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Textile Dye Removal from Aqueous Solution using Modified Graphite Waste/Lanthanum/Chitosan Composite

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Abstract. We investigated various pre-treatment processes of graphite waste using thermal, mechanical and chemical methods. The aim of this work is to study the performance of modified graphite waste/lanthanum/chitosan composite (MG) as adsorbent for textile dye removal from aqueous solution. Effect of graphite waste resources, adsorbent size and lanthanum concentration on the dye removal were studied in batch experiments. Selectivity of MG was also investigated. Pre-heated graphite waste (NMG) was conducted at 80°C for 1 h, followed by mechanical crushing of the resultant graphite to 75 µm particle size, giving adsorption performance of ~58%, ~67%, ~93% and ~98% of the model dye rhodamine B (concentration determined by UV-vis spectroscopy at 554 nm), methyl orange (464 nm), methylene blue (664 nm) and methyl violet (580 nm), respectively from aqueous solution. For this process, the system required less than ~5 min for adsorbent material to be completely saturated with the adsorbate. Further chemical modification of the pre-treated graphite waste (MG) with lanthanum (0.01 – 0.03 M) and chitosan (0.5% w/w) did not improve the performance of dye adsorption. Under comparable experimental conditions, as those of the 'thermal-mechanical-pre-treated-only' (NMG), modification of graphite waste (MG) with 0.03 M lanthanum and 0.5% w/w chitosan resulted in ~14%, ~47%, ~72% and ~85% adsorption of rhodamine B, methyl orange, methylene blue and methyl violet, respectively. Selective adsorption of methylene blue at most to ~79%, followed by methyl orange, methyl violet and rhodamine B with adsorption efficiency ~67, ~38, and ~9% sequentially using MG with 0.03 M lanthanum and 0.5% w/w chitosan.

1. Introduction

Availability of graphite waste from ex-electrolysis process is very abundant with availability of 1,000 ton per month and having very low price [1]. So far, the graphite electrode waste is only used as filler in steel manufacturing. It is widely known that the main compound in graphite electrode waste is carbon and has the ability to adsorb some dye, heavy metal ions and CO₂ [2]. From our previous research, these graphite waste contained the carbon is about 80% that can be utilized as sorbent [2].

In textile industry, the synthetic dyes that commonly used are rhodamine B, methyl orange, methylene blue (MB) and methyl violet (MV) and so on. These synthetic dyes are organic compounds that are not easily biodegraded by nature and could be easily deposited in the body. Both methylene blue and methyl violet are cationic dye and toxic [3]. Textile dyes deposited *in vivo* will accumulate in the food chain and may harm to human body [3].



In this study, we investigated various pre-treatment processes – thermal, mechanical and chemical treatments, for the utilization of graphite waste as sorbent for the selected of dye models in textile wastewater. Chitosan and lanthanum were selected as modifier to increase the adsorption capacity of graphite waste. Chitosan is used as adsorbent because of chitosan has amine group (NH₂) [4] which is able to bind chemically with the dye textiles. Besides, chitosan is a biodegradable material [5,6]. Lanthanum is used to help the adsorption of anion because lanthanum is cationic and contains empty orbitals that can bind the dye molecules [7]. Herein, we study on the preparation of modified graphite waste/lanthanum/chitosan composite as adsorbent for textile dye removal from aqueous solution. The aim of this work is to evaluate the adsorption efficiency of the selected dye models, rhodamine B, methyl orange, methyl violet, and methylene blue, from aqueous solution onto the prepared adsorbents. Effect of graphite waste resources, adsorbent size and lanthanum concentration on the dye removal were studied in batch experiments. Selectivity of modified graphite waste/lanthanum/chitosan composite (MG) was also investigated.

2. Method

2.1. Modification of adsorbent. Graphite waste was oven-dried at a temperature of 80°C for 1 h. Graphite waste that was dried then mashed with a grinder and filtered with a filter size of 150 microns. These steps are repeated with variations in the size of 100 and 75 μm. Graphite (5 g) was immersed and soaked in 50 mL of 0.01 M La³⁺ for 1 h. Results filtered with filter paper soaked cake then oven-dried at a temperature of 80°C for 2 hours. The dried cake weighed and then placed in an oven at 80°C for 1 hour on a regular basis to make sure the cake does not contain any water at all. The solids graphite re-soaked in a solution of 0.5% chitosan in 1% acetic acid solution for 3 h. After filtration, soaked cake then oven-dried at a temperature of 80°C for 2 h. The dried cake weighed and then dried again in an oven at 80°C for 1 hour on a regular basis to make sure the cake does not contain any water at all. All method was repeated using the La³⁺ ions concentration from 0.02 and 0.03 M.

2.2. Characterization. Nitrogen adsorption measurement was conducted at 77.2 K (-195.8°C), using an ASAP 2020 V4.02 unit gas adsorption analyzer, at an equilibration interval of 5 sec, with a sample mass from 0.28 to 0.30 g. The surface area of the adsorbent was determined using the Brunauer, Emmet, and Teller (BET) equation, and the microspore volume of the adsorbent was measured using the t-plot method. The pore size distribution was calculated according to the Barrett, Joyner, and Halenda (BJH) model, and the surface morphology was determined by field emission scanning electron microscopy and energy dispersive x-ray (FESEM-EDX) analysis.

2.3. Batch adsorption. 0.1 g of sorbent was soaked in 20 mL of dye with a concentration of 10 ppm for 5 minutes. The resulting mixture is filtered and the filtrate was taken to measure its concentration. The amount adsorbed of dye in filtrate was measured by using UV-Vis spectroscopy at wavelengths of 464, 554, 580, and 664 nm. The process is repeated using a textile dye concentrations of 20, 30, 40, and 50 ppm. Mixture of textile dye solution (rhodamine B, methyl orange, methyl violet, and methylene blue) is made with a concentration of 10 mg/L by the way each one mg dye dissolved into 100 mL of distilled water. 20 mL of the selected dye model is taken and mixed with 0.1 g of sorbent for 5 minutes. The resulting mixture was filtered and the filtrate was taken to measure its concentration. The absorption of filtrate was analyzed using UV-Vis spectroscopy with wavelength (λ) at 464, 554, 580, and 664 nm.

$$Q_e = \frac{V(C_0 - C_E)}{W} \quad (1)$$

The value of C_0 is the initial concentration taken from the initial concentration before the sorbent was soaked in textile dyes solution. C_E obtained from UV-Vis spectroscopy measurements were compared with a calibration curve. V is the volume of solution used. W is the mass of adsorbent used.

3. Results and Discussion

3.1. Characteristics adsorbent. The morphology of non-modified graphite (NMG), modified graphite (MG), and modified graphite after adsorbs dyes (MGA) were observed with FESEM-EDX (see Figure 1A-C).

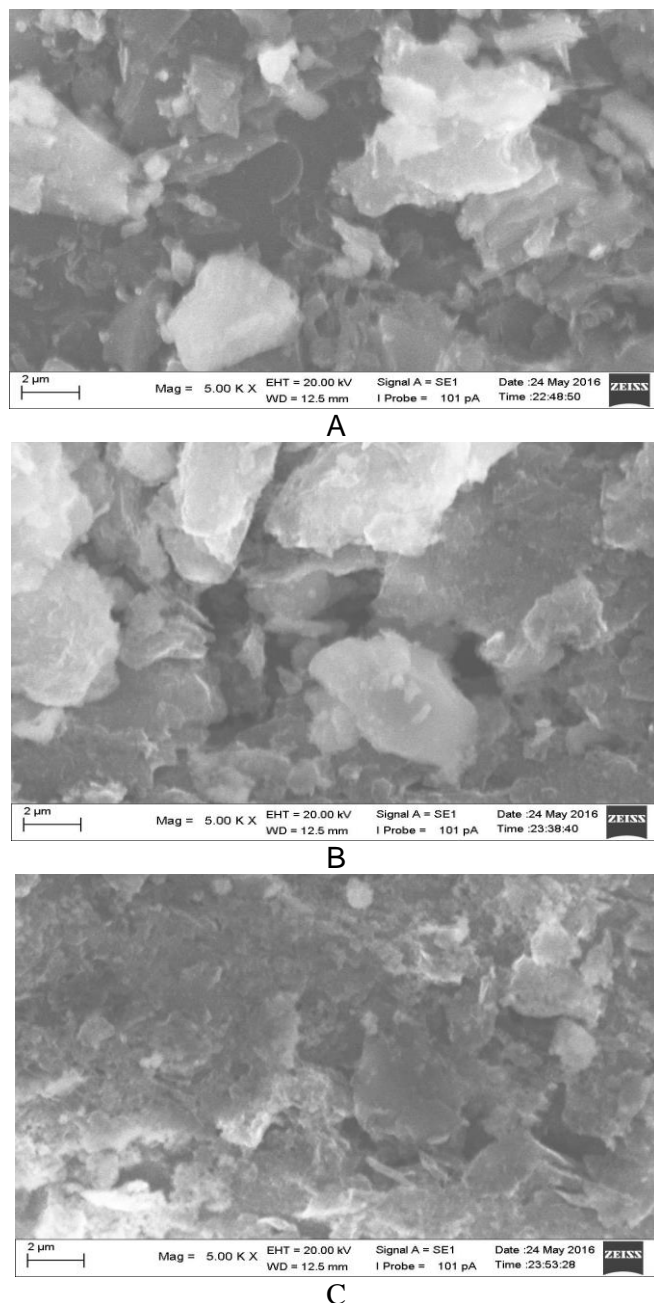


Figure 1. FESEM images of (A) non modified-graphite (NMG) with 200 mesh (75µm), (B) Modified graphite (MG) with lanthanum concentration of 0.03 M, and (C) Modified graphite after adsorption (MGA) with magnification of 5000x

Figure 1(a) shows that the NMG has uneven surface with small crystalline impurities. The NMG has pores ranging between 1 - 4 μm , with impurities crystal size ranges between 2 - 5 μm . After modification, the graphite surface shows larger size crystals with a lighter colour (Figure 1(b)) compared to Figure 1(a). This large crystals are lanthanum nitrate crystals with a size of 3 - 6 μm , while the bright side shows chitosan that blanketed graphite and lanthanum in which the composition can be seen in MG has a pore diameter of 1.5 - 5 μm . Figure 1(c) shows the surface of MGA becomes dark and some possible dyes aggregates appear. After carefully examining the pore diameter, pore diameter graphite after adsorbs reduced to range from 0.5 to 2.5 μm , which indicates pore filling by dye molecules.

The elemental composition of sorbents was summarized in Table 1. The carbon (C) content of NMG and MG slightly decreased because the addition of lanthanum and chitosan modification, and shows the lanthanum ions and chitosan were covering the graphite waste. Lanthanum was detected in MG and MGA indicating lanthanum is attached on the surface of graphite waste. After adsorption of the dyes, the composition of carbon in MGA increase due to molecularly adsorbed dyes. Fe content was not observed in both MG and MGA. Very little content of Si was observed in both NMG and MG. It is similar observed for non-modified graphite waste as previously reported [2].

Table 1. EDX composition of graphite waste before and after adsorption process

Component (wt %)	NMG	MG	MGA
C	81.25	75.79	83.09
O	6.43	3.97	4.41
F	8.05	12.78	7.19
Na	1.91	1.52	0.48
Al	0.67	0.99	0.55
Si	0.12	0.06	-
S	0.76	0.08	0.23
Ca	0.62	0.65	0.86
Fe	0.20	-	-
La	0.0	0.3	0.3

In accordance with Table 2, physical properties of MG such as surface area, pore volume and pore size are larger than the NMG. This properties enhancement increases possible contact of dye molecules with graphite. However, there is also a possibility that the concentration of lanthanum is used is still less optimum for improving dye adsorbs chemical substances. The results of the BET surface area calculations suggests that the graphite waste modified by lanthanum and chitosan has larger surface area (up to 84%).

Table 2. The physicochemical properties of graphite waste before and after modification

Parameter	NMG	MG
BET Surface area (m^2/g)	5.9	10.8
BJH adsorption cumulative surface area of pores (m^2/g)	3.5	9.0
t-Plot mesopore area (m^2/g)	2.1	0.5
Mesopore volume (cm^3/g)	1.1×10^{-3}	1.3×10^{-4}

BJH adsorption cumulative volume of pores (m^2/g)	1.6×10^{-2}	4.2×10^{-2}
Adsorption average pore (nm)	11.9	16.1
BJH adsorption average pores diameter (nm)	18.5	18.7
Average nanoparticle size (nm)	1025.1	556.7

3.2. Effect of Conditions in Adsorption of Textile Dyes

3.2.1. Effect of Graphite Waste Resources. At the same condition treatment of graphite waste (cathode, anode and a mixture of sequential), adsorption ability of textile dyes of sorbents are shown in Figure 2. The types of graphite waste sources are used in this research that influenced the ability to adsorb textile dyes. This is caused by the type of the structure possessed by each graphite with different percentage amount of impurities. In general, non-modified graphite (NMG) waste from cathode has better performance compared to other sources of graphite waste.

3.2.2. Effect of Adsorbent size. At the same condition treatment of graphite waste non modification (NMG) from three source (cathode, anode and mixed) with different particle sizes from 75 to 150 μm in sequence, adsorption of textiles dyes of adsorbent are shown in Figure 2. It is caused by the surface area increases as the particle size gets smaller. However, graphite waste from anode shows some anomaly where 100 μm particle size gave better adsorption than 75 μm .

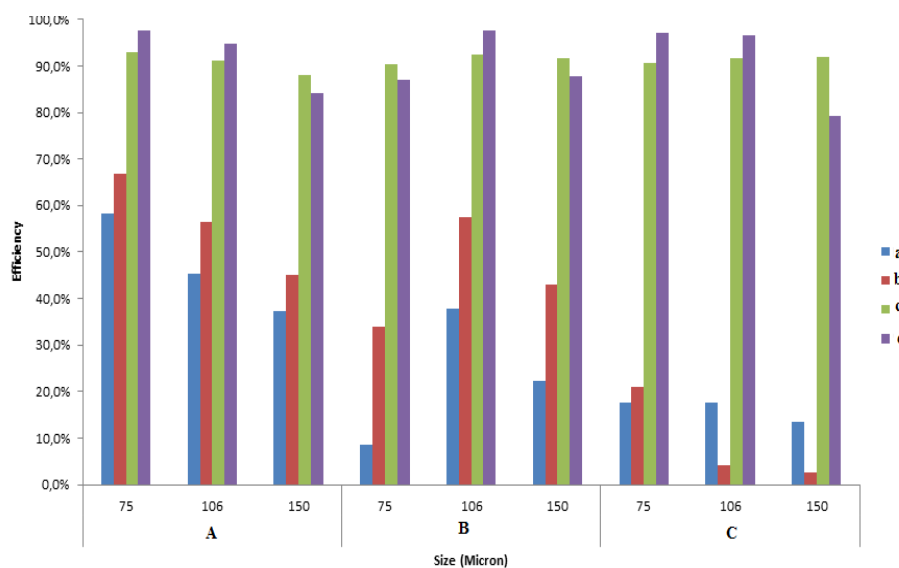


Figure 2. Adsorption efficiency of NMG with three graphite waste sources for (A) cathode, (B) anode and (C) mixture, where a = rhodamine B, b = methyl orange, c = methylene blue, and d = methyl violet,

3.2.3. Effect of lanthanum concentration on dye removal. At the same condition treatment of graphite anode, cathode, and a mixture of sequential, adsorption of textiles dyes of adsorbent dyes are shown in Figure 3. Figure 3 illustrates the adsorption of MG with varying concentrations of lanthanum and 0.5% chitosan and its comparison to a prior modified. Researcher using modified graphite (MG) with chitosan 0.5% as control (lanthanum concentrations of 0 M). Figure 3 also shows that the concentration of lanthanum is used to modify the graphite waste into the adsorbent effect on adsorption ability of the adsorbent. If the concentration of lanthanum increases the adsorption ability, this is in accordance with the initial hypothesis which lanthanum provides an empty orbital space to be chemically bound to the textile dye that acts as a ligand complexes on lanthanum.

The best results in this study were at concentrations of lanthanum of 0.03 M. However, as we can see in Figure 3, the performance decreases when the concentration of 0.02 M and then its adsorption ability climbed back in the concentrations of 0.03 M. This anomaly occurs because of the concentration of 0.02 M is the minimum concentration to indicate chemical adsorption adsorbent works well and balanced with physical adsorption adsorbent.

Adsorption capability of the entire MG when compared to NMG decreased. It can be caused by the presence of competition space textile dye adsorption by chitosan used in the modification. Both types of these compounds are organic substances that having empty electron, which found to be capable on binding to the ligand and lanthanum as the van der Waals with graphite waste, but it has possibility that the concentration of lanthanum was too small, thus, there is no positive change. It can be concluded chitosan does not have any positive impact on the ability of the textile dye adsorbs.

MG sorbents have different capabilities for different textile dyes. This is caused by the structure of the textile dyes used in this study. MG sorbents are more binding on methyl violet and methylene blue when compared with rhodamine B and methyl orange. This is because methyl violet and methyl orange contains the same properties, which are a cationic dye, while methyl orange dye which is anionic. Rhodamine B is also a cationic dye such as methyl violet and methylene blue, rhodamine B, but the particle size is greater than the methyl violet and methylene blue because it has a molecular mass that is much larger. Both of these causes leads to adsorption on methyl violet and methylene blue amounted to 84.9% and ~72%, respectively, compared to rhodamine B and methyl orange by ~14% and ~47%.

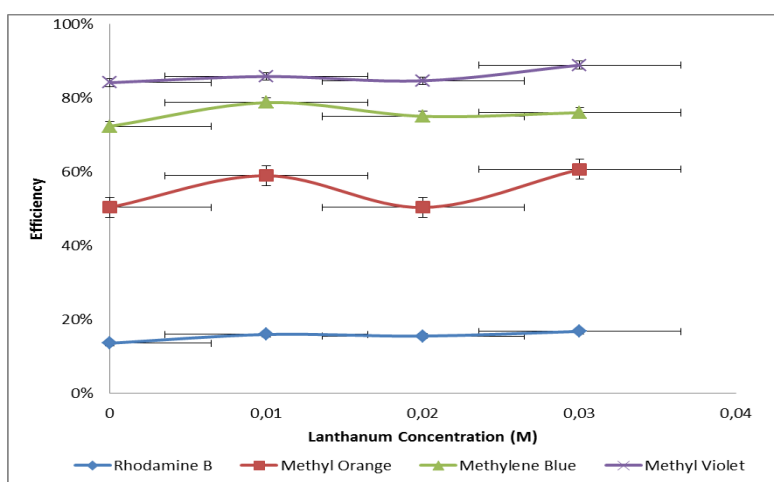


Figure 3. Effect of lanthanum concentration in modified graphite (MG) on dye removal in textile wastewater

3.3. Selectivity. The final concentration of each dye in Figure 4 illustrates the adsorbent selectivity against multiple types of dyes. The adsorbent has a selective adsorption of methylene blue at most to ~79%, followed by methyl orange, methyl violet and rhodamine B with adsorption ~67, ~38, and ~9% sequentially using MG with 0.03 M lanthanum and 0.5% w/w chitosan. The adsorption efficiency of methylene blue (MB) and methyl violet (MV) using modified graphite (MG) are lower than found using nanocomposite of hydrolyzed polyacrylamide grafted onto xanthan gum and incorporated-nanosilica had efficiency of 99.4 – 81.6% and 99.1 - 87.7%, respectively [3]. In the explanation for the modified graphite (MG) adsorption test and according to the literature review, the type of content and particle size affects the ability of the dye adsorbs an adsorbent. In this test of selectivity, adsorbent found to be

more compatible with dye, which has a mass of dye molecules that are smaller or smallest particle size of the dye. Sorbent prefer this type of cationic textile dyes because the surface of the adsorbent is negative due to the influence of the hydroxyl (OH) groups of chitosan is more dominant in neutral or alkaline pH. As we know that, the adsorption efficiency for removal dye from aqueous solution depend on the adsorbent dose, initial concentration of dye, pH, particle size of sorbent, type of sorbent, the chemical modifier of sorbent as well as temperature of the solution. It is similar was observed for removal of congo red dye from aqueous solution using modified xanthan gum/silica hybrid nanocomposite [8] and activated carbon/cobalt ferrite/alginate composite beads [9].

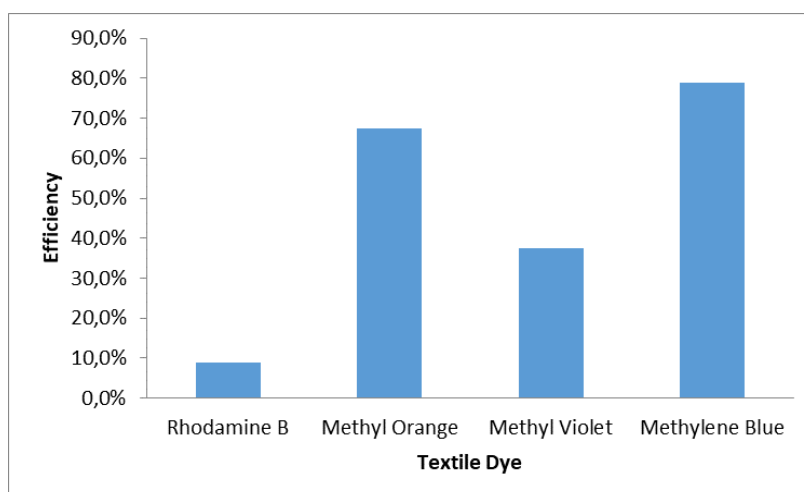


Figure 4. Selectivity of modified graphite (MG) with 0.03 M lanthanum and 0.5% w/w chitosan on textile dye removal

4. Conclusion

In conclusion, the thermal-mechanical pre-treatment of graphite waste (NMG) features the potential as the much-sought effective yet low cost technology for removal of dyes in textile wastewater. Further chemical modification of the pre-treated graphite waste with La (0.01 – 0.03 M) and chitosan (0.5% w/w) did not improve the extent of dye adsorption.

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