



Hybrid adsorbent material for sustainable removal of heavy metals from industrial wastewater

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Abstract

Industrial manufacturing is often associated with the discharges of wastewater, this wastewater usually contains toxic substances such as heavy metals which are detrimental to the environment and public health. In this work, 3-aminopropyltrimethoxysilane functionalized Fe_3O_4 /graphene oxide ($\text{MGO@SiO}_2\text{-NH}_2$) was synthesized and applied as adsorbent for removal of heavy metals from rice mill and textile effluent samples using batch adsorption technique. The adsorbent was characterized by FTIR, FESEM-EDX, TGA and VSM. Analyzing the adsorption efficiency of $\text{MGO@SiO}_2\text{-NH}_2$ for heavy metals at normal conditions using atomic absorption spectroscopy (ASS), $\text{MGO@SiO}_2\text{-NH}_2$ showed 76-100% removal efficiency for the heavy metal ions present in the two effluent samples. Furthermore, the adsorbent responded well to the external magnetic field which facilitated separation of the adsorbent from the effluent samples after adsorption.

Keywords: Adsorption, Graphene Oxide, Heavy metals, Wastewater, Magnetic

1. Introduction

Heavy metal contamination of water resources due to industrialization poses a serious threat to the environment and public health due to their toxicity effect on the human body even at lower concentrations [1]. These metals often contaminate public streams and other water bodies as a result of discharge from industrial effluents into the environment. Heavy metals such as lead (Pb) and mercury (Hg), arsenic (As) are toxic even at low concentrations causing serious health issues including cancers, kidney failure, malfunction of the nervous system and other serious diseases [2]. Thus, effluent from polluting industries needs to be properly treated before discharge into the environment in conformity with environmental standards and regulations. Conventional methods used in removing heavy metals from industrial effluents involve precipitation, coagulation and flocculation. These methods are either inefficient or involve the production of toxic sludge. Consequently, disposal of the toxic sludge could have a detrimental effect on the environment. Thus, the adsorption technique is considered feasible and versatile in removing heavy metals from industrial wastewater [3 - 4]. Materials such as silica gel, activated carbon and resins have been used as adsorbents for heavy metal ions. However, the improvement of adsorbent's capacity for heavy metal ions involves the immobilization of special functional groups with high affinity for metal ions onto the matrix of the adsorbent [4]. For example, the immobilization of sulphur or nitrogen compounds onto carbon-based materials such as graphene oxide (GO),

which is a carbon-based material obtained through graphite oxidation with specific surface areas of about $2620 \text{ m}^2/\text{g}$ could be a good material for this application [5].

In this study, Fe_3O_4 /graphene oxide (MGO) was synthesized and further functionalized using 3-aminopropyltrimethoxysilane ($\text{SiO}_2\text{-NH}_2$) to produce $\text{MGO@SiO}_2\text{-NH}_2$ as adsorbent for removal of heavy metals from industrial effluents using batch adsorption technique. The modification of GO with magnetite (M) is to ease separation without going through filtration and centrifugation processes after adsorption.

2. Materials and Methods

2.1 Chemicals and Materials

Analytical grade graphite ($44 \mu\text{m}$ particle size), HNO_3 (65%), KMnO_4 , H_2O_2 (30%), H_2SO_4 (97%), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, NaOH, toluene, 3-aminopropyltrimethoxysilane (APTMS), and NH_3 were purchased from Shanghai Chemical Reagent Corporation (PR China).

2.2 Instrumentation

$\text{MGO@SiO}_2\text{-NH}_2$ was studied using FTIR, TGA, FESEM-EDX, and VSM. The FTIR was a Perkin-Elmer TM 400 with a KBr pellet (Waltham, MA, USA), and transmission was observed from 400 cm^{-1} to 4000 cm^{-1} . However, FESEM coupled with EDX JSM-6701F JEOL (Tokyo, Japan) were used for morphological and elemental analysis of the adsorbent respectively. Thermal analysis was conducted using Perkin-Elmer TGA 8000 (Waltham, MA, USA) using an N_2 atmosphere with $100 \text{ mL}/\text{min}$ flow and heating rate of $10^\circ\text{C}/\text{min}$. Redox meter

MW500 (Milwaukee, USA) and EC meter HI9813-5(Woonsocket, USA) were used for redox potential and salinity measurements of the effluent samples respectively.

2.3 Synthesis

2.3.1 Graphene oxide Synthesis

Modified Hummer's method [6] was applied to synthesise graphene oxide (GO) through the oxidation of graphite. 2 g of graphite powder was dissolved in a mixture of 40 mL H₂SO₄ (97%) and 25 mL HNO₃ (65%), stirred for 12 h. 2g of KMnO₄ was added stepwise and the mixture was heated to 60°C for 18h. The mixture was then cooled and 3 mL H₂O₂ (30%) was added to the mixture until it turned yellow. Then, 800 mL of distilled water was added and allowed to stay overnight at room temperature. A precipitate was formed (GO), decanted and rinsed to neutral pH with distilled H₂O [7].

2.3.2 Fe₃O₄/graphene oxide (MGO) synthesis

Fe₃O₄ nanoparticles (MNPs) were first synthesized through the co-precipitation method. FeCl₂ (0.2 g) and FeCl₃ (0.4 g) were dissolved in 100 mL de-ionized water, stirred and heated to 60°C. 6 mL NH₃ (25%) was added and stirred for 6h at room temperature to produce a black precipitate (Fe₃O₄). 1g of GO was added to the Fe₃O₄ and stirred for 24h at 50°C to produce (Fe₃O₄/GO) which was then washed using distilled water (200 mL), then oven dried at 80°C for 24 h [7].

2.3.3 Synthesis of MGO@SiO₂-NH₂

1g of MGO was dispersed in 50 mL toluene and 15 mL 3-aminopropyltrimethoxysilane (APTES) was added dropwise. The mixture was refluxed for 24 hours to produce the adsorbent (MGO@SiO₂-NH₂) which was then oven-dried overnight for further application [8].

2.4 Application of MGO@SiO₂-NH₂ to effluent samples

To analyze the efficiency of MGO@SiO₂-NH₂ in the removal of heavy metal ions from industrial effluents. Two effluent samples were collected from a textile company and a rice mill plant, in Northwest Nigeria, respectively. Suspended solid particles were removed from the effluent samples, and then 20mg of MGO@SiO₂-NH₂ was applied to 50 mL of each of the raw effluent samples without further pretreatment to evaluate the performance of the adsorbent in raw effluents for 30 min. at normal conditions. But, before AAS analysis, the effluent samples were digested with concentrated HNO₃. The percentage removal for each metal ion present was calculated according to equation 1 [9]. All experiments were repeated in triplicates.

$$\%R = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

Where %R is percentage removal, C_i (mg/L) is the initial concentration and C_f(mg/L) is the final concentration.

3. Results and Discussion

3.1 Characterization

The FTIR spectrum of GO is compared with MGO and MGO@SiO₂NH₂ as shown in Fig. 3.1 GO IR peak (Fig.3.1a) appearing at 3400 cm⁻¹ assigned to O-H stretching vibrations and 1715 assigned to C=O stretching vibrations [10]. The IR spectra of GO, as the starting material show similarity with the IR spectra of MGO (Fig 3.1b), but the appearance of an IR peak at 601 cm⁻¹ assigned to Fe-O bending vibrations indicates magnetic nanoparticles (Fe₃O₄) on MGO [11]. However, the appearance of IR peaks at 1650 cm⁻¹ (N-H, bending vibrations) and 1086 cm⁻¹ (Si-O stretching) in Fig 3.1c, suggested successful grafting of SiO₂NH₂ onto MGO, thus forming the adsorbent MGOSiO₂-NH₂. Furthermore, other new peaks appeared at 650 cm⁻¹ and 480 cm⁻¹ in Fig.3.1c after grafting SiO₂NH₂ onto MGO [11-12].

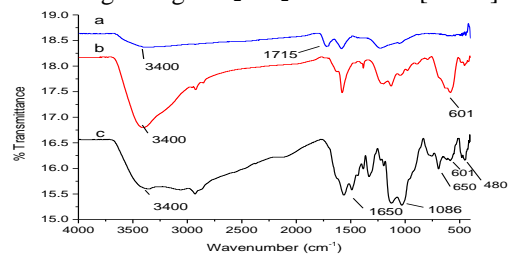


Figure 3.1: FTIR plot for (a) GO, (b) MGO, (c) MGOSiO₂-NH₂

SEM images for the morphologies of GO, MGO and MGO@SiO₂-NH₂ are shown in Fig.3.2 Open GO sheet layers are seen in Fig. 3.2a, while in Fig. 3.2b, Fe₃O₄ nanoparticles slightly filled and covered the GO sheets and in between GO layers. In Fig. 3c, the MGO is seen coated with a gel-like material; presumably, SiO₂-NH₂, which suggests successful synthesis of MGO@SiO₂-NH₂.

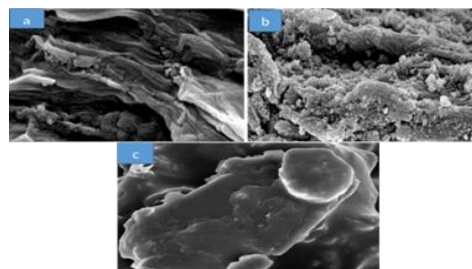


Figure 3.2: SEM image of (a) GO, (b) MGO, (c)MGO@SiO₂-NH₂. Mag. 3.500k.

The element analysis (EDX) of the synthesized adsorbent (MGO@SiO₂-NH₂) confirms the presence of the elements C, N, O, Si and Fe. Fig.3.3 shows the EDX spectra for GO, MGO and MGO@SiO₂-NH₂ respectively, while Table 3.1 presents the percentage number of atoms of the elements present in the adsorbent. It can be seen that, for GO (Fig 3.3a) only C and O atoms are present, while following the incorporation of Fe₃O₄, the presence of Fe is observed in addition to C and O (Fig

3.3b), which showed MGO is formed. As expected, the presence of Si and N is observed in MGO@SiO₂-NH₂ (Fig.3.3c) in addition to C, O and Fe, suggesting successful synthesis of the adsorbent (MGO@SiO₂-NH₂).

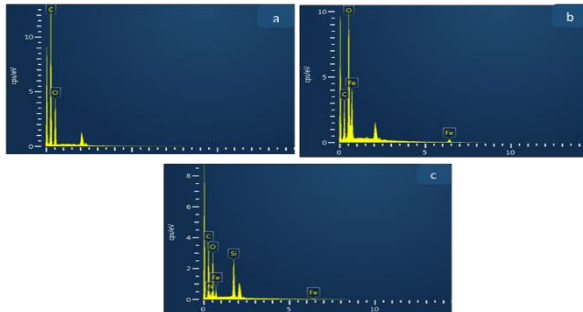


Figure 3.3: EDX spectra of (a) GO, (b) MGO, (c) MGO@SiO₂-NH₂

Table 3.1: EDX percentage number of atoms of constituent elements in MGO@SiO₂-NH₂

Material	%C	%O	%Si	%N	%Fe
GO	76	24	-	-	-
MGO	45.8	39.2	-	-	15
MGO@SiO ₂ -NH ₂	40.1	32.8	8.3	7.1	11.7

Thermal stability of GO, MGO and MGO@SiO₂-NH₂ was determined using TGA (Fig. 3.4). First stage of degradation within 20–200°C could be attributed to the degradation of volatile functional groups such as OH and water vapour [13]. Here, GO showed 7% weight loss, MGO 4%, while MGO@SiO₂-NH₂ showed a very slight weight loss. This suggests fewer volatile substances in MGO@SiO₂-NH₂ compared to GO, MGO. At 400°C, MGO showed more weight loss of 15%, probably due to the decomposition of Fe₃O₄, the GO is stable at this temperature while MGO@SiO₂-NH₂ is relatively stable, showing slight weight loss. Furthermore, the weight loss from 600 to 1000°C is due to the combustion of carbon, while inorganic residues are found at 1000°C. At this temperature range, GO and MGO showed 70% and 50% weight loss respectively, due to the iron (Fe) residue in MGO. While MGO@SiO₂-NH₂ showed higher stability with only 28% weight loss, due to further modification with SiO₂-NH₂ that will probably be left behind Si, as the inorganic residue in addition to Fe [8] [13-14].

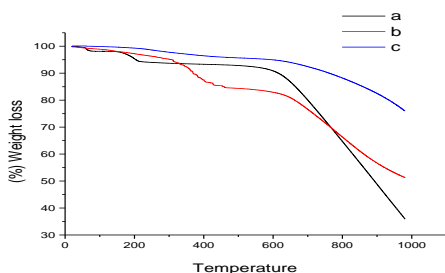


Figure 3.4: TGA Plot of (a) GO (b) MGO and (c) MGO@SiO₂-NH₂

The magnetic hysteresis loop for MGO and MGO@SiO₂-NH₂ is presented in Fig. 3.5. The materials attained saturation magnetization values of 65 and 50 emu/g for MGO and MGO@SiO₂-NH₂, respectively. It can be seen that the magnetization value of MGO@SiO₂-NH₂ is lower compared to MGO, due to coating with APTES. Nevertheless, MGO@SiO₂-NH₂ responded well to the external magnetic field and was separated from the aqueous solution within 50s.

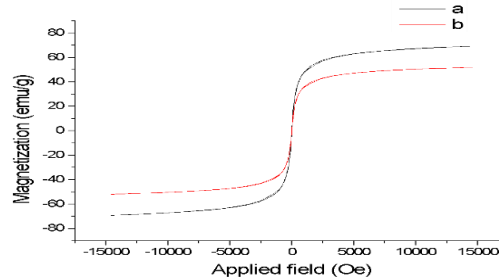


Figure 3.5: VSM analysis plot of (a) MGO and (b) MGO@SiO₂-NH₂

3.2 Application result of MGO@SiO₂-NH₂ to effluent samples.

Tables 3.2 and 3.3 present the heavy metals composition of rice mill and textile effluents respectively, before and after treatment, using 20 mg of MGO@SiO₂-NH₂ for 30 minutes in 50 mL sample volume at normal conditions, for each effluent sample. It was observed that the adsorbent achieved 76 – 100 removal efficiency for all the metal ions present. However, based on salinity values of 319 and 423 μS/cm for rice mill and textile effluents respectively, based on the values, the effluent can be identified as non-saline [15]. This suggested that MGO@SiO₂-NH₂ could effectively remove heavy metals from non-saline oxidizing effluents.

Table 3.2: Composition of rice mill effluent before and after remediation with MGO@SiO₂-NH₂

Parameter	Initial Conc. (mg/L)	Conc. after treatment (mg/L)	% Removal
Pb(II)	3.3	0.2	94
Ni(II)	1.1	0.0	100
Cd(II)	0.2	0.0	100
Cr(III)	1.3	0.3	76
Cu(II)	0.9	0.1	89
Zn(II)	1.7	0.0	100
Mn(II)	1.9	0.4	79
pH	6.2		
Salinity	319 μS/cm		
Redox potential	+179mV		

Table 3.3: Composition of textile effluent before and after remediation with MGO@SiO₂-NH₂

Parameter	Initial Conc. (mg/L)	Conc. after treatment (mg/L)	% Removal
Pb(II)	1.3	0.0	100
Ni(II)	4.1	0.7	83
Cd(II)	3.3	0.1	97
Hg(II)	2.2	0.0	100
Cu(II)	1.0	0.2	80
Zn(II)	2.6	0.4	85
Co	3.9	0.2	94
Fe(II)	1.4	0.2	86
pH	4.3		
Salinity	423 μS/cm		
Redox potential	+224 mV		

4. Conclusions

3-aminophenyltrimethoxysilane was successfully used to functionalize GO to produce chelating material, GO@SiO₂-NH₂ as an effective adsorbent for the removal of heavy metal from rice mill and textile effluent at normal conditions. Furthermore, the adsorbent showed high thermal stability during TGA analysis, which suggests that the adsorbent could be used at elevated temperatures without thermal degradation. The adsorbent showed a good efficiency of 76-100 removal efficiency for the respective metal ion. However, further optimization studies would improve the performance of the adsorbent.

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