthesis routes that might not be compatible with the inherent nature of DESs. Herein, however, the discussion is more closely related to the methodologies adopted for integrating DESs within such systems and the behavior of DESs under the set synthesis/functionalization conditions of the DES-ADS. Some of these methodologies were adopted from the literature on ionic liquids, which behave fundamentally differently than DESs. Therefore, it is crucial to understand the chemical and thermal behavior of the DESs and examine the syntheses schemes and methodologies for developing (and characterizing) DES-ADS as means to eliminate potential scientific gaps, which otherwise are masked by the pragmatic performance exhibited by such DES-based products. It should also be noted that the synthesis routes discussed herein are related to the DES involvement, not the full synthesis of the adsorbent as this can have multiple synthesis and preparation steps, which might not require a DES.

### *7.1. Synthesis routes for preparation of DES-ADS*

Developing a particular adsorbent can involve multiple exhaustive steps designed in a specific sequential order. These steps may or may not require the use of polar (sometimes organic) solvents such as methanol, ethanol, or simply water. The synthesis route varies with the type and nature of the base material being synthesized, and the moiety/functional group being functionalized onto/within that particular adsorbent material. After examining all the papers referenced herein for the preparation of adsorbents with the use of DESs, it was possible to categorize the methodologies of all the developed DES-ADS into three major synthesis routes. Notwithstanding to the specific keywords used within each article to describe the conditions of the DES-ADS development, the major synthesis routes can be practically classified as shown in Fig. 17 to: (I) Mixing, (II) Dispersion, or (III) Solvothermal methods. It should be noted that this section is to identify the methods adopted in DES-ADS literature only. A further discussion on the adequacy of using DESs within the experimental conditions of such methods will follow. Moreover, the classification of the synthesis route is exclusive for the DES-related step and no other preceding or subsequent steps in the synthesis of the adsorbent, as the full synthesis procedure might include other steps (oxidation, exfoliation… etc.) that are not directly affected by the used DES(s). Hence, the classification herein identifies the major routes in the literature used for incorporating DESs within different adsorbent materials.

#### *7.1.1. Route I: Mixing*

In terms of 'Mixing' or 'Dilution' methods (Route I), the procedure involves the use of solvents, including organic (e.g., ethanol, methanol) or inorganic solvents (e.g., DI water, Phosphate buffer solution), of which the adsorbent base material + DES + any other agents are added to the solvent then reacted together at certain conditions. Parameters such as reaction time, temperature, and stirring speed vary on a case-by-case basis. Nevertheless, the generalized illustration (I) of Fig. 17 describes the preparation route of such type of DES-ADS. Usually, the DES in route (I) assumes either the role of a functional monomer, providing the necessary building block for the synthesis of MIPs, or used as a reaction medium to carry out the synthesis (or part of the synthesis) procedure. For instance, DES-ADS from the biochar of dried pomelo-peel were reportedly loaded through the impregnation of ChCl:Gly 1:2 DES within the synthesized $Fe_3O_4$-biochar composites [170] (Fig. 18). After synthesizing the $Fe_3O_4$-biochar composite, it was dispersed along with 10 mL of the DES into a 50 mL methanol solution, stirred at mild conditions and then vacuum dried. In a different approach, Wei et al.[61] reported the functionalization of an $Fe_3O_4$-MOF composite adsorbent using a APTMACl:Sorbitol (1:1) DES in order to be used for dye removal from aqueous media. The synthesis and extraction procedure are illustrated in Fig. 19. Briefly, after fabrication of $Fe_3O_4$, functionalization with $–NH_2$ groups, and synthesis of MOFs (HKUST-1) nanoparticles, 0.5 g of $Fe_3O_4$-HKUST-1 composite was added to a 100 mL of ethanol, along with 5 mL of the synthesized DES. The mixture was then condensate-refluxed (70 °C for 12 h), washed with DI water, and dried at 75 °C. The synthesized composite ($Fe_3O_4$-MOF-DES) underwent another reaction following a seeded emulsion polymerization method [187] as means to reach a poly(DES) functionalized adsorbents. The later reaction involved dispersing the $Fe_3O_4$-MOF-DES particles in a DI water/ethanol solution and other reagents (crosslinker, initiators,… etc.) [61]. Finally, the (poly) DES-functionalized adsorbents ($Fe_3O_4$-MOF-PDES) were washed with DI water and dried overnight. Regarding the use of the DES as functional monomers for MIP synthesis, a direct example is illustrated in Fig. 20 of which a DES from polymerizable constituents of poly(vinyl pyrrolidone) (VP) and malonic acid (MlnA) was used to provide the functional monomers for the MIPs [147]. This DES-ADS was collectively synthesized from $Fe_3O_4$, GO and MIPs for the L-asparaginase adsorption. After exfoliation of GO and synthesis of $Fe_3O_4$ using conventional methods, the MIPs incorporating VP:MlnA DES were synthesized through a polymerization process in an ethanol–water medium (9:1 v/v). The resulting DES-ADS was then washed with MeOH, NaOH solution, and DI water. Other methods have

been also considered as in Fig. 21.

On the other hand, the use of DES as a reaction medium was also reported for the development of several adsorbent composites following route (I). For example, a ChCl:U 1:2 DES was used to dissolve the precursor materials for CoFe oxide [51]. Another study reported dissolving cellulose in ChCl:MalA DES, followed by several subsequent dilution/mixing steps for developing $Fe_3O_4$-MIP-cellulose adsorbent [109]. Moreover, an example of using the DES as a porogen (within the reaction medium) for the synthesis of MIPs in a benign aqueous environment was reported by Wang et al. [92] where the DES (as a porogen) enhanced the surface area of the synthesize MIPs while simultaneously promoting template dissolution.

Overall, it was referred to this route as 'dilution' or 'mixing' as it involves mixing the adsorbent and the DES in a specific medium, which results in the dilution of the DES within such medium. Accordingly, with dilution, the inherent properties of the DES are, in fact, disrupted [188] as the hydrogen bond network will not be maintained between the DES [189,190] In the specific examples where the final mixture was vacuum dried (as mentioned above; Fig. 18), the DES constituents can be maintained within the structure of the adsorbents, provided that the copious washing step using solvents such as ethanol, methanol or DI water, did not wash out one or both of the DES constituents. However, most studies disregard these aspects when using DESs, which effectively results in the dilution and flushing of the DES with the solvent, or the washing out of the DES from the adsorbent.

### *7.1.2. Route II: Dispersion*

The second synthesis route (II) traced within the DES-ADS literature – referred to as'Dispersion' – involves the addition of adsorbent base material(s) + any other reagent directly into a prepared DES (Fig. 17-II). The whole mixture is then reacted under specific operating conditions (i.e., time, temperature and stirring speed). Hence, the main role of the DES is as a reaction medium to aid in the synthesis of the adsorbent/composite, or to act as a functionalization agent via providing the needed functional groups to the dispersed adsorbent within the DES system. On that front, the functionalization if CNT via different DES for the extraction of some heavy metals ($Pb^{2+}$, $As^{3+}$, $Hg^{2+}$) [73–75] was reported. After preparing the DES and oxidizing pristine CNTs with $KMnO_4$ separately, 200 mg of the oxidized CNTs were dispersed in 7 mL of DES for 3 h at 65 °C. The mixture was then washed several times with DI water and filtered via 0.45 μm PTFE membranes. Likewise, the modification of boron nitride (BN) material was carried out in a similar method by dispersing 200 mg of BN within the DES through ultrasonication (10 min) followed by heat-stirring for 24 h at 60 °C [172], however, the washing step was not clearly discussed. The DES-modified BN was then used in the synthesis of MIPs. In a report by Meharbi et al. [57], a GO-$Fe_3O_4$ nanohybrids where synthesized at different ratios via dispersion in a ChCl:U 1:2 DES. The hypothesis was to use a DES with abundant amine groups (i.e., ChCl:U) as a reaction medium for the functionalization of GO, and later its conjugation with $Fe_3O_4$ [57]. The resulting composite was synthesized and applied for the adsorption of both lead and MB dye; however, its stability was not thoroughly evaluated through different regeneration cycles, and the magnetism of the synthesized GO-$Fe_3O_4$ was not tested. In another work, DES-based Chitosan beads were synthesized via the dissolution of chitosan flakes in a ChCl:U and ChCl:Gly DES [167]. After dispersing the chitosan in the DES, the mixture was suspended in a 0.5 M NaOH solution to synthesize the beads. A different study evaluated the functionalization of choline groups onto cotton fibers via dispersing the fibers (0.1 g) in a ChCl:U 1:2 DES (5 g) by adding 0.372 g of NaOH [131]. After heat-stirring the mixture, the functionalized cotton fibers were washed with copious amount of DI water.

Type (II) of synthesis procedures, basically depends on the role of the DES as a medium to carry out different functions during the preparation of the adsorbents. On the one hand, the DES is solely used as a green medium, which, although not mentioned clearly within the reviewed articles, limits the use of hazardous organic solvents. On the other hand, the DES, in addition to being used as a reaction medium, is required for the potential functional groups to equip the adsorbent's base material. Using conventional DESs (e.g., ChCl:U/EG/Gly) to introduce specific functionalities might not be a proper approach, as the target application might require a more specific, tailor-made DES to introduce such functionalities. Moreover, in certain cases, only one of the DES' constituents is essentially needed in the final structure of the adsorbent under analysis (to provide the needed function). Therefore, the question arises whether using a DES is even required in the first place rather than just using a sole HBA or HBD material for its function. This highlights the need for a bottom-up methodology for selecting the required materials based on the function of every constituent in the DES as well as their collective role as a DES. Moreover, in numerous cases, the dispersed adsorbents (in DES) undergo several washing steps using DI water or organic solvents such as acetone and ethanol. If the DES is to serve as a functionalization agent for the adsorbents, then it is crucial to study the actual mechanism that the DES' constituents are attached to the adsorbents as well as understand the type of bonds keeping the DES-ADS intact, ensuring that the use of such organic solvent for washing is not disrupting such bonds. For instance, in the earlier example using the synthesis route (I) for introducing a DES into biochar material (Fig. 18), the DES itself was diluted in methanol during the synthesis of the adsorbent, yet it was not washed out of the adsorbents as the mixture was vacuum dried, leaving the DES constituents impregnated within the biochar material; this does not eliminate the propensity of washing out the DES if it was not stable enough when the DES-based biochar adsorbent in contacted with aqueous environments or with harsh solvents. On the contrary, simply dispersing an adsorbent material in a DES, and washing it with copious amounts of solvents or aqueous solutions can disrupt the interactions between the DES (or one of its constituents) and the adsorbent.

### *7.1.3. Route III: Solvothermal*

As for the last synthesis route (Fig. 17-**III**), the procedure mostly involves the synthesis of adsorbent material under high temperature and/or pressure conditions (i.e., solvothermal method). Although few, most of the studies that discussed the synthesis of DES-ADS using this method were selective for the DES neat components. This is mainly because the role of the DES in such a procedure is to provide the precursor materials for the synthesis of the DES-ADS. The DESs used in these reports also act as a reaction medium for dissolving other precursor materials. But in both cases, the DES (as a precursor) or the DES + precursor materials were subjected to

extreme temperature and/or pressure conditions to forge the final DES-ADS for application. On that front, a couple of studies reported the synthesis of carbonous materials doped with N-atoms [60] or codoped with N,S-atoms [71]. The former study used a mixture of glucose and urea to form a DES, which was later heated and dried using a microwave (900 W; 5 min). The produced black foam-like material was then carbonized for up to 900 °C (Fig. 22), and ultimately used for the adsorption of organic contaminants (MB dye and nitrophenol) [60]. Similarly, Chen et al. [71] reported the synthesis of FLP using a ternary DES (Fructise:Urea:Thiourea). After the formation of the ternary DES, it was heated in an oven followed by carbonization of the material via the addition of sulfuric acid (Fig. 23). A couple of studies by Li & Chang and coworkers considered the synthesis of Mg-based materials (MgAl LDH [64] and MgO [52]) for the adsorption of dyes from water. In both cases, a DES composed of $MgCl_2$•6H2O and urea was prepared and sealed in an autoclave at 150 °C for 6 h. For the MgAl LDH, an additional DES ($AlCl_3$·6$H_2O$:PEG200) was used to introduce the Al composite. The obtained precipitate was then centrifuged and washed with DI water and ethanol before further use. In a similar method, Ni-based DES was sealed and heated in an autoclave to obtain $Ni_2CO_3(OH)_2$ nanosheets [53]. Lanthanum titanate adsorbents were also prepare in a similar procedure but with the precursor material ($La_2O_3$ + $TiO_2$) added to the DES (ChCl:U 1:2) until homogenized, followed by calcination at 800 °C for 1 h [72]. Aside from these MOs, the synthesis of COVs was also reported, however following a slightly different procedure. In these studies, the COV precursors were added into a glass tube containing the DES. In one case, 1,3,5-Triformylphloroglucinol + 2,5-Diaminobenzoic acid were added into a TBABr:IM DES in a glass tube for 12 h at 90 °C; The resulting red solid material was then filtered, washed with water and ethanol, and vacuum dried at 120 °C [59]. In another case, 1,3,5-Tris(4-aminophenyl)-benzene + 2,5-dihydroxyterephthalaldehyde were added into a ChCl: HFP 1:2 in a sealed glass amplitude tube; following a freeze–pump–thaw method (3 cycles), the mixture was set at 80 °C for 2 days, washed with acetone, and vacuum dried at 60 °C [93].

The solvothermal method, usually, during the synthesis of the adsorbents, involves the use of high temperature and/or pressure, which jeopardizes the DES structure and its stability. The neat components of the DESs can undergo certain side reactions or even degradation when subjected to elevated temperatures. Moreover, in this synthesis route (III), the carbonization/calcination of DESs effectively eliminates their nature as DESs. Hence, in the case of using DESs as precursor materials, a question arises of what might be the difference between preparing a DES from such materials (as was applied in the previous studies) vs. simply carbonizing the DES constituents directly (via autoclave / sulfuric acid… etc.), and whether the hydrogen bonding and mixing of the DES' constituents prior carbonation/calcination is advantageous to the overall reaction. It should be noted here that the influence of the DES in enhancing the structural properties of the synthesized carbonous material is not discussed, as it is the focal point of other detailed reviews [191]. The imposed question is on the systematic investigation of such effect and whether using a DES system in a solvothermal synthesis apparatus differs from simply mixing starting constituents.

### *7.2. Shortcomings in the development of DES-based adsorbents*

The synthesis routes for developing DES-ADS (Fig. 17) were generalized and categorized based on the DES' position within the synthesis procedure of the adsorbents. The DESs are also categorized based on their role and function contributed to the final synthesized adsorbent. The same DES might assume different roles based on the intended objective it is used for. As mentioned briefly above, each synthesis routes endorses specific operational conditions which might not be compatible with the DES nature.

One of the major mishaps when handling DES – within the scope of synthesizing DES-based adsorbents – is the dispersion of DESs in huge volumes of other organic solvents such as methanol, ethanol, or simply DI water. The dilution in such solvents disrupts the hydrogen bond network within the DES and yields a solution comprising the DES constituents. This practice is usually common in synthesis routes (I) and (II), where the DES is used to provide a functional monomer (in the case of MIPs) or as a functionalization agent. In such cases, the DES is either diluted in a relatively huge volume of an organic solvent (route I) or washed out with copious amounts of water and/or organic solvents (route II). The stability and integrity of the DES are questionable in both situations.

With regards to the operating conditions, exposing the DES to elevated temperatures (as in synthesis routes II and III) can produce certain undesired side reactions (e.g., esterification of organic acids). Accordingly, the DES might exhibit a different behavior, which might not reflect its promoted eutectic nature. Moreover, in some of the DES-ADS synthesis methodologies (routes II and III), the DES was subjected to elevated temperature > 150 – 200 °C, resulting in the decomposition of one or both constituents. This issue has been raised by researchers, especially in the field of MIPs [22], calling for the need to have a solid understanding of the DES' chemistry and thermal behavior prior its utilization in MIP synthesis. The report also highlighted the need to understand the role of the DES within the synthesis procedure of MIPs. This is also applicable for other DES-based adsorbents as well, and the identification of DES's role in the overall synthesis procedure must be accompanied by proper selection of the HBAs and HBDs fulfilling this role. The use of DESs as green synthesis media can be justified in that sense, as the objective of using the DES is most likely determined beforehand (e.g., regulating agent, material dissolution, elimination of hazardous solvents). However, using the DES to equip the adsorbent material with specific functional groups is a more intricate task, which should be approached via a clear bottom-up framework. This framework was missing in most of the reviewed articles in this work, and the justification for the DES selection was not clearly called out. Furthermore, the function/contribution of both DES' components (HBA and HBD) should be separately identified, as the preparation and use of DES might not be necessary if one of the constituents is sufficient to achieve the desired objective from using a DES.

Lastly, the synthesis of DES-ADS via solvothermal method (route III) subjugates the DES to extremely high temperatures (>400 – 800 °C), which essentially breaks the hydrogen bonding amongst the components of the DES as well as causes degradation of the starting DES components. As mentioned earlier, in most cases, the material selection for the DES – as precursor material – is done according to an intended objective (e.g., doping N-atoms, constricting FLPs, introducing metal oxides…etc.). Nevertheless, since the DES will undergo carbonization using thermal (via autoclave) or chemical (via acids) means, the need to prepare the DES prior to

carbonization is to be questioned. In contrast to such methods, Wang et al. [192] used the same solvothermal method to develop different types of metal chalcogenides with alkylammonium-based DESs as structural directing agents as well as reaction media. The DES constituents were added to the pressure container and heated along with other reagents and precursor materials without previously heat-stirring the HBA and HBD to form a separate DES. Although, technically speaking, merging all constituents in this approach cannot be termed as 'DES,' a holistic approach combining and comparing both methods can give a clearer indication of the influence of the DES' hydrogen bond network on the final adsorbent during and after carbonization.

## 8. Recommended stepwise framework for the development of DES-based adsorbent

In order to have a clear understanding of the nature of DESs and their associated molecular behavior when used for the development of adsorbents, it is vital to construct a stepwise bottom-up approach taking into consideration the effect of the HBA, HBD, and their collective/synergetic combination on the final adsorbent material (DES-ADS). In most cases, it is not applicable to prepare a DES and add it to a pre-structure adsorbent preparation method. The main criteria that must be considered in the preparation of DES-based adsorbents reflect those aspects analyzed in this review (Applications, Materials, and DESs). According, the development of DES-ADS can be discussed from the perspective of DES-related criteria and adsorbent-related criteria.

### *8.1. DES-related criteria*

Among the many features of DESs, designability, or the ability to prepare task-specific DESs through the combination of different types of constituents into binary and ternary mixtures, is one of the most lucrative features for the separation industry. However, as mentioned in *section 3*, these mixtures are not considered new compounds, and both HBA and HBD(s) retain their original molecular properties. Their combination, however, exhibits different unique characteristics compared to that of the neat components. Considering this, subjecting a DES to any of the conditions of the synthesis routes in *section 7.1* (i.e., dilution, washing with water or solvents, elevated heating, or carbonization) is critical to the DES stability. Dilution, practically, reduces the DES into a solution of its starting components. Excessive washing of the adsorbent after presumably functionalizing it with DES will result in flushing the DES (or one of its components) from the DES-ADS, unless the DES components are functionalized though more stable mechanisms than hydrogen bonding. Excessive heating can induce certain reactions between the DES components (e.g., esterification, precipitation) thereby changing its eutectic nature. Lastly, carbonization or calcination effectively breaks the DES components into solid carbonous materials. Therefore, identifying the (a) objective of using the DES and (b) the function of its components, supports the adequate and productive selection of DESs, taking into consideration the compatibility with adsorbent material and the suitability for the intended application. The flow chart in Fig. 24**(a)** illustrates the first step in developing a DES-based adsorbent. This step is mainly concerned with the preparation of a DES with the proper selection of starting components based on compatibility with adsorbent material and suitability for intended application. The objective of using a DES can be for various reasons, such as providing green synthesis medium, enhancing selectivity towards target analyte, or improving adsorbent properties. On the other hand, the functional role of the HBA and HBD is related to the specific contribution of each component, such as providing functional monomers (building blocks), functional groups, or precursor materials for the adsorbent material.

It is important to identify the distinct role of each of the DES' components before the development of the DES-ADS. This step will serve two important points; If one of the DES components does not provide a specific function for the intended application, then the inclusion of a DES preparation step is essentially redundant and only incurs a loss of time and materials. Thus, only the component providing the needed functionality will be used for the adsorbent synthesis, and the authors will have to drop some flashy keywords from their article title. On the other hand, if both of the DES components serve necessary functionalities for the intended application, then the study will evolve to more intricate analyses with the opportunity to explore the individual and/or collective features contributed by the DES and its components. Henceforth, novel or synergetic effects can be validated between the DES components and the adsorbent material. In Fig. 24**(a)**, after determining the intended objective of using a DES, it is important to select adequate components to fulfill the functions introduced from this DES. In simple cases, if the objective of using the DES is to have a green synthesis medium for adsorbents' synthesis, then the function of the DES components is to form a stable solvent that is compatible with both adsorbent materials and reagents. In more specific cases, the DES components are to be used as building blocks for the synthesis of the adsorbents, such as the use of MAA-based DES for MIP synthesis [22,81,97,112] or the use DES materials as precursors for adsorbent synthesis [60,71]. In the former case, if the MAA molecule is used as a functional monomer for the MIPs, then the contribution of the ChCl or other alkyl ammonium salts (as HBA) should be accompanied by solid justifications and empirical investigations.

One of the characteristics that should be satisfied by the DES' constituents is their ability to be functionalized onto the adsorbent materials, specifically for DES-ADS of which the DESs are used to functionalize the adsorbent material. The presence of functionalizable moieties and their counterparts on the adsorbent material ensures a clear functionalization route through identifiable mechanisms. Most of the studies, however, seem to dismiss the attachment mechanism stabilizing the DES with the adsorbent. Moreover, the characterization techniques used for identifying the presence of the "DES" within the adsorbent material after functionalization are inconclusive. Most of the techniques used are detecting a change in the physical or chemical properties of the functionalized adsorbent as compared to the plain one without clearly discerning the active presence of DES. Several researchers depended on FTIR spectra to identify the presence of functional groups that characterize one or both DES constituents. Yet, the exact nature, distribution, and ratio of these constituents cannot be quantified by these techniques. Likewise, the use of SEM or even TEM microscopy can only detect certain alterations occurring to the adsorbent without clearcut concluding the presence of a DES. Therefore, it is important to follow a

mechanistic approach to identify the presence of each of the DES constituents and the associated influence it contributes.

After choosing DES constituents based on their functions, it is important to ensure their suitability for DES formation at the desired molar ratio. Most studies that included a DES preparation step proposed the formation of a DES once a clear homogeneous liquid was formed. Nevertheless, and given the specificity of the "deep" qualificative in the DES literature [6], if the constituents used for the DES preparation are novel, then further analytical characterization is needed to identify the mixture of such compounds as actually a DES. On that front, preliminary information on the thermal properties and the solid–liquid phase equilibria of the DES can give a clearer understanding of its fundamental behavior under different conditions [4].

### *8.2. Adsorbent-related criteria*

The next phase, after identifying a working DES with functional, compatible constituents, is the preparation of the adsorbent according to one of the major roles contributed by the DES (i.e. synthesis or functionalization). It is important to distinguish the individual influence of each of the DES constituents on both the characteristics of the adsorbent material and its performance in the specified measurable metrics (adsorption capacity of certain analyte, stability, selectivity). After studying the individual influence contributed by each of the DES' constituents, the collective effect resulting from functionalizing both constituents onto the adsorbent material should be investigated on both levels as well, i.e. adsorbent properties and performance. This methodical procedure allows for identifying the individual characteristics of the HBA- and HBD-functionalized adsorbents in comparison to their DES-based complement and aids in decerning any synergetic effects that might occur in the DES-ADS. Fig. 24**(b)** illustrates the stepwise investigations to follow for discerning those effects. Ultimately, the characteristic properties and performance of the DES-ADS will reflect the successful association/interaction of the DES with the adsorbent material and will determine the influence of using such a neoteric solvent system for adsorption.

Aside from using the components as a DES (blue line) for the preparation of the overall DES-ADS, the procedure might also dictate the synthesis/functionalization to follow a sequential order (HBA then HBA, or vice versa), depending on the nature of the HBAs, HBDs and their stabilities at different reaction conditions. Therefore, even after identifying the individual effect of each DES component on the adsorbent's properties and performance, it is worthwhile investigating this alternative technique for preparing DES-based adsorbents, as it allows for tuning the reaction conditions during adsorbent preparation for each of the DES components. Moreover, the DES components in DES-ADS, provided they were synthesized successfully, might have a varying stoichiometric ratio compared to that of the liquid DES state. Therefore, it is also of interest to investigate the type and degree of hydrogen bonding on the surface of the functionalized adsorbents. Again, it should be highlighted that DES-ADS of which the DES is not present in the final solid adsorbent (e.g., DES as a reaction medium) are excluded from the previous discussion, as the objective of using the DES does not entail its incorporation – into the molecular level – with the adsorbent material.

## 9. Conclusion and outlook

Nuances in green chemistry deserve the attention of the scientific community, which was the case for neoteric solvents such as DESs, a class of solvents known for their unique characteristics such as simplicity of preparation, biodegradability, cost-efficiency and, of most, tunability. The advent of DESs into different fields and across numerous applications was promoted given their enhanced performance and pragmatic outcomes within the separation industry in general whether in liquid–liquid separation processes, solid–liquid ones or even gas separation. Concurrently, given that DES' field is still relatively recent, fundamental investigations and theoretical studies are still being brought up and discussed in literature. The integration of DESs within the parameters of other fields is of wide interest, especially for the solid–liquid processes, since DESs provide this green platform for the development and application of various materials and composites. Nevertheless, this integration should be delineated with basic principles which governs the thermal and physicochemical behavior of DESs—a practice that has been often dismissed in the literature.

This work thoroughly and critically scrutinized the integration of DESs with adsorption processes, shedding light on the major advancements in the development of DES-based adsorbents – DES-ADS. The reviewed literature herein was discussed from different perspectives, taking into consideration the different applications of DES-ADS, the materials of which DES-ADS are composed of, and the HBAs and HBDs used in their preparation. In terms of fields of application, the following was observed:

- Within the reviewed DES-ADS literature, the fields of applications were in different categories including water & wastewater treatment (55.1 %), protein isolation (12.7 %), extraction from food (12.7 %), extraction from biomass (7.6 %), medical applications (3.4), and other applications (8.5 %).
- The majority of DES-ADS studies were in the field of water & wastewater treatment (55.1 %) which itself is subdivided into different categories including dye removal (21.6 %), heavy metals (13.1 %), pharmaceuticals (11 %), phenols (4.2 %), and other applications (5.1 %).
- Most of the DES-ADS used for dye adsorption were developed from DESs comprising HBA of alkyl ammonium/phosphonium salts with anions as Cl- or Br-. Such studies reported the electrostatic interactions to be a primary mechanism. Other mechanisms come into play for dye removal using these DES-ADS including hydrophobic, hydrogen bonding and π-π interactions.
- DES-ADS showed high potential for heavy metals extraction, yet the extraction mechanism and selectivity of such DES-ADS must be further evaluated.
- Applications in protein isolation and extraction of certain substances from food both had the theme of using MIPs as adsorbents due to the specificity of such target analytes which requires tailor-made templating technology.

With regard to the base materials used for the development of DES-ADS, it is often the case that more than one material used in conjunction with other materials forming a binary (or ternary) hybrid/composite:

- The major categories of base materials used for the development of DES-ADS are $Fe_3O_4$ (18.2 %), MIPs (23.1 %), CNTs (8.5 %), Chitosan/Cellulosic material (7.3 %), metal oxides & hydroxides (6.7 %), and graphene oxide (6.7 %), biochar (4.2 %), silica particles (3.6 %), cyclodextrin (3 %), MOFs (2.4 %), and a wide variety of rare use cases as "others" (16.4 %).
- The significant and recurring use of $Fe_3O_4$ in conjunction with numerous other base materials is mainly attributed to its unique magnetic properties, which ease its separation and recovery process.
- MIPs, comprising the largest slice of adsorbent material used within DES-ADS was mostly hybridized with $Fe_3O_4$. Likewise, GO was mostly functionalized with $Fe_3O_4$ to introduce magnetic properties into the synthesized DES-ADS.
- CNTs were mostly studied by a few research groups, of which it was rarely hybridized with other base-materials.

In terms of the different DESs used for the synthesis or functionalization of adsorbents, different patterns were observed:

- The HBAs used in the preparation of DESs were mainly ChCl (60 %), other alkyl ammonium/phosphonium salts (20 %) or metal salts (5 %), among other HBAs. As for HBDs, the main components were glycerol (12 %), ethylene glycol (17 %), urea (18 %), a wide variety of organic acids (20 %), methacrylic acid (and its derivatives) (14 %), sugar diols (7 %) and other HBDs.
- The use of ChCl-based DESs was prevalent in most of the studies, with one-third of the studies using such DESs via the specific combinations of ChCl:EG, ChCl:Gly or ChCl:U – at the molar ratio 1:2. This is mainly due to the rich repository of information available for such DESs. Most of these studies dismissed the reasoning for selecting such DESs or regarding their green merit as a sole justification for their use. Although ChCl-based DESs are among the well-established, legacy DESs, such DESs might not be the best for the target application.
- Different organic acids such as malonic and caffeic acids as well as (meth)acrylic acid and its derivatives were mainly used—as DES components—to provide functional monomers during the synthesis of MIPs.

After describing the status of the DES-ADS field, the second part of this review scrutinized the different methodologies and approaches for the synthesis of DES-ADS. Notwithstanding to the specific terminologies and keywords used in the literature by various authors, the different methodologies were essentially categorized into three standardized main synthesis routes: (I) Mixing, (II) Dispersion, or (III) Solvothermal methods. Moreover, it was noticed that the intrinsic nature and thermophysical behaviors of DESs was not considered during the synthesis routes. As a result, the preparation of DES-ADS suffered several drawbacks which incur redundant use of both material and cost. These shortcomings are highlighted as follows:

- Dilution/Mixing of DESs in huge volume of organic solvents (route I) essentially breaks down the hydrogen bond network within the DES and renders the mixture as merely a solution with dissolved DES constituents.
- Washing of impregnated/functionalized DES with copious amounts of water and/or organic solvents (route II), disrupting the interactions between the DES (or one of its constituents) and the adsorbent material.
- Exposing the DES + adsorbent mixture to elevated temperature conditions (route II, III), which might lead to certain unwanted side reactions such as esterification, or even degradation of certain DES constituents.
- Exposing the DES material to harsh temperature and pressure conditions (route III) effectively eliminates the nature of the DES via carbonization/calcination.
- An exception is the use of DESs as green reaction media or as a solvent for the synthesis process, where, unlike DES-functionalized adsorbents, the final adsorbents are not claimed to have DES functional groups.
- These drawbacks were mostly masked by the pragmatic performances observed by certain DES-ADS.

Ideally, the diverse functional roles fulfilled by DESs and the intended objective(s) of using such DESs within the adsorption framework should be clearly identified. A DES can assume one or more functional roles during the preparation of DES-ADS, including being used as reducing agents, functionalization agents, reaction media, functional monomers, porogens and precursor materials among other functions. On the other hand, the objectives of utilizing DESs withing the framework of advanced materials is often of a broader purpose such as incorporating different functional groups onto/within the adsorbent material to enhance its adsorption capacity or selectivity, replacing hazardous organic solvent medium with a green one, or modifying the adsorbent's properties (hydrophobicity, stability, electronegativity). Yet, the objective of using a DES is often not explicitly mentioned, with the majority of articles using "*off the shelf*" DESs for their adsorption study without prior reasoning behind such selection. To address this step within the DES-ADS development process, a more methodical framework was postulated herein following a bottom-up approach for the careful considerations towards the DES's individual constituents, their collective mixture, and compatibility with the adsorbent material.

The framework is organized into two criterions, a DES-related and adsorbent-related one; The DES-related criteria begin with detailing the objective(s) behind the use of DESs for the intended process. This is followed by the careful selection of DES's starting components (HBA and HBD) of which the role/function of each is identified and tested. The suitability of the DES' components for incorporation with the adsorbent's base materials is postulated based on its chemistry and molecular information, where it will be later checked for its compatibility with the adsorbents. The formation of a DES is then attempted and checked if its properties are fulfilling the intended objective(s). As for the adsorbent-related criteria, it involves more empirical steps towards determining the individual

influence of each of the DES components (HBA/HBD) on the selected adsorbent. Ultimately, this systematic approach allows for decerning the effectiveness and contribution of each component towards the synthesized DES-ADS as well as determining any synergies that might occur from their collective use as a DES.

The use of this approach, however, might be met with certain limitations in terms of the tedious analysis steps and the efficiency of the overall DES-ADS preparation process thereof, and the question arises of whether such steps are necessary or not. Nevertheless, identification of such scientific gaps, especially within the DES field, allows for utilizing such class of neoteric solvents for its full potential, which is realized in their remarkable tunability. In addition, scientific, academic, collaborative research, as an elementary tool for industrial scale-up, requires such an investigative framework to reduce redundant expenses in both material and time. Ultimately, this framework allows researchers to take the necessary steps toward answering the research question(s) and can be extrapolated into other fields to develop various DES-based adsorbents, membranes, or other functional materials.

Lastly, it should be acknowledged that the scope of this review, although comprehensive and critical, leaves some part of the discussion for the readers' investigations and personal reflections. Therefore, we decided to make the database acquired during this search available within the supplementary material of this work in the form of an interactive, user-friendly spreadsheet (Fig. 25). The file contains multiple entries with specific information about each article/research work, covering aspects such as application, process, material, DES, feed properties, adsorbent dose, adsorption capacity, target analytes, regeneration cycles, isotherms, synthesis route and more. We hope readers are inspired to interact and query this database for their own research or to unveil more trajectories worth studying.

## CRediT authorship contribution statement

**Ghaiath Almustafa:** Writing – original draft, Visualization, Formal analysis, Data curation, Conceptualization. **Rawan Abu Alwan:** Writing – original draft, Formal analysis, Data curation. **Ho Kyong Shon:** Writing – review & editing, Resources, Project administration. **Jorge Rodriguez:** Writing – review & editing, Visualization, Project administration, Methodology, Funding acquisition. **Inas AlNashef:** Writing – review & editing, Validation, Supervision, Methodology.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.pmatsci.2025.101501.

## Data availability

Database is available in the Supplementary Info. file.

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