

# **Adsorptive removal of antibiotics from water and wastewater: progress and challenges**

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## **Abstract**

Antibiotics as emerging contaminants are of global concern due to the development of antibiotic resistant genes potentially causing superbugs. Current wastewater treatment technology cannot sufficiently remove antibiotics from sewage, hence new and low-cost technology is needed. Adsorptive materials have been extensively used for the conditioning, remediation and removal of inorganic and organic hazardous materials, although their application for removing antibiotics has been reported for ~30 out of 250 antibiotics so far. The literature on the adsorptive removal of antibiotics using different adsorptive materials is summarized and critically reviewed, by comparing different adsorbents with varying physicochemical characteristics. The efficiency for removing antibiotics from water and wastewater by different adsorbents has been evaluated by examining their adsorption coefficient ( $K_d$ ) values. For sulfamethoxazole the different adsorbents followed the trend: biochar (BC) > multi-walled carbon nanotubes (MWCNTs) > graphite > clay minerals, and for tetracycline the adsorptive materials followed the trend: SWCNT > graphite > MWCNT = AC > bentonite = humic substance = clay minerals. The underlying controlling parameters for the adsorption technology have been examined. In addition, the cost of preparing adsorbents has been estimated, which followed the order of BCs < ACs < ion exchange resins < MWCNTs < SWCNTs. The future research challenges on process integration, production and modification of low-cost adsorbents are elaborated.

**Keywords:** adsorption, antibiotic, biochar, activated carbon, carbon nanotube, regeneration

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## **1. Introduction**

Antibiotics are unique among medicines in that they act selectively on bacteria, among them the pathogens, while leaving human cells and tissues unaffected (Sköld, 2011). Antibiotics can be classified by either their chemical structure or mechanism of action (Table 1). There are over 250 different antibiotic entities registered for use in human and veterinary medicine (Kümmerer and Henninger, 2003). Most of these substances have a microbial origin, but they can also be semi-synthetic or totally synthetic. Antibiotics are the potent medicines that have

been used for several decades in both human and animals, for therapeutic treatment of infections related diseases, and for protecting their health (Sapkota et al., 2008). Among the various pharmaceuticals, antibiotic usage has been rapidly increased all over the world thus it has received widespread attention (Kasprzyk-Hordern et al., 2009). Of particular concern are antibiotic residues in the environment which can induce antibiotic resistant genes (ARGs) from extended exposure at relatively low concentrations (Dantas et al., 2008). The past and ongoing usage of antibiotics produces significant residues which are directly or indirectly introduced into the aquatic and terrestrial environments (Sarmah et al., 2006), and residues of human and veterinary antibiotics have been detected in many different matrices (Batt et al., 2006; Feitosa-Felizzola and Chiron, 2009; Hirsch et al., 1999; Jacobsen et al., 2004; Lindsey et al., 2001; Mompelat et al., 2009; Ternes, 1998) .

Antibiotics have different half-lives in the environment, some are highly persistent (Daughton and Ternes, 1999), and therefore their contamination levels in the environment have been increasing. Several studies (Ji et al., 2012; Lai et al., 2009; Wollenberger et al., 2000) showed significant impacts that exposure to antibiotics ( $\mu\text{g/L}$  -  $\text{mg/L}$ ) may cause on aquatic organisms on their survival, growth and body weight. The release of antibiotics into the natural water bodies mainly comes from the effluents of municipal sewage treatment plants (STPs) and pharmaceutical manufacturing plants. As reviewed by Michael et al. (2013) and Rizzo et al. (2013), urban wastewater treatment plants are likely to be hotspots for the release of antibiotics and ARGs in the natural environment. Thus pharmaceutical chemicals especially antibiotics are gaining the recognition of emerging environment contaminants as being classified as recalcitrant bio-accumulative compounds (Chen and Zhou, 2014), hence antibiotics are regarded as toxic and hazardous chemicals (Hartmann et al., 1998; Lee et al., 2001; Wollenberger et al., 2000) .

Before discharging wastewater into the environment it is highly important for antibiotic residues to be removed but it usually involves high cost. Case studies of providing cost effective solutions for antibiotic removal are urgently needed (Kim et al., 2005; Košutić et al., 2007; Watkinson et al., 2007). Although processes such as advanced oxidation can convert antibiotic molecules into simple compounds or even mineralize them completely but these processes are very expensive (Mehrzouei et al., 2014) and difficult to maintain for the total removal of compounds including antibiotics at industrial scale. Thus physicochemical technologies are proving to be highly suitable treatment option for organic contaminants. (Homem and Santos, 2011; Wang et al., 2007). Adsorption process is very efficient (Hao et al., 2012; Zhou et al., 2012), simple to design and operate; and it is relatively inexpensive and unaffected by the potential toxicity as for biologically based processes (Ahmaruzzaman, 2008). Adsorption processes are widely used to remove organic contaminants from contaminated stream onto adsorbent surfaces (Han et al., 2008; Homem and Santos, 2011), although their application to antibiotic removal has been reported for around 30 compounds so far. The efficiency of adsorption processes is highly affected by the type of adsorbent, adsorbate properties, and the compositions of waste stream (Aksu and Tunç, 2005). Several adsorptive materials including activated carbon (AC), carbon nanotubes (CNTs) especially multi-walled carbon nanotubes (MWCNTs), natural clay materials such as bentonite, ion exchange materials and biochar (BC) are reviewed for antibiotic removal. However, other adsorbents such as hollow silica nanospheres, MgO particles, MgO nanoparticles, ZnO-MgO nano-composites and kaolinite are not reviewed (Fakhri and Behrouz, 2015).

Upon realising the significance of antibiotic removal by adsorption technology, the aim of this study is to review and analyze the published studies on the application of adsorptive materials for antibiotic removal. Specifically this review will cover (i) the behaviour of adsorptive materials for removing antibiotics from wastewater in both static and dynamic regimes; (ii) the mechanism, kinetics and equilibria of adsorption process; and (iii) the

progress and future challenges of the adsorptive materials including cost consideration and regeneration studies.

## **2. Adsorptive processes for antibiotic removal**

The term adsorption is the accumulation of matter from a gas or liquid phase to the surface of an adsorbent, which could involve physical and/or chemical adsorption. Although adsorption is a well-known process, in the past decades the study of this technology for antibiotic removal has not been extensively explored. The most widely reported adsorbents for antibiotic removal include ACs, CNTs, bentonite, ion exchange resins and BCs. Overviews of published journal articles for antibiotic removal by adsorptive materials are presented in Tables 2-6. In most of the adsorption studies, the concentrations of antibiotics used are at mg/L level, which are significantly higher than environmentally relevant concentrations (ng/L -  $\mu\text{g/L}$ ). To ensure a consistent comparison between different adsorbents, the discussion often referred to the linear range of the adsorption isotherms by calculating the adsorption coefficient ( $K_d$ ). The adsorption efficiency is directly related to the adsorbent's properties such as specific surface area (SSA), porosity (macro or micro porosity), pore diameter and functional groups (Estevinho et al., 2007).

### **2.1. ACs**

ACs have been widely used to remove organic contaminants from water and wastewater in industrial scale applications and more recently in removing pharmaceuticals from sewage effluent (Grover et al., 2011). High degree of micro porosity, well developed surface area, and high adsorption capacity are the key features of ACs (both granular and powdered) that make them suitable as adsorbent for the removal of organic contaminants (Huang et al., 2011; Jain et al., 2004; Roosta et al., 2014a; Roosta et al., 2014b). However, the main drawbacks of ACs are their high production cost and high regeneration costs (Aksu and Tunç, 2005), and the

adsorption of antibiotics on their surface is significantly influenced by their characteristics such as surface physical morphology and functionality (Foo and Hameed, 2012). Recent studies on using ACs for antibiotic removal have shown that ACs or modified ACs have potential applications for significant remediation of various antibiotics from wastewater, with an efficiency varying from 74% to 100% (Torres-Pérez et al., 2012; Pouretedal and Sadegh, 2014). During batch adsorption of nitroimidazoles on AC, it was found that the pH of the medium and the electrolyte concentration did not influence the adsorption process (Rivera-Utrilla et al., 2009). A 90% removal efficiency of nitroimidazoles and trimethoprim was obtained by using AC (PAC and GAC) (Kim et al., 2010; Méndez-Díaz et al., 2010) as shown in Table 2. In another study over 90% adsorption removal efficiency (Tables 2) for trimethoprim, sulphonamides (sulfachloropyridazine, sulfadimethoxine, sulfamerazine, sulfamethazine and sulfathiazole), carbadox and tetracycline was achieved using PAC as adsorbent (Adams et al., 2002; Pouretedal and Sadegh, 2014, Torres-Perez et al., 2012).

As shown in Table 2, in a study of the adsorptive removal of amoxicillin using AC and bentonite, high removal efficiencies were achieved by AC (95%) than by bentonite (88%) (Putra et al., 2009). Another study reported that 99% amoxicillin was removed by  $\text{NH}_4\text{Cl}$ -induced AC at pH 6 and 50°C (Moussavi et al., 2013). Using AC produced from vine wood it was found that the removal of different classes of antibiotics such as amoxicillin, cephalixin, cephalosporin, penicillin G and tetracycline varied between 74% and 88% as summarized in Table 2 (Pouretedal and Sadegh, 2014). In addition, even 100% removal of sulfamethoxazole (Stackelberg et al., 2007) and other pharmaceuticals (Grover et al., 2011) was observed. Furthermore, it was reported that NaOH-AC produced from macadamia nut shells presented a high surface area ( $1524 \text{ m}^2/\text{g}$ ) with a maximum adsorptive capacity (Table 2) for the removal of tetracycline from aqueous solution (Martins et al., 2015). Although AC, in particular GAC has higher rate of success for the removal of antibiotics from aqueous medium, its high cost

and difficulty of regeneration are two major disadvantages constraining its wider application at commercial scale (Crisafulli et al., 2008).

## 2.2. CNTs

Engineered CNTs (single and multiwall) have recently shown great promise for many remediation applications including pharmaceutical chemicals such as antibiotics since the discovery of CNTs in 1991 (Kim et al., 2014b; Singh et al., 2014). CNTs contain cylindrical layered graphite sheets with a characteristically large surface area which have high van der Waals index (Schwarzenbach et al., 2005). The benzenoid rings of graphite sheets have high polarizability due to the presence of  $sp^2$ -hybridized carbon atoms. These properties of CNTs make them super hydrophobic materials that can interact with aromatic pollutants by  $\pi$ - $\pi$  coupling stacking (Long and Yang, 2001; Lara et al., 2014). The removal of antibiotics such as sulphonamides, lincomycine, and amoxicillin by CNTs has been studied in fixed bed columns or batch mode under a broad range of conditions, and great removal success (80% to > 90%) has been reported (Ji et al., 2009b; Kim et al., 2014a; Mohammadi et al., 2015).

In recent remediation of antibiotics from aqueous environments, about 90% removal of lincomycin and sulfamethoxazole (sulphonamides) was found from aqueous solutions on SWCNT and MWCNT (Kim et al., 2014a). Kim et al. (2014a) also reported that SWCNT had a greater efficiency than other adsorbents in the order: SWCNT > PAC > MWCNT as detailed in Table 3. In another study it was reported that about 96% adsorptive removal of sulfamethoxazole and sulfapyridine occurred in a fixed bed column of CNTs, where contact periods were only 2 h (Tian et al., 2013). In batch mode, an adsorptive removal efficiency of sulfamethoxazole and sulfapyridine on CNTs and graphite was found to be 80% as shown in Table 3 (Ji et al., 2009b). An 86.5% adsorptive removal of amoxicillin from aqueous media was also found using MWCNT (Table 2) (Mohammadi et al., 2015). However, CNTs may not



be widely applicable due to their high material cost (Esawi and Farag, 2007). In future, the low cost production of CNTs should be a high priority in adsorption research.

### **2.3. Clay mineral (bentonite)**

Clay mineral e.g. bentonite is an adsorbent of aluminium phyllosilicate, which has high surface area and pore volume. Bentonite can act as an adsorbent for the remediation of antibiotics from water and wastewater. Up to now, antibiotic removal by bentonite has not been widely explored, only a few literature reports have been found. In batch mode, the adsorption of ciprofloxacin from aqueous solution on bentonite was found to be very high with 99% removal efficiency, with a contact time of 30 min at pH 4.5 (Genç et al., 2013). In another study (Table 4) for the removal of ciprofloxacin on using bentonite, AC, zeolite and pumice, it was observed that bentonite achieved the highest removal capacity (Genç and Dogan, 2015). They also calculated the Gibbs free energy ( $\Delta G^\circ$ ) values of adsorption by bentonite, zeolite, AC and pumice which appeared in the order: bentonite > AC > zeolite > pumice.

On the other hand, during amoxicillin removal from real wastewater on bentonite and AC, bentonite efficiency (88%) was found to be less than using AC (95%); and neither adsorbent can completely remove amoxicillin due to the sorption competition from other substances which were also present in the wastewater (Putra et al., 2009). Thus the performance of bentonite is sometimes higher or almost comparable with AC in the removal of antibiotics such as amoxicillin and ciprofloxacin from wastewater (Genç et al., 2013; Putra et al., 2009)..

### **2.4. Ion exchange resins**

Ion exchange is a process in which cations or anions in a liquid medium are exchanged with cations or anions on a solid sorbent, and electro-neutrality is maintained in both phases. Overall it was found that ion exchange resin materials can remove antibiotics from water and

wastewater with efficiency up to 90%. As shown in Table 5, the adsorption removal efficiency of tetracyclines and sulphonamides on ion exchanger were > 80% and ~90% respectively (Choi et al., 2007). In another study on the removal of sulfamethazine using ion exchange materials about 100% sulfamethazine removal was achieved in all cycles (Fernández et al., 2014b). However for the removal of quinoxaline derivatives (carbadox) and sulphonamides (sulfachloropyridazine, sulfadimethoxine, sulfamerazine and sulfathiazole) using ion exchange resin, it was reported that ion exchange method may not be appropriate (Adams et al., 2002). In batch mode, the removal of a mixture of sulfamethoxazole and sulfamethazine using a strong anionic resin was successfully carried out with a higher capacity of adsorption for sulfamethoxazole; furthermore, 100% of both compounds were recovered during the elution stage (Fernández et al., 2014a). Ion exchangers can therefore remove some antibiotics from wastewater significantly. However the problems associated with this type of materials are backwashing and regeneration, with additional problems such as the appearance of fouling and potential irreversible accumulation (Üstün et al., 2007).

## **2.5. BCs**

The interest for alternative adsorbents rather than AC is growing with the purpose of finding new low-cost yet effective adsorbents, from by-products or waste materials derived from industrial or agricultural processes. BC is a potential alternative to AC that could be used for antibiotic removal. The raw materials for BC production can be obtained from agricultural biomass and solid waste which are abundant with little cost (Xu et al., 2013). BC can be prepared by various methods and has many interesting properties such as low cost, highly porous structure and high removal capacities for organic and inorganic pollutants from aqueous solution (Ahmed et al., 2014b). For example, BC is usually produced under a temperature range of 300-1000°C in the presence or absence of minimal oxygen ( $\leq 2\%$ ) through the process of slow or fast pyrolysis. These kinds of treatment convert the biomass

materials into products with a high surface area owing to porous structure. In addition, enriched surface functional groups make BC suitable to be used as a prominent adsorbent for antibiotic removal from aqueous stream (Rajapaksha et al., 2014). As an adsorbent, BC has the porous structure almost similar to AC and thus can act as an efficient sorbent for the removal of diverse pollutants from water and wastewater (Chen et al., 2007; Faria et al., 2004; Nakagawa et al., 2004). BC can be produced at a lower cost than AC, where higher temperature and additional activating agent may be required. In most cases, BC does not require additional activation process like AC for the removal of antibiotics although some researchers (Azargohar and Dalai, 2008; Uchimiya et al., 2012) have performed BC activation using different activating materials. In particular, it is speculated that activation of BC by steam and/or N<sub>2</sub> purging may enhance its sorption tendency (Rajapaksha et al., 2014; Rajapaksha et al., 2015). Thus, the overall production of BC is significantly cheaper than AC as reported in the literature (Cao et al., 2009; Zheng et al., 2010; Karakoyun et al., 2011; Ahmad et al., 2012a; Lu et al., 2012).

Antibiotic sorption to BC may vary greatly according to antibiotic properties as well as BC properties (Yao et al., 2012; Zhang et al., 2013). Moreover, BCs exhibited similar or even better adsorption capacity than commercially available ACs as being reported in several studies (Karakoyun et al., 2011; Xue et al., 2012; Zhang et al., 2012; Yang et al., 2014). BC can act as a dominant adsorbent for the removal of antibiotics as it has shown very high degrees of removal (up to 100%) depending on antibiotic classes. In studying the adsorptive removal of sulfonamides (sulfamethoxazole and sulfapyridine) on BC (Table 6), it was reported that pinewood BC which was prepared under different thermochemical conditions exhibited strong adsorption capacity (Yao et al., 2012; Xie et al., 2014). In addition, the high removal efficiencies of up to 100% for antibiotics florfenicol and ceftiofur were achieved on pinewood BC (Table 6) which demonstrated the potential of BC as an effective adsorbent for removing antibiotics from sewage and other contaminated effluents (Mitchell et al., 2015).

Teixido et al. (2011) reported a high  $K_d$  value ( $10^6$  L/kg) for the removal of sulfamethazine on BC while Liu et al. (2012) observed the maximum adsorption capacity (58.8 mg/g) for tetracycline on biomass-derived BC.

Based on the available data for different adsorbents such as BC, MWCNT, graphite and clay minerals (Zheng et al., 2013; Ji et al., 2009b; Thiele-Burhn et al., 2004), the relationship between  $K_d$  for sulfamethoxazole and adsorbents is shown in Figure 1, suggesting that these adsorptive materials followed the general trend of BC600 > BC 500 > MWCNT > graphite = clay minerals. However for the removal of tetracycline (Figure 2), adsorptive materials followed a different trend: SWCNT > graphite > MWCNT = AC > bentonite = humic substance = clay minerals (Ji et al., 2009a).

In summary, adsorption technology can be applied for removing different antibiotics from water and wastewater containing a whole suite of other inorganic and organic components, often with a very high efficiency. To ensure the wide application of adsorption technology at commercial scale, the cost reduction in the preparation of effective adsorbents will remain to be a constraining factor, and to that end BC preparation has the greatest potential for exploitation as a research topic (Liu et al., 2012; Teixido et al., 2011; Yao et al., 2012).

### **3. Antibiotics removal: kinetics, isotherms and mechanism**

#### **3.1. Adsorption kinetics**

The kinetics of adsorption not only determine the rate of antibiotic removal from water and wastewater, but also the size and capital cost of actual adsorption system required for commercial applications. Adsorption kinetics typically involve four steps: bulk transport, film transport, intra-particle transport and adsorption on the adsorbent. Often the rate controlling step is film transport which is governed by molecular diffusion in the boundary layer. Kinetic modelling is performed to investigate the rate of the controlling steps during the removal of antibiotics from solution by adsorbents. There are different differential equations being used

for kinetic modelling in both batch and continuous system; these equations are solved by using integral method (Han et al., 2009). Many different kinetic models have been used including zero order, first order or pseudo first order, second order or pseudo second order and third order to describe the kinetics of adsorption. Kinetic parameters such as the rate constants, equilibrium adsorption capacities and related correlation coefficients for pseudo first-order and second-order kinetic models were discussed and summarized in Tables 7a and 7b. Some of the parameters are described below, including the effects of initial concentrations of adsorbate and adsorbent and contact time on the kinetics of adsorption.

#### **Effect of initial concentrations of adsorbate and adsorbent**

The initial relative concentrations of adsorbate and adsorbent will determine when the adsorption becomes saturated, with the consequence of adsorbate leaving without treatment causing a breakthrough. Thus different antibiotics will potentially have different equilibration time to reach their maximum efficiency. For example, the breakpoint time was found to decrease from 37.4 to 25.6 min for sulfamethoxazole, and from 51.8 to 25.5 min for sulfapyridine as the initial concentration of the antibiotics was quadrupled (Tian et al., 2013). In general, an increase in adsorbate concentration can lead to a lower removal efficiency. On the other hand, an increase in adsorbent dosage will result in a better removal efficiency although the operating cost will increase.

#### **Effect of contact time between adsorbent and adsorbate**

The contact time between adsorbate and adsorbent is a key kinetic parameter. In general, it is preferred that the contact time between adsorbate and adsorbent will be kept at minimum while maximum removal can be achieved. However, due to adsorption kinetic controls longer than minimum time, i.e. optimum time is required to ensure sufficient removal of antibiotics is obtained by reaching a dynamic equilibrium (Genç et al., 2013). For example, the rate of penicillin removal was found to reach equilibrium after 48-72 h regardless of the nature of carbon adsorbents, where most of the uptake occurred within the first 24 h (Ania et al., 2011).

A complete adsorptive removal of amoxicillin occurred on 50 mg/L of  $\text{NH}_4\text{-Cl}$  induced AC (NAC) within first 20 min. The high  $r^2$  value of NAC and standard AC for the adsorption of amoxicillin indicated that the kinetic results were best described by the pseudo second order kinetic model (Moussavi et al., 2013). Good fitness to pseudo second order model was also found for the adsorption of amoxicillin onto AC and bentonite at pH 2.31 (Table 7b) (Putra et al., 2009). The kinetics of tetracycline adsorption onto ACs (Table 7a) followed a very fast decrease in concentration within the first 12 h, followed by a slow decrease depending on the adsorbent materials (Torres-Pérez et al., 2012). Based on the correlation coefficients ( $r^2 > 0.98$ ) of adsorption kinetic models of different antibiotics (amoxicillin, cephalexin, penicillin G and tetracycline) on AC (Table 7b), it was found that pseudo second order provided the best fit; and the adsorption mechanism was suggested to be chemisorption (Pouretedal and Sadegh, 2014). The equilibrium contact time was found to be 8 d to reach for the adsorptive removal of imidazoles when using 0.1 mg/L of AC (Rivera-Utrilla et al., 2009). On the other hand, the equilibrium contact time of sulfamethoxazole adsorption on waste based carbon was found to be significantly faster at 15 to 30 min (Table 7a) (Calisto et al., 2015). It was also mentioned that the experimental data was best described by pseudo second order with a  $r^2$  value of 0.991, and maximum adsorption capacity ( $q_{\text{max}}$ ) was found to be 118 mg/g. On the other hand, tetracycline adsorption on NaOH-induced AC reached an equilibrium at about 120 min with a  $r^2$  value of 0.960 (Table 7a), which indicated that the adsorption kinetics followed pseudo second order (Martins et al., 2015).

Adsorption of sulfamethoxazole on BC (Table 7a) reached equilibrium within 72 h and neutral sulfamethoxazole ( $\text{SMX}^0$ ) was dominant at pH 1.0-6.0, and above 7.0 BC surface became negatively charged while the sorption of negatively charged sulfamethoxazole ( $\text{SMX}^-$ ) species increased with increasing pH (Zheng et al., 2013). It is shown in Table 7b that the adsorption of lincomycine on SWCNTs and MWCNT reached an equilibrium within 100 h and adsorption kinetics involved two phases: a rapid step which was followed by a slow step.

It was also found that SWCNT had the higher potential to adsorb lincomycin and sulfamethoxazole than MWCNT (Kim et al., 2014a).

In using bentonite as adsorbent, it was reported that the pseudo second order model (Table 7b) fitted the kinetic data very well ( $r^2 > 0.99$ ) at low pH value, which was due to the chemisorption of amoxicillin being dominant (Ho, 2006; Putra et al., 2009). In a batch kinetic study for the adsorption of sulfamethazine on bentonite (Table 7a), it was found that 120 min was needed to reach an equilibrium (Fernández et al., 2014b). For adsorptive removal of ciprofloxacin (Table 7b) on bentonite, AC, zeolite and pumice, it was observed that the pseudo second order kinetic model was the best model for fitting the data with  $r^2$  value of 0.999 (Genç & Dogan, 2015). The equilibrium time (Table 7a) for batch adsorptive removal on strong anion exchanger was found to be 120 min and 100 min, respectively for sulfamethoxazole and sulfamethazine, and for sulfamethazine (Fernández et al., 2014a; Fernández et al., 2014b), which is relatively fast for the adsorption process.

### **3.2. Adsorption isotherms**

Equilibrium isotherms are widely used to represent the relationship between the adsorbed concentration in the adsorbent phase and the dissolved concentration at equilibrium. Such isotherms are a characteristic feature for a specific system at particular environmental conditions. There are several adsorption isotherm models such as the Langmuir, Freundlich, Brunauer–Emmett–Teller (BET), Temkin, Frumkin, Harkins–Jura, Smith, and Dubinin–Radushkevich (D-R) isotherms. The Langmuir model assumes monolayer adsorption on adsorbents which have homogeneous energy distribution, the Freundlich isotherm is an empirical model suitable for heterogeneous surface adsorption, and the D-R isotherm model is valid for the adsorption of low concentration of contaminants onto both homogeneous and heterogeneous surfaces. The equilibrium adsorption isotherms for some antibiotic compounds are shown in Tables 7a and 7b. For BC adsorbent, the adsorption of antibiotics

sulfamethoxazole and sulfapyridine was well fitted with the Freundlich sorption model ( $r^2 > 0.96$ ). For three BC samples namely BC400, BC500 and BC500H, it was found that the adsorption isotherms were highly nonlinear and the degree of nonlinearity followed the order: BC500H > BC500 > BC400 (Xie et al., 2014). The isotherms of sulfamethoxazole sorption on nondeashed BC was found to be fitted by both Freundlich and Dubinin models with the adjusted coefficient  $r^2 > 0.952$  (Table 7a) (Xie et al., 2014). The isotherms of sulfamethoxazole on BC was almost linear ( $n = 0.919$ ), implying that the antibiotic partitioning into the non-carbonized organic matter was dominant (Chen et al., 2008a). With increasing pyrolytic temperature from 300 to 600°C, the  $n$  values were decreased to 0.198, which revealed more heterogeneous glassy, hard or condensed sorption dominating on BC surfaces with high sorption distribution energy (Xing et al., 1996; Zhang et al., 2011).

For CNT adsorbent, the adsorption of lincomycine was not well fitted by the Langmuir isotherm ( $r^2 < 0.70$ ), indicating that the adsorption was not of pure monolayer type. In comparison, the Freundlich model (Table 7a) was better suited to the adsorption data with  $r^2 > 0.93$ , and values of  $n$  were substantially smaller than 1 suggesting more heterogeneous adsorption sites on the adsorbents. The highest value of Freundlich affinity constant ( $K_F$ ) obtained from the isotherms was from SWCNTs, and the general trend was SWCNT > PAC > MWCNT (Kim et al., 2014a). It was proposed that the attraction of acceptor-acceptor, and acceptor-donor pairs between the antibiotics (sulfamethoxazole and sulfamethazine) and the CNTs were responsible for the observed strong adsorption of antibiotics onto CNTs at lower pH values (Tian et al., 2013). In another study of the adsorption of amoxicillin on CNT, three models namely the Langmuir, Freundlich and D-R were found to provide a good fit to the adsorption data ( $r^2 > 0.91$ ), and the Langmuir isotherm (Table 7b) provided the best fit ( $q_{\max}$  value 23.458 mg/g,  $b_L$  value  $2.5 \times 10^{-5}$  L/mol,  $r^2 > 0.99$ ), indicating saturated monolayer sorption (Mohammadi et al., 2015). The Freundlich adsorption isotherm provided the best fit for the removal of sulfonamide with adsorption nonlinearity (as indicated by the smaller  $n$



values) (Ji et al., 2009b). The adsorption isotherms of sulfamethoxazole, tetracycline, and tyrosine were also well fitted by the Freundlich isotherm model (Table 7a) ( $r^2 > 0.98$ ) with  $n$  value significantly smaller than 1, which reflected that the adsorption was consistently highly nonlinear (Ji et al., 2010).

For AC adsorbent, the  $r^2$  values of the Langmuir isotherm were greater than those of other isotherms which indicated that amoxicillin molecular adsorption occurred as monolayer (Table 7b). It was also found that the maximum monolayer adsorption capacities were 262 and 437 mg/g, respectively for standard AC and  $\text{NH}_4\text{-Cl}$  induced AC (Moussavi et al., 2013). Another study on standard AC for the adsorption of tetracycline revealed that the Freundlich model proved to be the best fit ( $r^2 > 0.985$ ), and the maximum adsorption capacity ( $q_{\text{max}} = 817$  mg/g) was observed for a commercially available GAC2 (Torres-Pérez et al., 2012). It was also found (Table 7b) that the Langmuir isotherm ( $r^2 > 0.980$  and higher  $b_L$ ) provided the best fit for the removal of amoxicillin, cephalixin, penicillin G and tetracycline on AC (Pouretedal and Sadegh, 2014). The correlation coefficient value ( $r^2 > 0.99$ ) on AC (Table 7b) indicated that the Langmuir isotherm was the best fit and the constant ( $b_L$ ) increased in the order: dimetroimidazole > metronidazole > ronidazole > tinidazole, which might be related to the decreased solubility of these nitroimidazoles in water with increasing absorption energy (Rivera-Utrilla et al., 2009). Sulfamethoxazole adsorption on waste based AC was found to be best matched with the Freundlich isotherm ( $r^2 = 0.987$ ) with  $K_F$  value of  $0.308 \pm 0.008 \text{ L}^n \text{ mmol}^{1-n}/\text{kg}$  (Calisto et al., 2015). For the adsorption of tetracycline on  $\text{NH}_4\text{-Cl}$  induced AC (Table 7a), isotherm models of the Langmuir, Freundlich and Temkin also provided a good fit to the experimental data (Martins et al., 2015). The  $n$  value (14.63) from the Freundlich isotherm indicated that the physisorption was favourable.

For bentonite adsorbent, the Langmuir model was found to provide the best fit for the adsorption of amoxicillin (Putra et al., 2009) with  $r^2$  of 0.9886 and  $q_{\text{max}}$  of 53.9 mg/g. Similarly the Langmuir model was found to be more suitable than the Freundlich model for

the adsorption of ciprofloxacin on bentonite with  $r^2$  value of 0.939 and  $q_{\max}$  value of 147.1 mg/g (Genç et al., 2013).

For ionic exchange resins (Table 7a), the adsorption isotherm of sulfamethazine on strong anionic resin in a fixed bed showed that the Langmuir model correlated with the experimental data well, with  $r^2$  value of 0.981 and  $q_{\max}$  value of 110 mg/g (Fernández et al., 2014b). In another study, it was found that the Langmuir model was the best fit for the adsorption of sulfamethoxazole and sulfamethoxazole on strong anion exchanger resin (Fernández et al., 2014a).

It can be summarized that antibiotic adsorption on different adsorbents followed different pattern, with BC and CNT following multi-layer coverage whilst AC, bentonite and ion exchange resin followed monolayer coverage.

Some of the factors that affect adsorption isotherms are described below:

#### **Affinity of adsorbate to adsorbent**

Affinity of adsorbate is a prime factor that governs the mechanism of adsorptive materials. In general, if the affinity of adsorbate molecule to adsorbent surface is high then there is a high tendency for adsorption to take place. The adsorption of ionic compounds was greatly governed by the electrostatic interaction between adsorbent surface and adsorbate (Lertpaitoonpan et al., 2009; Tolls, 2001). It was found that the strength of adsorbate-adsorbent interactions may modify due to a screening effect in the presence of electrolyte solution (Radovic et al., 2001). The affinity of adsorbate is also dependent on the properties of the adsorbate molecules.

#### **Physicochemical characteristics of adsorbate and adsorbent**

The surface of adsorbent raw materials such as bentonite appears to be closely packed flacks in contrast to the ragged appearance of the thermal activated structure (Toor and Jin, 2012). After thermal activation, adsorptive materials gave the appearance of a more porous structure due to interlayer spaces collations. Moreover, some chemical activation of adsorptive

materials generated a more porous structure as well as more oxygenated functional groups on their surfaces than thermal activation only (Malik et al., 2006; Toor and Jin, 2012). The changes in molecular structure and chemical composition of the adsorbents depend upon the activation methods and conditions to be used for specific adsorbate removal. Excessive heating may lead to irreversible collapse of structure and interlayer spaces of the adsorbents.

The edges of the platelets porous surface are first to be attacked by the adsorbate molecules as it is more virgin. Thus different interactions between adsorbate and adsorbent surface occur between surface of the adsorbent and the active site of the adsorbate. In general, the increase in surface area of adsorbents provides a better chance for more interactions with adsorbate molecules. The pore size of the adsorbent may be either macro or micro in nature depending on the raw material and activation methods.

### **Effect of temperature**

The effect of temperature on the adsorption of antibiotic molecules by adsorbent can be calculated by thermodynamic equations:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad (1)$$

$$\Delta G^{\circ} = -RT \ln K_c \quad (2)$$

where  $\Delta G^{\circ}$  is the Gibbs free energy,  $\Delta H^{\circ}$  is the total enthalpy of the solution,  $\Delta S^{\circ}$  is the entropy of the reaction in solution, R is the universal gas constant (8.314 J/mol K),  $K_c$  is the equilibrium constant representing the ability of the adsorbent to retain the adsorbate and extent of movement of the adsorbate within the solution, and T is the absolute temperature (K). In general, the adsorption reactions are exothermic and spontaneous with negative  $\Delta H^{\circ}$  and  $\Delta G^{\circ}$  values and higher degree of randomness for positive  $\Delta S^{\circ}$  value (Lian et al., 2009; Pouretedal and Sadegh, 2014). For the endothermic adsorption reactions, positive value of  $\Delta H^{\circ}$  indicates that the adsorption of organic molecules onto the surface of the solid involve a chemical reaction which may be due to the protonation, hydrogen bond formation or van der Waals forces (Pouretedal and Sadegh, 2014). For example, in studying the adsorption of 40

mg/L of ciprofloxacin using bentonite and AC, negative  $\Delta G^\circ$  values (-4340 and -843 J/mol), positive  $\Delta H^\circ$  values (8662 and 7739 J/mol), and positive  $\Delta S^\circ$  values (44.1 and 29.1 J/mol K) were observed for bentonite and AC, respectively at 22°C. The results indicated that some structural changes were occurring on the adsorbent surfaces, and the randomness at the solid-liquid interface was increased during the adsorption process (Genç and Dogan, 2015).

### **Effect of solution pH**

The solution pH is a critical parameter for an effective interaction between adsorbate and adsorbent (Acemioğlu, 2004). The influence of pH on adsorption is mainly dependent on the type of carbonaceous materials and the target contaminants. It not only affects the adsorbent surface charge but also affects the degree of ionization and speciation of the adsorbate (Kołodzyńska et al., 2012; Li et al., 2013; Regmi et al., 2012). As carbonaceous materials carry various surface functional groups mainly oxygen containing groups e.g.  $-\text{COOH}$  and  $-\text{OH}$ , thus the behaviour of these functional groups changes with solution pH. When the pH of the solution is increased or decreased then the percentage of removal may change as a result, thus the optimum pH for the effective removal of specific antibiotics should be determined. For example, in the pH range of 1.0-6.0,  $\text{SMX}^0$  was dominant and the BC surface was negative; but at  $\text{pH} > 7.0$ ,  $\text{SMX}^-$  was dominant ( $> 71.5\%$ ) and the BC surfaces were strongly negative (Zheng et al., 2013). Therefore, the molecules being adsorbed and the extent of their adsorption are highly dependent on solution for those ionisable compounds. It was observed that NaOH-induced AC showed approximately 100% removal of tetracycline at pH 3.0, 80% at pH 4.0, and 70% at pH greater than 5.0, hence the optimum pH was 3.0 for tetracycline removal (Martins et al., 2015). However, for some antibiotics solution pH did not have a major effect for their removal as shown for nitroimidazoles when solution pH was between 4 and 11 (Rivera-Utrilla et al., 2009).

The adsorption of adsorbate molecule may be dominated by the specific driving force, e.g.  $\pi$ - $\pi$  electron-donor-acceptor (EDA) interaction with  $\pi$ -electron rich surface and the aromatic ring of adsorbents.

### 3.3. Adsorption mechanism

In general, electrostatic interaction (cation and anion attractions), hydrophobic effect (hydrophobic interaction), hydrogen bonds, partition into un-carbonized fractions, pore filling, and other processes (surface precipitation,  $\pi$ - $\pi$  interactions) are the main mechanism for the adsorption of antibiotics onto the carbon-based adsorbents such as AC and BC (Tan et al., 2015). Adsorption phenomenon of contaminants involves four steps: (i) solute transportation in the bulk, (ii) film diffusion of adsorbate, (iii) pores diffusion of adsorbate diffusion, (iv) adsorption - interaction between adsorbate and porous structure. These interactions are strong and more specific than physical adsorption and they are limited to the monolayer coverage (Cooney, 1999).

The potentially different and diverse adsorption mechanism by which antibiotics bind to carbon materials (BC, CNT and AC) are shown in Figure 3. The internal properties of adsorptive materials play a major role in the adsorption of organic compounds as those materials have heterogeneous surface area due to co-existing carbonized and non-carbonized fractions, which possess different adsorption mechanism. It was suggested that sulphonamides adsorption on different BCs well correlated with the amount of graphitization which indicated that  $\pi$ - $\pi$  EDA interaction between the adsorbate molecules and the graphite surfaces of the BC was the predominant adsorption mechanism (Xie et al., 2014). Sorption of sulfamethoxazole on BC at low pH (1.0-6.0) was dominated by the specific driving force,  $\pi$ - $\pi$  EDA interaction of the protonated aniline ring with the  $\pi$ -electron rich graphite surface referring to as  $\pi^+$ - $\pi$  EDA, rather than ordinary electrostatic cation exchange. Above pH 7.0 anionic

sulfamethoxazole species sorption was increased and became regulated via charge-assisted hydrogen bonds (Teixidó et al., 2011; Zheng et al., 2013).

By studying the kinetic data, it was assumed that the mechanism of antibiotic adsorption on AC was a chemical reaction i.e. chemisorption (Pouretedal and Sadegh, 2014). It was mentioned that the electronic density of nitroimidazoles with their aromatic rings increased their adsorption on AC and enhanced the chance of  $\pi$ - $\pi$  adsorbate-adsorbent dispersion interactions. Hence the adsorption process was mainly determined by the adsorbent-adsorbate dispersion interactions (Rivera-Utrilla et al., 2009). However, it was reported that  $\text{NH}_4\text{Cl}$  induced AC may show similar mechanism i.e. electrostatic interaction, hydrogen bonding formation, electron donor-acceptor, and  $\pi$ - $\pi$  dispersion interaction (Vargas et al., 2011; Martins et al., 2015).

Adsorption heterogeneity and hysteresis are two features of antibiotic-CNT interactions. However, different mechanism may act simultaneously, mainly hydrophobic interactions,  $\pi$ - $\pi$  bonds, electrostatic interactions and hydrogen bonds, hence the prediction of antibiotic adsorption on CNTs is not straightforward. The dominant adsorption mechanism is different for different types of antibiotics (such as polar and nonpolar), thus different models may be needed to predict antibiotic-CNT interaction. Adsorption mechanism will be better understood by investigating the effects of properties of both CNTs and antibiotics along with the environmental conditions such as solution pH, temperature and matrix (Pan and Xing, 2008). It was reported that the adsorption of very hydrophilic antibiotics (lincomycine and sulfamethoxazole) on SWCNTs might include electrostatic interactions and hydrogen bonds, in addition to hydrophobic interactions (Kim et al., 2014a). On the other hand, it was highly expected that sulfamethoxazole interacted with the polarized aromatic rings on the surface of CNTs via the mechanism of  $\pi$ - $\pi$  electron coupling (Ji et al., 2009b). It was proposed that  $\pi$ - $\pi$  EDA interaction between  $\pi$  electron acceptor compounds and the  $\pi$  electron rich regions of the grapheme surface of CNTs, and graphite occurred during

adsorption (Chen et al., 2008b; Ji et al., 2009a). A similar mechanism was found on KOH-activated CNT for the adsorption of sulfamethoxazole, tetracycline and tyrosine (Ji et al., 2010).

In general, bentonite has different mechanisms for adsorptive removal of contaminants (Putra et al., 2009). The first mechanism was cation exchange where low valence cations in bentonite structure ( $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$ ) were exchanged by protonated functional groups within amoxicillin (amoxicillin has positive charge due to the protonation of amoxicillin carboxyl and amine groups by the presence of free  $\text{H}^+$  ions in the solution). For carboxyl and amine groups the protonation took place as follows but phenol groups were not protonated on amoxicillin (Andreozzi et al., 2005).



The second mechanism was via interactions between the protonated groups (aluminol and silanol) in bentonite and carboxyl groups in antibiotics. The dominant mechanism of ciprofloxacin adsorption on bentonite was cation exchange. FQ molecules appear to be better suited for cation exchange than for cation bridging or surface complexion. At pH 4.5, cation exchange between the protonated heterocyclic (N atom) of positively charged ciprofloxacin ( $\text{CIP}^+$ ) and negatively charged montmorillonite surface occurred at pH 7.0, the carboxylic anion was the dominant species and thus carboxylic group of negatively charged ciprofloxacin ( $\text{CIP}^-$ ) interacted with montmorillonite surface (Genç and Dogan, 2015; Pei et al., 2009; Yan et al., 2013b).

#### **4. Adsorbent regeneration and adsorbent production cost estimation**

##### **4.1. Adsorbent regeneration**

Recovery of saturated adsorbent is one of the most important steps in the adsorptive removal of contaminant, as the feasibility of an industrial adsorption process largely depends on the cost of regeneration of spent adsorbents which can be reused subsequently. After being saturated with contaminants, the regeneration of adsorptive precursors is dependent on the type of adsorbents. For example, for carbonaceous materials (AC, BC and CNT) thermal decomposition processes are most widely used. There are three thermal methods for the regeneration of carbonaceous materials namely (i) pyrolysis, (ii) pyrolysis-gasification and (iii) gasification. Pyrolysis and gasification techniques for AC regeneration in a thermo balance at different ranges were carried out using air or CO<sub>2</sub> (200 cm<sup>3</sup>/min) under N<sub>2</sub> flow, and it was observed that air gasification achieved the best result as air had no cost with minimum time contact of 3 h (Sabio et al., 2004). Other regeneration methods involve chemical and solvent (e.g. NaOH, HCl, NaCl), microbiological, electrochemical, ultrasonic, and wet air oxidation approaches. If the solvent regeneration method is to be used then solvent consumption should be much less than that by water (Tamon et al., 1990). For example, the regeneration of AC was done using 5%w/w of NaOH (Pouretedal and Sadegh, 2014).

To regenerate CNT columns loaded with sulfamethoxazole and sulfapyridine, a solution containing 30 g/L NaCl and 1.5 g/L NaOH of pH 12 was used, with an excellent recovery of 97% for sulfamethoxazole and 91% for sulfapyridine, respectively (Tian et al., 2013). Tian et al. (2013) also observed that each regeneration cycle reduced the capacity of the adsorption bed by 8-26% for both antibiotics, but permitted the column to be reused multiple times with an acceptable antibiotic sorption capacity. It was also reported that total amoxicillin from MWCNT can be regenerated using 0.1 mol/L of NaOH and HCl, followed by distilled water (Mohammadi et al., 2015). Bentonite can be regenerated using NaOH as solvent (Peng et al., 2005), and can also be regenerated by thermal treatment (Lin and Cheng, 2002). Once desorbed, the antibiotic-loaded solvents should be disposed carefully e.g. by incineration to



eliminate pollution as well as utilizing the energy content of solvents, as otherwise antibiotics will be transferred from water to another phase. For highly concentrated chlorine containing solvents, flue gas from incineration should be purified for removing chlorine before emission.

#### **4.2. Estimation of adsorbent production cost**

The adsorbent precursors are mostly produced from agricultural (e.g. biomass), industrial (e.g. timber) and municipal (e.g. sewage) solid waste. Each of individual preparation process of adsorptive precursors has different reagents and equipment cost. The total cost of adsorptive materials can be calculated by equation 3:

$$\text{Total cost} = \text{Production cost} + \text{Regeneration cost} + \text{Process loss cost} \quad (3)$$

The production cost involves raw material and adsorbent preparation, and in most cases the raw material cost is relatively low or even negligible, depending on local precursor availability. Using BC as an example, its cost depends on the local supply of raw materials, processing requirement, reactor availability, pyrolysis parameters, value added co-products production, and material recycling in their life cycle (Mohan et al., 2014).

For CNTs, their operational cost in wastewater treatment could be lower than for other commercial carbon sorbents such as ACs (Tian et al., 2013). CNTs can perform as better adsorbents under many circumstances than ACs (Pan and Xing, 2008). But the problem associated with CNTs is that in most cases their adsorption is not reversible and production cost therefore becomes too high. For example, by studying 44 commercially available CNTs, it was found that the average price was in the range of \$1,500-\$10,000/kg and \$45,000-\$140,000/kg, respectively for MWCNTs and SWCNTs (Cho et al., 2008; Apul and Karanfil, 2015). In comparison, ACs can be available at a substantially lower price range of \$2-5/kg (Babel and Kurniawan, 2003; Lin and Juang, 2009).

Furthermore, BCs as adsorbents are inexpensive or even have negligible cost. Their production technique is also very inexpensive and does not consume costly reagents, in

comparison to AC production and activation which require high temperature and expensive reagents. Based on literature data, the cost of different BC production has been calculated and summarized as being in a range of \$0.2-0.5/kg based on the frequently reported data, and focusing on the woody waste BC rather than hardwood as environmentally and socially it is more sustainable to utilize woody wastes than hardwood (Dickinson et al., 2014). The authors therefore concluded that BC as an effective adsorbent can potentially be produced with low carbon foot print, hence highly beneficial for water treatment whilst minimizing other environmental damage such as greenhouse effect. Other adsorbent such as ion exchange resin may cost up to \$150/kg (Wang et al., 2011). A comparative price chart showed that the adsorbent cost followed the order of SWCNTs > MWCNTs > ion exchange resins > ACs > BCs (Figure 4).

## **5. Integration of adsorption process into existing treatment framework**

Currently antibiotics are removed from water or wastewater either by batch process or continuous process using adsorptive materials such as ACs, CNTs, bentonite, ion exchange resins and BCs. As one treatment technology cannot remove all contaminants from wastewater completely, it is necessary to combine more than one treatment into an integrated system. In future, considering the different treatment processes and advantages of the adsorption technology, it is necessary to study the integration of adsorption process into existing wastewater treatment system. Already, some integrated or hybrid systems (Purnell et al., 2015; Quist-Jensen et al., 2015; Rondon et al., 2015) have been developed and used by combining with other technologies such as membrane reactor (MR), membrane bioreactor (MBR), high retention membrane bioreactor (HR-MBR) (Luo et al., 2014), anaerobic membrane bioreactor (AMBR), enhanced membrane bioreactor (eMBR), filtration, osmosis, reverse osmosis, ozonolysis, chlorination, photocatalysis, aeration, anaerobic and aerobic bioreactors. These technologies may be merged or supplemented with the adsorption

technology. Some of the new integration treatment systems can be (i) MBR → adsorptive process, (ii) MBR → activated sludge → adsorptive process, (iii) MBR → biological AC → adsorptive process, (iv) MBR → biological AC → adsorptive process → photocatalysis, (v) AMBR → biological AC → adsorptive process → photocatalysis, (vi) AMBR → adsorptive process → UV filtration → photocatalysis, and other potential combinations. The combined treatment will improve the removal of recalcitrant or poorly degraded antibiotics and other trace organic contaminants, as a result of the highly efficient adsorption technology.

## **6. Challenges and future perspectives in removing antibiotics from contaminated water**

Water is becoming ever more polluted in various ways leading to concern for human and animal health. The extensive use of antibiotics for therapeutic treatment of infections related diseases in human and animals has caused antibiotic contamination of different water bodies globally. The rapid growth and development in and around urban areas and industrial complexes together with population growth have raised both the importance and requirement of appropriate wastewater treatment facilities with increasingly complex implementation. Thus, the important challenges for the 21<sup>st</sup> century in the field of antibiotics removal from wastewater in general and adsorptive technology specifically include addressing (i) the role of science in the development of stringent regulations and water quality standards preventing antibiotics being discharged from different sources; (ii) issues with establishing infrastructure for the centralized collection of antibiotic contaminated wastewater; (iii) advanced wastewater treatment technology targeted at effective antibiotic removal; (iv) waste-derived low cost adsorptive materials with a high capacity for antibiotic removal; (v) final disposal of antibiotics-loaded adsorbents; and (vi) life cycle analysis of novel adsorptive materials in order to minimize their carbon footprint.

Some of the future research perspectives include:

- In-depth cost-benefit analysis of adsorptive materials (e.g. BCs) including their production and regeneration using different methods.
- Development of fully-integrated adsorption systems combining different technologies by considering all the important factors such as treatment requirement.
- Establishing large-scale supply chains for the continuous production of adsorptive materials with high yield and low cost.
- Development of effective and low-cost regeneration techniques for BCs and other similar adsorbents.
- Maximizing the adsorptive capacity of adsorbents by modifying their surface structure with novel functional groups in order to achieve high selectivity and specificity.
- Experimenting with multiple or mixture adsorbents with potentially better performance.
- More studies are needed to examine the effect of competition from co-solutes in solution on antibiotic removal by adsorption.

## 7. Conclusions

The removal of antibiotic residues from water and wastewater by adsorption technology has been critically reviewed based on extensive scientific reports. It can be summarized that adsorption is an effective method for antibiotic removal from contaminated waters with an efficacy of 90-100% at mg/L concentration range. The most widely used adsorbents with effective removal are ACs, CNTs and BC. For the removal of sulfamethazole, it was found that adsorptive materials followed the order of BC600 > BC500 > MWCNT > graphite = clay minerals, while for the removal of tetracycline, adsorptive materials followed the trend: SWCNT > graphite > MWCNT = AC > bentonite = humic substance = clay minerals. The high material cost and potential high regeneration costs are the major drawbacks for both ACs and CNTs. In comparison, BCs can be prepared at a significantly lower cost with equal or better adsorptive capacity for antibiotic removal, hence should be explored further. It was

found that the cost of adsorbents followed the order of SWCNTs > MWCNTs > ion exchange resins > ACs > BCs. Adsorption equilibrium was well modelled by either the Langmuir isotherm or the Freundlich isotherm, while adsorption kinetics often followed pseudo second order. The mechanism of antibiotic adsorption potentially involved  $\pi$ - $\pi$  EDA interactions, electrostatic interactions, hydrophobic interaction, hydrogen bonds, and pore filling. Further research should focus on improved understanding of adsorption mechanism, in order to prepare functionalized adsorbents with better specificity and selectivity for antibiotics. In addition, research efforts should be directed to pilot scale or even commercial scale adsorption experiments so that the operating cost of adsorption technology can be fully evaluated. With thorough knowledge of molecular adsorption mechanism, better methods of regenerating spent adsorbents, and full cost-benefit analysis of commercial adsorption columns, the application of low-cost and highly effective adsorbents such as BCs in removing antibiotic residues from waste streams will become widely adopted in safeguarding our precious water resources.

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**Table 1**

Physicochemical properties of major types of antibiotics investigated by different studies.

Class	Compound	Acronym	CAS number	$\log k_{ow}$	$pK_a$	Molecular mass	Molecular formula	Reference
Chloramphenicols (CPs)	Chloramphenicol	CAP	56-75-7	1.14		323.13	$C_{12}H_{12}Cl_2N_2O_5$	Yan et al. (2013a)
	Thiamphenicol	TAP	15318-45-3	-0.27		356.22	$C_{12}H_{15}Cl_2NO_5S$	
	Florfenicol	FF	76639-94-6	0.37		358.21	$C_{12}H_{14}Cl_2FNO_4$	
Macrolides (MLs)	Erythromycin	ETM	59319-72-1	3.06	8.9	731.95	$C_{38}H_{69}NO_{12}$	Yan et al. (2013a)
	Roxithromycin	RTM	80214-83-1	2.75	9.17	837.05	$C_{41}H_{76}N_2O_{15}$	
Sulfonamides (SAs)	Sulfadiazine	SD	68-35-9	-0.34	2.0/6.48	250.28	$C_{10}H_{10}N_4O_2S$	Qiang and Adams (2004), Yan et al. (2013a), Yang et al. (2011)
	Sulfamerazine	SM	127-79-7	0.44	2.06/6.90	264.30	$C_{11}H_{12}N_4O_2S$	
	Sulfamethazine	SMT	57-68-1	0.14	2.65/7.65	278.34	$C_{12}H_{14}N_4O_2S$	
	Sulfamethoxazole	SMX	723-46-6	0.89	1.6/5.7	253.28	$C_{10}H_{11}N_3O_3S$	
	Sulfathiazole	ST	72-14-0	0.05	2.2/7.24	255.32	$C_9H_9N_3O_2S$	
	Sulfapyridine	SP	144-83-2	0.35	2.9/8.54	249.29	$C_{11}H_{11}N_3O_2S$	
Tetracyclines (TCs)	Tetracycline	TC	60-54-8	-1.37	3.3	444.43	$C_{22}H_{24}N_2O_8 \cdot HCl$	Qiang and Adams (2004), Yan et al. (2013a), Yang et al. (2011)
	Chlortetracycline	CTC	64-72-2	n/a	3.3/7.55	515.34	$C_{22}H_{23}ClN_2O_8 \cdot HCl$	
	Oxytetracycline	OTC	2058-46-0	-0.9	9.5	496.90	$C_{22}H_{24}N_2O_8 \cdot HCl$	
	Doxycyclinehyclate	DXC	24390-14-5	2.37	3.02/7.97	544.98	$C_{22}H_{24}N_2O_9 \cdot HCl$	
Flouroquinolones (FQs)	Norfloxacin	NFC	70458-96-7	-0.46	3.11/6.10	319.33	$C_{16}H_{18}FN_3O_3$	Qiang and Adams (2004), Yang et al. (2011)
	Enrofloxacin	EFC	93106-60-6	0.70	3.85/6.19	359.4	$C_{19}H_{22}FN_3O_3$	
	Ciprofloxacin	CIP	85721-33-1	0.28	6.09	331.34	$C_{17}H_{18}FN_3O_3$	
	Ofloxacin	OFC	82419-36-1	-0.02		331.34	$C_{18}H_{20}FN_3O_3$	
Imidazoles	Metronidazole, fenbendazole, oxfendazole			-0.02-3.9	2.4	171.5-315.3		Thiele-Bruhn (2003)
$\beta$ -Lactams	Penicillins, ampicillin, meropenem, cephalosporins, ceftiofur, penicillin G, cefotianm			0.9-2.9	2.7	334.4-470.3		Thiele-Bruhn (2003)
Others	Carbadox	CARB	6804-07-5			262.2	$C_{11}H_{10}N_4O_4$	Qiang and Adams (2004)
	Lincomycin	LNCM	859-18-7		7.80	443.0	$C_{18}H_{34}N_2O_6S \cdot HCl$	
	Trimethoprim	TRMP	738-70-5		3.24/6.76	290.3	$C_{14}H_{18}N_4O_3$	

**Table 2**

Summary of the antibiotic removal by AC adsorbents applied in the treatment of contaminated water.

Antibiotic class/compound	Adsorbate concentration (mg/L)	Operating condition	Removal	Reference
$\beta$ -Lactams/amoxicillin	300	pH 2–7, 0.1–3.5 g AC, 30 °C	95%	Putra et al. (2009)
	50	0.4 g/L PAC, pH 6, >50 °C	99%	Moussavi et al. (2013)
	20	pH 2, 45 °C, 0.4 g/L AC, time 8 h	74–88%	Pouretedal and Sadegh (2014)
Cephalexin	20	pH 2, 45 °C, 0.4 g/L AC, time = 8 h	74–88%	Pouretedal and Sadegh (2014)
Imidazoles/nitroimidazoles	100–600	25 °C, pH 2–11, 0–0.1 M NaCl, 1 g/L AC		Rivera-Utrilla et al. (2009)
Dimetridazole				
Metronidazole				
Ronidazole	150	25 °C, 0.2–1 g/L AC, pH 7	90%	Méndez-Díaz et al. (2010)
Tinidazole				
Penicillins/penicillin G	20	pH 2, 45 °C, 0.4 g/L AC, time 8 h	74–88%	Pouretedal and Sadegh (2014)
	50	pH 6, batch process, 25 °C, time 48–72 h		Ania et al. (2011)
Quinoxaline derivatives/carbadox	50	Time 4 h, 0.66 g PAC, pH 7	>90%	Adams et al. (2002)
Sulphonamides/sulfamerazine	50	Time 4 h, 0.66 g PAC, pH 7	>90% for PAC	Adams et al. (2002)
Sulfamethazine				
Sulfathiazole				
Sulfachlorpyridazine				
Sulfadimethoxine				
Sulfamethoxazole		Time 1.5–3 min	100%	Stackelberg et al. (2007)
Ciprofloxacin	20–40	Batch: 22 °C, pH < 5.5, 0.0125 g GAC	87%	Genç and Dogan (2015)
Tetracycline	50, 100, 300	Batch, time 120 h, pH 3.4–11		Torres-Pérez et al. (2012)
	20	pH 2, 45 °C, 0.4 g/L AC, time 8 h	74–88%	Pouretedal and Sadegh (2014)
	600	pH 3–10		Martins et al. (2015)
Trimethoprim	50	Time 4 h, 0.66 g PAC, pH 7	>90% by PAC	Adams et al. (2002)
	50	pH 4–10, 25 °C, 0–3 g/L AC	>90%	Kim et al. (2010)

**Table 3**

Summary of antibiotic removal process by CNTs applied in the treatment of contaminated water.

Antibiotic class/compound	Adsorbate concentration (mg/L)	Operating condition	Removal	Reference
$\beta$ -Lactams/amoxicillin	80	Batch: 0.1–0.2 g MWCNT, pH 4.6, time 120 h	86.5%	Mohammadi et al. (2015)
Lincosamides/lincomycin	12,000	Batch: 20 °C, pH 6.0, time 100 h	>90%	Kim et al. (2014a)
Sulphonamides/sulfamethoxazole	12,000	Batch: 20 °C, pH 6.0, time 100 h	>90%	Kim et al. (2014a)
Sulfamethoxazole	200	Fixed bed column: pH 3.0–9.0, time 2 h	96%	Tian et al. (2013)
Sulfapyridine				
Sulfamethoxazole	0.21–2.50	Batch: 15 mg MWCNT, pH 5.7–6.2	80%	Ji et al. (2009b)
Sulfapyridine				

**Table 4**

Summary of antibiotic removal by clay material (bentonite) applied in the treatment of contaminated water.

Antibiotic class/compound	Adsorbate concentration (mg/L)	Operating condition	Removal	Reference
$\beta$ -Lactams/amoxicillin	300	pH 2–7, 0.1–3.5 g adsorbent, 30 °C	88%	Putra et al. (2009)
Flouroquinolones/ciprofloxacin (CIP)	50–500	Batch: contact time 30 min, pH 4.5, 2.5 g/L bentonite	99%	Genç et al. (2013)
	20–40	Batch, 22 °C, pH < 5.5, 0.0125 g adsorbent	87–91%	Genç and Dogan (2015)

**Table 5**

Summary of antibiotic removal by ion exchange resins applied in the treatment of contaminated water.

Antibiotic class/compound	Adsorbate concentration (mg/L)	Operating condition	Removal	Reference
Sulphonamides/sulfachloropyridazine	10	pH 7.0, 25 °C, time 15 d	~90%	Choi et al. (2007)
Sulfadimethoxine		MIEX <sup>®</sup> resin treatment: pH 7.0, 25 °C,		
Sulfamerazine		0.5–5.0 mL/L resin, time 24 h		
Sulfamethazine				
Sulfamethoxazole				
Sulfamonomethoxine				
Sulfathiazole				
Sulfamerazine	50	Time 4 h, 0.66 g ion exchange resins, pH 7	>90% for PAC	Adams et al. (2002)
Sulfamethazine				
Sulfathiazole				
Sulfachloropyridazine				
Sulfadimethoxine				
Sulfamethazine	200–400	Fixed bed: room temp., 1.3 g resin, time 100 min	100%	Fernández et al. (2014b)
Sulfamethoxazole	30–350	Batch and continuous, time 120 min		Fernández et al. (2014a)
Sulfamethazine				
Quinoxaline derivatives/carbadox	50	0.66 g strong-acid cation and strong-base anion resins, pH 7		Adams et al. (2002)
Tetracyclines/chlortetracycline	10	pH 7.0, 25 °C, time 1 d and 15 d, 0.5–5.0 mL/L resin	>80%	Choi et al. (2007)
Democycline				
Doxycycline				
Meclocycline				
Minocycline				
Oxytetracycline				
Tetracycline				
Trimethoprim	50	Sorption: time 4 h, 0.66 g ion exchange resins, pH 7		Adams et al. (2002)



**Table 6**

Summary of antibiotic removal by BC adsorbents applied in the treatment of contaminated water.

Antibiotic	Adsorbate concentration (mg/L)	Operating condition	Removal	Reference
Amphenicol/ florfenicol	50	Batch: 0.4 g BC, 22 °C, time 24 h	100%	Mitchell et al. (2015)
Ceftiofur	50	Batch: 0.4 g BC, 22 °C, time 24 h	98–100%	Mitchell et al. (2015)
Sulfamethoxazole	12.5	Batch: 35 rpm, time 72 h, pH 5		Zheng et al. (2013)
	10	0.1 g BC, 22 ± 0.5 °C		Yao et al. (2012)
Sulfamethazine	0.001–0.1	pH 5, 48 h, 20 ± 0.2 °C		Teixidó et al. (2011)
Sulfamethoxazole	50	Batch: 10–15 mg BC, pH 6		Xie et al. (2014)
Sulfapyridine				
Tetracycline	50–1000	0.1 g BC, 30 °C		Liu et al. (2012)

**Table 7a**

Model parameters for the equilibrium isotherms and kinetics of adsorptive materials during antibiotic removal from contaminated water.

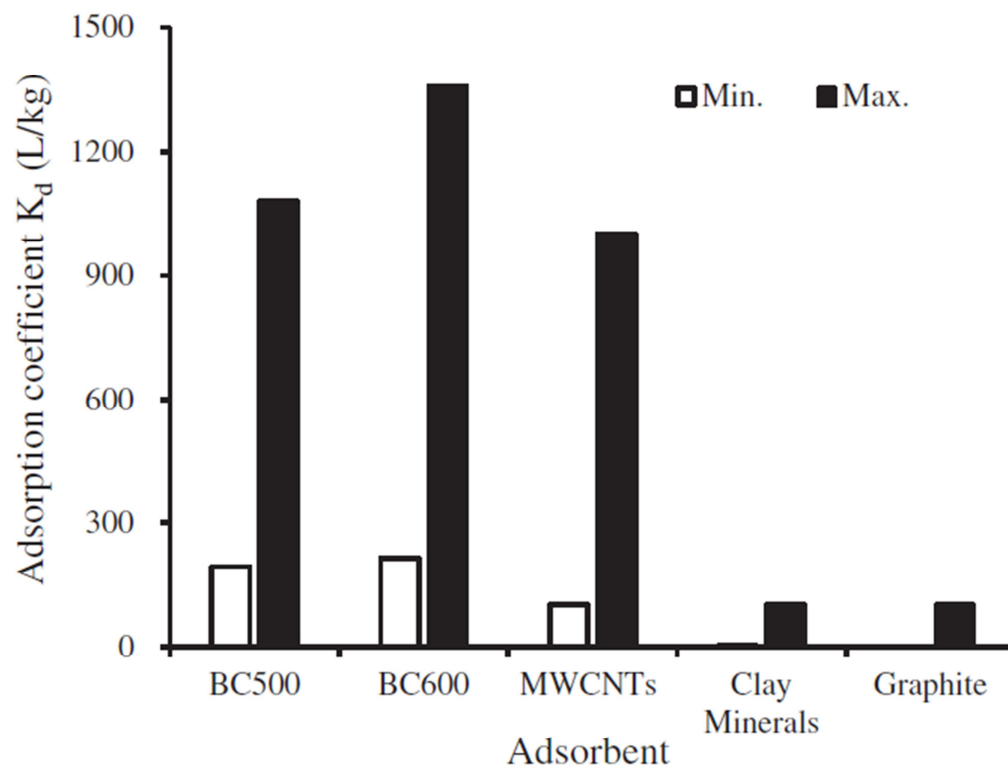
Antibiotic	Adsorbent	Equilibrium model						Kinetic model						Reference
		Langmuir parameters			Freundlich parameters			Pseudo 1st order			Pseudo 2nd order			
		q <sub>max</sub>	b <sub>L</sub>	r <sup>2</sup>	n	K <sub>F</sub>	r <sup>2</sup>	q <sub>e</sub>	k <sub>1</sub>	r <sup>2</sup>	q <sub>e</sub>	k <sub>2</sub>	r <sup>2</sup>	
Sulfamethazole	BC500H				0.20 ± 0.01	0.164 ± 0.009	0.98							Xie et al. (2014)
Sulfapyridine					0.16 ± 0.01	0.143 ± 0.008	0.96							
Sulfamethazole (SMX)	BC500				0.256 ± 0.012	2.54 ± 0.0197	0.952							Zheng et al. (2013)
	BC600				0.198 ± 0.011	2.94 ± 0.0106	0.955							
	WBC	118 ± 5		0.982	3.1 ± 0.2	0.308 ± 0.008	0.987	111	0.15	0.978	118	0.0021	0.991	Calisto et al. (2015)
	SWCNT				0.31 ± 0.06	6.38 ± 2.91	0.931							Kim et al. (2014a)
	MWCNT				0.48 ± 0.05	2.01 ± 0.51	0.986							
	PAC				0.30 ± 0.02	3.78 ± 0.46	0.993							
	SWCNT				0.40 ± 0.01	5.2 ± 0.400	0.992							Ji et al. (2010)
	MWCNT				0.347 ± 0.007	2.3 ± 0.100	0.996							
	Anion Exchange	263	0.017	0.997										Fernández et al. (2014a)
Sulfamethazine (SMZ)	Anion Exchange	110	0.043	0.981										Fernández et al. (2014b)
		110	0.043	0.995										Fernández et al. (2014a)
														Ji et al. (2010)
Tetracycline	SWCNT				0.095 ± 0.004	1.4 ± 0.300	0.976							
	MWCNT				0.104 ± 0.005	0.800 ± 0.020	0.977							
	BP-H <sub>2</sub> O	288.3	0.2075	0.990	0.15	0.30465	1.000							Torres-Pérez et al. (2012)
	PH-H <sub>2</sub> O	28.0	1.5393	0.972	0.10	0.0418	0.985							
	GAC1	133.1	0.0533	0.998	0.21	0.09607	0.999							
	GAC2	816.7	1.7809	0.987	0.10	1.2033	0.999							
	BP-H <sub>2</sub> O	308.8	0.0621	0.929	0.29	0.15457	0.969							
	GAC2	549.5	1.0944	0.990	0.06	0.9535	0.995							
	AC	1.98	1.87	0.980		0.54	0.960		0.002	0.910		0.233	0.990	Pouretedal and Sadegh (2014)
	NaOH-AC	455.8		0.97	14.63	0.7769	0.970	381.9	0.204	0.89	408.3	0.00073	0.960	Martins et al. (2015)

$q_e$ ,  $q_{\max}$  = mg/g,  $b_L$  = L/mol,  $K_F$  = ( $\text{mmol}^{1-n} \text{L}^n \text{kg}^{-1}$ ),  $k_1$  =  $\text{min}^{-1}$ ,  $k_2$  = ( $\text{mg g}^{-1} \text{min}^{-1}$ ), BC500-600 = BC from 500 °C and 600 °C, BC500H = 500 °C pyrolyzed BC with hydrogenation, WBC = Waste based carbon, PH-H<sub>2</sub>O = AC from peanut hulls with steam activation, BP-H<sub>2</sub>O = AC from beet pulp with steam activation, GAC1&2 = commercial GAC 1&2, SAC = standard AC, NAC = ammonium chloride induced AC.

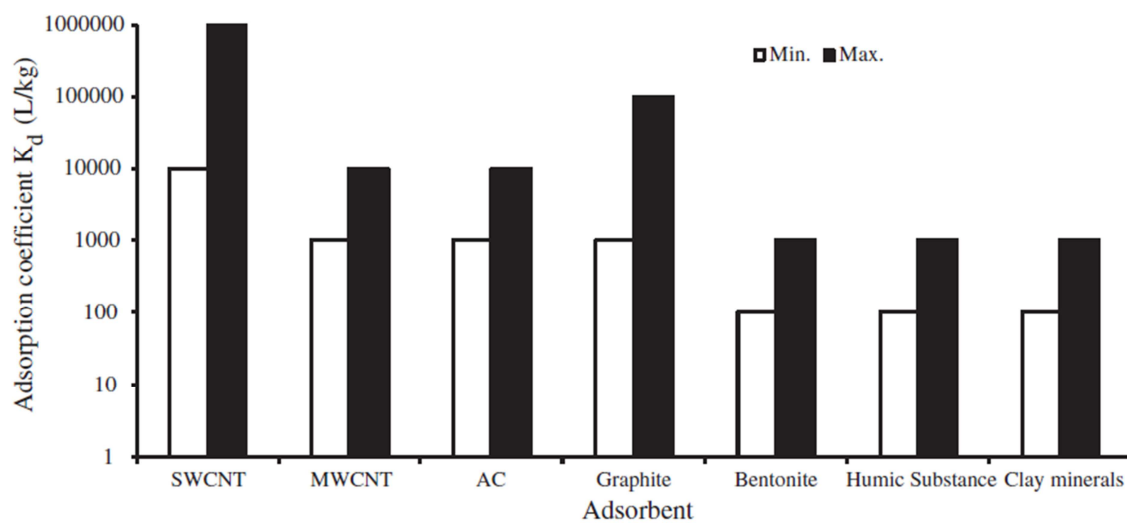
**Table 7b**

Model parameters for the equilibrium isotherms and kinetics of adsorptive materials during antibiotic removal from contaminated water.

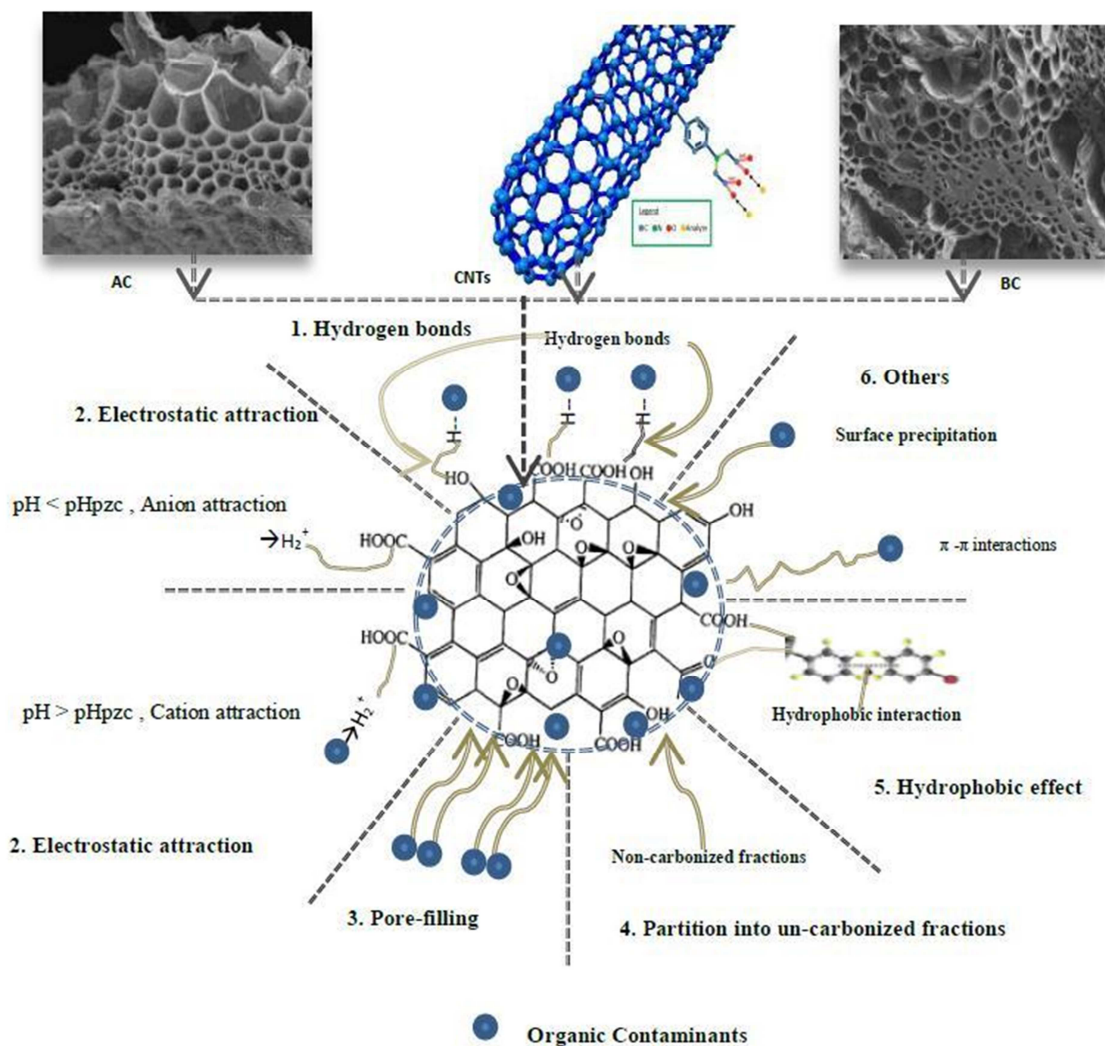
Antibiotic	Adsorbent	Equilibrium model						Kinetic model						Reference	
		Langmuir parameters			Freundlich parameters			Pseudo 1st order			Pseudo 2nd order				
		q <sub>max</sub>	b <sub>L</sub>	r <sup>2</sup>	n	K <sub>F</sub>	r <sup>2</sup>	q <sub>e</sub>	k <sub>1</sub>	r <sup>2</sup>	q <sub>e</sub>	k <sub>2</sub>	r <sup>2</sup>		
Amoxicillin (AMX)	MWCNT	23.458	2.50e−5	0.999	0.3749	3.000	0.918							Mohammadi et al. (2015)	
	SAC	261.8	0.166	0.998	4.95	0.2448	0.96	83.3	0.044	0.983	125	0.001	0.998		Moussavi et al. (2013)
	NAC	438.6	0.128	0.994	2.7	0.2086	0.959	40.29	0.099	0.961	126.6	0.013	0.999		
	AC	7.367	2.51	0.980		0.54	0.900		0.005	0.890		0.009	0.980		
Cephalexin	Bentonite	53.93		0.988		0.0044	0.965	19.55	0.009	0.979	20.82	5.243	0.993	Putra et al. (2009)	
	AC	221.868		0.994		0.0336	0.9905	24.29	0.229	0.988	26.71	0.021	0.998		
	AC	7.08	1.08	0.980		0.11	0.910		0.004	0.890		0.017	0.990		Pouretedal and Sadegh (2014)
	AC	8.41	3.10	0.990		0.89	0.910		0.004	0.910		0.094	0.990		
Penicillin G														Kim et al. (2014a)	
Lincomycine (LCN)	SWCNT				0.22 ± 0.02	1.03 ± 0.17	0.985								
	MWCNT				0.35 ± 0.03	0.287 ± 0.049	0.987								
	PAC				0.27 ± 0.03	1.00 ± 0.18	0.968								
Nitroimidazole	AC	287.532	0.0235	>0.999		1.451	0.932							Rivera-Utrilla et al. (2009)	
Metronidazole	AC	287.91	0.0233	>0.999		2.4478	0.893								
Dimetridazole	AC	257.162	0.0565	>0.999		0.8098	0.885								
Tinidazole	AC	378.283	0.0246	>0.999		1.807	0.928								
Ronidazole														Ji et al. (2010)	
Tyrosin	SWCNT				0.097 ± 0.004	0.910 ± 0.001	0.983								
	MWCNT				0.127 ± 0.004	0.650 ± 0.001	0.989								
Fluoroquinolone	Bentonite	147.1	0.0106	0.9392	2.61	0.04488	0.9006				99	0.3571		Genç et al. (2013)	
Ciprofloxacin (CIP)	Bentonite							137.1	0.065	0.817	138.9	0.0052	0.999		Genç and Dogan (2015)
	AC							93.49	0.049	0.952	95.24	0.0033	0.998		



**Fig. 1.** Adsorption coefficient ( $K_d$ ) for the removal of sulfamethoxazole by different adsorbents.



**Fig. 2.** Adsorption coefficient ( $K_d$ ) for the removal of tetracycline by different adsorbents.



**Fig. 3.** Adsorption mechanism during the adsorption of antibiotics by carbonaceous materials. Modified from Tan et al. (2015).

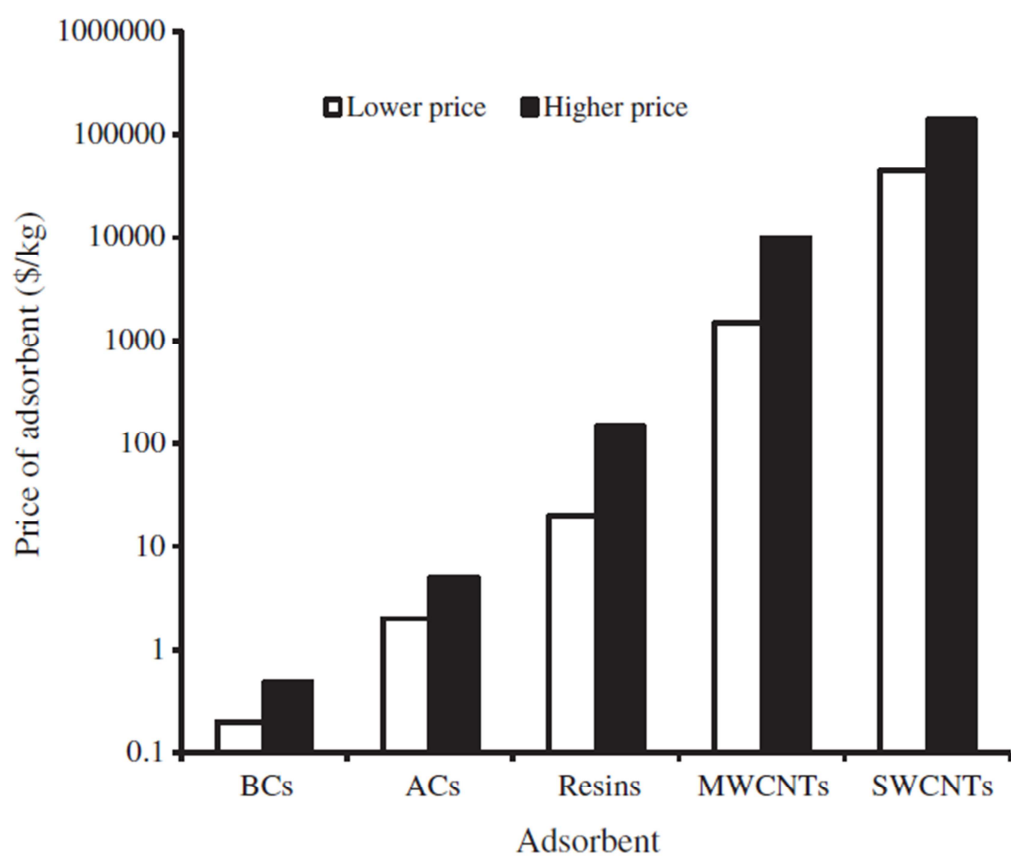


Fig. 4. The commercial price of different adsorbents.