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Competitive Removal of Cationic Pollutants Using GO and GO-NH2 Nano-adsorbents and Efficiency Comparison of Single and Binary Component Systems

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ABSTRACT: Many industrial wastewater containing various cationic pollutants including heavy metals and organic dyes with non-degradable structures that are considered as a serious threat to public health and the environment. In this study, nano-absorbers including graphene oxide (GO) and graphene oxide modified with 3-aminopropyltriethoxysilane ($GO-NH_2$) was successfully synthesized and characterized by Scanning Electron Microscope (SEM), X-Ray Diffraction (XRD) and Fourier Transform Infrared (FTIR) analysis. GO and $GO-NH_2$ were applied to remove Pb^{2+} and Cd^{2+} metal ions, and methylene blue (MB) cationic dye from aqueous solution in single and binary component systems (Pb^{2+}-Cd^{2+}, Pb^{2+}-MB, Cd^{2+}-MB). In the single component system, the maximum absorption of 99%, 72.5% and 49.5% was obtained for MB, Cd^{2+} and Pb^{2+}, respectively, by using GO. In the case of $GO-NH_2$, maximum absorption of 90%, 73% and 35% was obtained for Pb^{2+}, Cd^{2+} and MB, respectively, in single-component system. In the presence of MB dye, removal percentage of Pb^{2+} and Cd^{2+} showed a reduction of 10% compared to the single component system (R_q <1) by using GO. By using $GO-NH_2$, in the metal-dye binary systems, the removal percentage of Pb^{2+} and Cd^{2+} showed a reduction of 15% and around zero, respectively, to the single component system. The adsorption rate of MB onto GO and Pb^{2+} onto $GO-NH_2$ were in good agreement with pseudo-second order model (R^2=99; k_2=0.0002g mg^{-1} min^{-1}, R^2=95; k_2=0.001g mg^{-1} min^{-1} respectively).

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1- Introduction

Both dyes and heavy metals are commonly discharged by textile, printing, tanning industries, and are major concerns in natural water and wastewater systems. It is well known that some organic dyes and heavy metals are toxic to aquatic organism and are potential threats to human health [1]. Adsorption is considered one of the best methods to remove dyes and heavy metals from contaminated waters due to its ease of operation and insensitivity to toxic substances. However, most of adsorption studies have been conducted with test solutions containing either metal ions or dyes in single system [2]. For this reason the purpose of this work is to study the adsorption metal ions (lead, cadmium) and organic dye (methylene blue) in single and binary solutions using GO and chemically-modified $GO-NH_2$. The effects of pH, absorption dose and time on adsorption in a single-component system were investigated. In addition, kinetic models for pollutants with higher removal efficiency were studied with each of the adsorbents.

2- Methodology

2- 1- Synthesis of GO and $GO-NH_2$

The synthesis of GO was performed by natural graphite powder oxidation according to the Hummer method [3]. Surface of GO was modified by amine group by grafting method [4].

2- 2- Heavy metal ion and dye adsorption in single and binary systems

The batch adsorption experiments of Pb^{2+}, Cd^{2+} and MB in single and binary system (Pb^{2+}-Cd^{2+}, Pb^{2+}-MB, Cd^{2+}- MB) were carried out at pH=6 with a concentration of 9×10^{-2} mmo/L. Then 0.1 g/L of nano-adsorbents added to 50 mL metal ion and dye solution. After stirring 2 h, the residual metal concentration and dye in the aqueous solution were analyzed by atomic absorption spectroscopy(AAS) and visible spectrometry, respectively.

At equilibrium, the adsorbed amount of dyes and heavy metals per unit mass of adsorbent (qe, mg/g) and removal efficiency were determined according to the following Equations 1 and 2:

$$q_e = \frac{(C_o - C_e)V}{w} \tag{1}$$

$$R\% = \frac{(Co - Ce)}{Co} \times 100 \tag{2}$$

Where V is the liquid volume (L), C_o is the initial concentration in the solution (mg/L), C_e is the equilibrium concentration (mg/L), and W is the amount of the adsorbent sample on a dry basis (g), respectively. In order to evaluate the effect of each

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of the metals Pb^{2+}, Cd^{2+} and MB in a simultaneous adsorption system with each of the adsorbents, the absorption capacity ratio (R_q) of Equation 3 was used:

$$R_q = \frac{q_{b,i}}{q_{m,i}} \quad (3)$$

Where $q_{b,i}$ is the binary adsorption capacity for pollutant i and $q_{m,i}$ is the single component adsorption capacity of that pollutant at the same operating conditions. if $R_{q,i} > 1$, the presence of other pollutants in binary systems improves the adsorption of pollutant i (i.e., synergistic adsorption), (b) if $R_{q,i} = 1$, there is no effect on the multicomponent adsorption of pollutant i, and (c) if $R_{q,i} < 1$, the adsorption of pollutant i is reduced by the presence of other pollutants in the multicomponent solution (i.e., antagonistic adsorption) [5].

3- Results and Discussion

3- 1- Characterization

Figure 1 displays the morphology of GO using scanning electron microscopy (SEM).

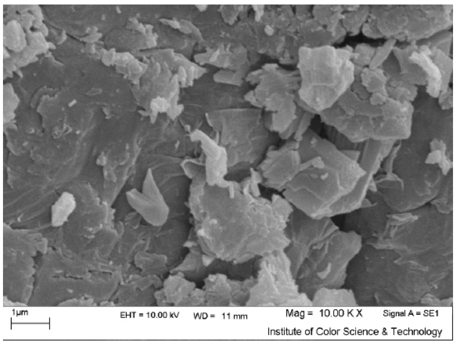

Figure 1. SEM Image of GO

Figures 2 and 3 show the structural characteristics, surface chemistry and identification of organic groups on the surface of synthesized nano-adsorbents by X-ray diffraction (XRD) and FTIR spectroscopy spectra.

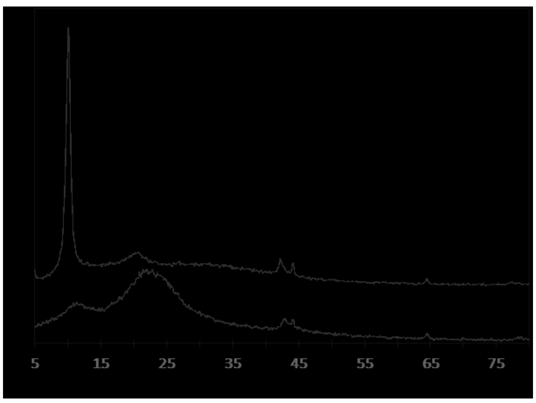

Figure 2. XRD analysis of GO and GO-NH$_2$

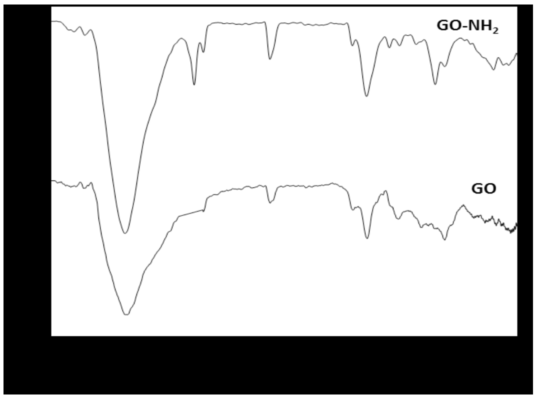

Figure 3. FTIR spectra of GO and GO-NH$_2$

3- 2- Adsorption of heavy metals and dye from wastewater using the GO and GO-NH$_2$ nano-adsorbent

Results of adsorption experiments using single component solutions are reported in Figure 4. The removal efficiency for heavy metal ions, Cd^{2+}, Pb^{2+} and MB using GO was equal to 70.5, 49.5 and 99%, respectively, and by GO-NH$_2$ was obtained 73, 90 and 35%, respectively.

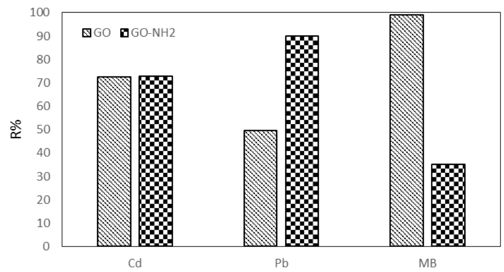

Figure 4. Single component removal efficiency of heavy metal and dye using GO and GO-NH$_2$ at pH 6

The multicomponent adsorption capacities and the values of $R_{q,i}$ for all pollutants of the binary systems reported in Table 1. Results indicateed that the simultaneous presence of pollutants in the absorption system, using both adsorbents, affects the percentage of adsorption.

3- 3- Effect of pH and adsorbent doses on the dye and heavy metal adsorption

For MB, the adsorption shows a slight increase at lower pH and sharply increases when the pH is higher than 6 by using GO. For Pb^{2+}, the removal efficiency by GO-NH$_2$ is also lower (7% at pH=2) while shows a significant increase (90%) at pH=6.

Increasing MB and Pb^{2+} removal efficiency by increasing the absorbents dose from 0.05 t0 0.1 was due to the increase of absorption sites in the adsorption process.

Table 1. Binary adsorption capacities of heavy metal and dye using GO and GO-NH_2 at pH 6

Binary system	GO					
	$q_{e,MB}$ (mmol/g)	$q_{e,Cd2+}$ (mmol/g)	$q_{e,Pb2+}$ (mmol/g)	$R_{q,MB}$	$R_{q,Cd2+}$	$R_{q,Pb2+}$
Cd^{2+}-MB	0.84	0.60	-	1.09	0.93	-
Pb^{2+}-MB	0.86	-	0.25	0.82	-	0.63
Cd^{2+}-Pb^{2+}	-	0.65	0.50	-	0.99	1.20
	GO-NH_2					
Cd^{2+}-MB	0.66	0.15	-	0.51	1.00	-
Pb^{2+}-MB	0.10	-	0.40	0.35	-	0.50
Cd^{2+}-Pb^{2+}	-	0.73	0.79	-	1.11	0.98

3- 4- Adsorption kinetic of the MB and Pb

Pseudo-first-order and pseudo-second-order kinetic models were used for study the adsorption MB and Pb^{2+}onto the GO and GO-NH_2. Results showed that the calculated qe values are mainly equal with experimental qe values and R^2 are relatively high for adsorption data (Table 2), which indicates that the adsorption of MB and Pb^{2+} onto GO and GO-NH_2 obeys the pseudo-second-order model.

Table 2. Kinetic adsorption models

pseudo-first-order model				
pollutants	Nano- adsorbent	$q_{e,Cal}$ (mg/g)	K_2 (min^{-1})	R^2
MB	GO	386	0.0006	0.90
Pb^{2+}	GO-NH_2	263	0.07	0.95
pseudo-second-order model				
MB	GO	294	0.0002	0.99
Pb^{2+}	GO-NH_2	189	0.001	0.95

4- Conclusions

In summary, GO and GO-NH_2 as adsorbents for cationic contaminants such as heavy metals (lead and cadmium) and dye (methylene blue) in a single and binary component system. According to the results, GO is effective absorbent for MB (99%). However, for the adsorption of heavy metals, the GO-NH_2 was more effective than GO (Pb^{2+}=90%, Cd^{2+}=73%). Finally, for the dye-metal binary adsorption, a clear competition of both cationic species (dye and metal) for the adsorption sites was observed (antagonistic effect). As a consequence, the removal efficiency of Pb^{2+} and Cd^{2+} onto GO decreased significantly from 49% to 34% and from 72% to 64%, respectively. The removal efficiency of Pb^{2+} decreased about 15% when compared to the values obtained in mono-component adsorption by using GO-NH_2. The sorption kinetics of MB and Pb^{2+} were well described by pseudo second-order model.

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