

Kinetic and Equilibrium Studies for Dual Functional Adsorbent with Amino Group Magnetite

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Abstract

A dual functional adsorbent (EDA/MMA/OA/Fe₃O₄) with amino group magnetite has been synthesized to behave as an anionic or cationic adsorbent (for the adsorption of phosphate or copper) by adjusting the pH value to make amino group protonic or neutral. The adsorptions of phosphate and copper ions by the dual functional adsorbent were investigated using kinetic, equilibrium, thermodynamic, and surface characteristic experiments. The adsorption behaviors for both copper ions and phosphate by EDA/MMA/OA/Fe₃O₄ were in good agreement with the Langmuir adsorption isotherm with the maximum adsorption capacities of 7.096 for the copper ion and 34.5071 mg g⁻¹ for phosphate, respectively. The optimum conditions for the desorption of copper ions and phosphate were 0.1M HNO₃ and 0.05 M NaOH, respectively. After three cycles, the adsorption capacity of the recycled EDAMMA/OA/Fe₃O₄ for copper ions and phosphate exhibited a loss of about 17.1% and 28.1%, respectively.

Keywords: Adsorb; Copper ions; Magnetic; Adsorbent; Phosphate

Introduction

Pharmaceuticals and personal care products (PPCPs) are a class of emerging contaminants which include commonly used medicinal, cosmetic and personal hygiene products [1]. Great concern has been raised about PPCPs due to their potential adverse impacts on ecological safety and human health [2]. Among the contaminants of PPCPs, cosmetic wastewater is the main contributor due to its large quantities. The main components of wastewater from a cosmetic manufacturing facility before further treatments include the surfactants, heavy metals, cations, and anions [3]. In this study, trace concentrations of copper and total concentrations of phosphorous were 16.8 µg L⁻¹ and 4.89 mg PL⁻¹, respectively.

Removing copper ions from wastewater is an important treatment procedure as copper is a highly toxic heavy metal since it causes stomach and intestinal distress, liver and kidney damage, and anemia [4,5]. Traditional metal ion treatment processes include chemical precipitation, ion exchange, electrolysis, reverse osmosis, adsorption, etc. [5,6]. Besides, excess phosphate in rivers can lead to significant eutrophication and water quality problems, including harmful algal blooms, as well as depletion of dissolved oxygen, which subsequently results in the decline of aquatic life [7]. In order to reduce or reuse the amount of phosphate in water, several techniques have been developed to remove phosphate from aqueous media, such as chemical precipitation, biological treatment, and adsorption [8,9]. Among these treatment methods, adsorption has been considered one of the most suitable and effective methods for the removal of both copper ions and phosphate [9-11].

The application of magnetic adsorbent technology to solve environmental problems has received considerable attention in recent years. Magnetic adsorbents (various magnetic particles, Fe₂O₃ and Fe₃O₄) can be used to adsorb contaminants from aqueous or gaseous effluents [12,13]. After the adsorption is carried out, the adsorbent can be separated from the medium by a simple magnetic process [14,15]. These adsorbents have a variety of surface functional groups which can be tailored for use in specific applications. Poly (2-hydroxyethylmethacrylate), poly(oxy-2,6-dimethyl-1,4-phenylene), polyvinyl-butyril, and chitosan are typical adsorbents which are used in different applications [15-17].

The objective of this study was to investigate the removal of both phosphates and copper ions from aqueous solutions using amino group magnetite. Kinetic, equilibrium, and characteristic experiments were performed to characterize the phosphate and copper ions of the amino group magnetite. Sorption kinetic and equilibrium isotherm models were used for data analysis. This will open up a potential broad application in cosmetic wastewater treatment (Table 1).

Materials and Methods

Adsorption and desorption

In adsorption experiments, the adsorbent concentration was controlled at 0.5 g in a 50 mL solution, and the equilibrium time was considered as 24 h [18]. Effects of the pH (2.0-6.0), kinetic experiments (0~90 min), adsorption isotherm (initial phosphate concentration 400~800 mg L⁻¹ and initial copper ion concentration 50~150 mg L⁻¹), and thermodynamic studies (283~313 K) on adsorption were studied. The pH value of the solution was controlled by adding 0.1 N HNO₃/NaOH.

Desorption experiments were carried out with HNO₃/HCl solutions

Magnetic catalyst	Surface area (m ² g ⁻¹)	Treatments	Adsorption (mg g ⁻¹)		
			1 st cycle	2 nd cycle	3 rd cycle
EDA/MMA/OA/Fe ₃ O ₄	34.99	Phosphate	11.71	9.70	8.42
		Copper ion	5.97	5.23	4.95
Fe ₃ O ₄	18.06	-	-	-	-

Table 1: The Brunauer-Emmett-Teller surface area and reuse performance of Fe₃O₄ and EDA/MMA/OA/Fe₃O₄.

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in the concentration range of 0.001~1 M. A 0.5 g amount of the EDA/MMA/OA/Fe₃O₄ adsorbent adsorbed with copper ion/phosphate was placed into 50 mL of an HNO₃/HCl solution with thermostatic shaking for a time period of up to 24 h. The desorption efficiency (DE) was determined from the following equation (Equation (1)):

$$DE = \frac{C \times V}{q \times m} \times 100\% \quad (1)$$

where C (mg L⁻¹) is the concentration of copper ions or phosphate in the desorption solution, V is the volume of the desorption solution, q (mg g⁻¹) is the amount of copper ion/phosphate adsorbed on the adsorbents before the desorption experiment, and m (g) is the amount of the adsorbent used in the desorption experiments.

Synthesis and instruments

The preparation methods of the dual functional adsorbent (EDA/MMA/OA/Fe₃O₄) follow up our previously study [19]. The magnetic polymer particles (MMA/OA/Fe₃O₄) were prepared by using methyl methacrylate (MMA) as the functional monomer, ethylene glycol dimethacrylate (EDGMA) as the cross-linking agent, polyvinyl pyrrolidone (PVP) as the stabilizer, 2,2-azodiisobutyronitrile (AIBN) as the radical initiator and ethanol as the solvent. As shown in Figure 1,

MMA/OA/Fe₃O₄ modified with amino group (EDA/MMA/OA/Fe₃O₄) was prepared by using ethylenediamine (EDA) and acetonitrile as a solvent and separated by an external magnetic field.

The concentrations of copper ions were determined by standard spectrophotometric methods using a polarized Zeeman atomic absorption spectrophotometer (Z-2000, Hitachi, Japan). The concentration of phosphate was determined using standard methods [20] using a spectrophotometer (Lambda 25, Perkin Elmer, USA).

Results and Discussion

Point of zero charge (PZC) analysis

PZC analysis can estimate the adsorption behavior of materials at a certain pH and provide reliable evidence of the mechanism of adsorption of copper ion or phosphate onto the adsorbent. As can be seen in Figure 2, the PZC results for Fe₃O₄, SiO₂/Fe₃O₄, MMA/OA/Fe₃O₄ and EDA/MMA/OA/Fe₃O₄ were 7.0, 6.2, 6.0 and 8.1, respectively, and these results were similar to results [21].

Effect of pH on adsorption of copper ion and phosphate ion

The performance of the EDA/MMA/OA/Fe₃O₄ adsorbent in

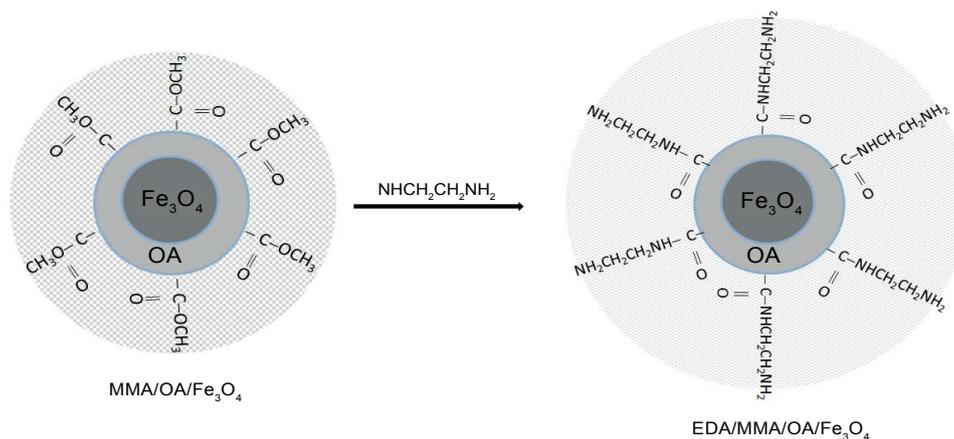


Figure 1: Preparation and molecule structure of EDA/MMA/OA/Fe₃O₄.

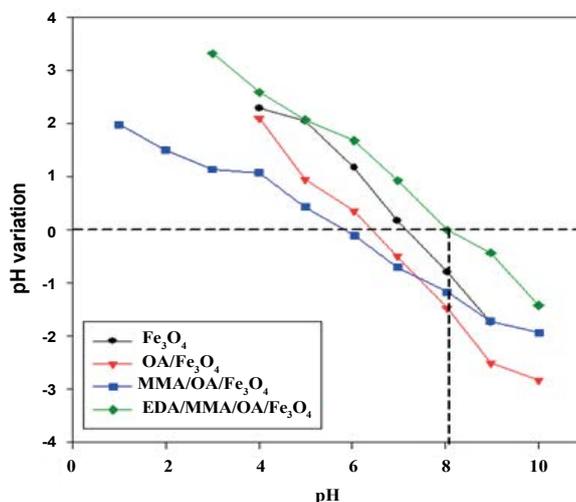


Figure 2: Effect of pH values on zeta potential of Fe₃O₄, SiO₂/Fe₃O₄, MMA/OA/Fe₃O₄ and EDA/MMA/OA/Fe₃O₄.

adsorbing copper and phosphate ions in solutions with different pH values is shown in Fig. 3. Experimental conditions included initial concentrations of copper ion = 100 mg L⁻¹ and phosphate ion = 500 mg L⁻¹, EDA/MMA/OA/Fe₃O₄ = 10 g L⁻¹, reaction time = 24 h, and temperature (T) = 298 K. The results revealed that the adsorption behavior of EDA/MMA/OA/Fe₃O₄ with copper ions and phosphate ions is strongly pH-dependent.

The amino groups (-NH₂) of EDA/MMA/OA/Fe₃O₄ are or are not protonated (NH₃⁺), depending on the pH values of the solution. The amine forms of NH₃⁺ and NH₂ will attract anions [22] and cations [23], respectively. In a solution with pH 3, the adsorption efficiency of Cu²⁺ by EDA/MMA/OA/Fe₃O₄ was nearly zero, but for phosphate ions it was relatively higher (22.1%). In solutions with low pH values, a relatively high concentration of protons would strongly compete with the copper ions for amine sites, so that the adsorption of copper ions was significantly decreased.

Furthermore, the protonation of the amino groups led to strong electrostatic repulsion of the copper ions to be adsorbed. As a result, it became difficult for the copper ions to come into close contact with the adsorbent surface and be adsorbed onto it; this resulted in poor adsorption performance for copper ions in a solution with pH ≤ 3. On the other hand, the protonated amines possess a strong electrostatic attraction to phosphate ions, which leads to a high adsorption capacity. Thus, the phosphate ion adsorption increased with the decrease in pH value because the dominant phosphate forms in the solution are H₃PO₄ and H₂PO₄⁻. The solution's pH value determines whether the amino groups on the synthetic magnetic adsorbent are protonated [24]. Protonated amino groups can adsorb phosphate anions. Lower solution pH values make EDA/MMA/OA/Fe₃O₄ more protonated, thus, attracting more phosphate anions.

As a result, the optimum pH values for phosphate ion adsorption were found to be in the pH range from 2 to 3, and all further adsorption experiments were carried out with a solution pH of 3 for PO₄³⁻. due to the consideration of actual engineering application and the overdose of acid.

At higher solution pH values from 4 to 6 (lower proton concentrations), regarding copper ions, the competition between protons and copper ions for the amino groups became less significant, and more of the amino groups existed in their neutral form, which reduced the electrostatic repulsion of the copper ions. Furthermore, the unpaired electrons of the amino groups could create coordinate bonds with the copper ions. More copper ions could thus be adsorbed onto the surfaces of EDA/MMA/OA/Fe₃O₄, resulting in an observed increase in Cu²⁺ adsorption on the adsorbent. With regard to phosphate ions, in solutions with a higher pH, fewer protons are available to protonate the amino groups (-NH₂) of EDA/MMA/OA/Fe₃O₄ to form NH₃⁺, thereby decreasing the electrostatic attractions between negatively charged anions; this decrease is attributed to the lower degree of adsorption.

There was a complete removal of copper ions from the solution when the solution's pH value exceeded 6.5. This took place because copper ions began to precipitate as Cu(OH)₂. Therefore, copper ions were removed by both adsorption and precipitation when the solution's

pH value exceeded 6.5 [25]. As a result, the optimum pH values for Cu₂₊ adsorption were found to be in the pH range from 5 to 6, and all further adsorption experiments were carried out in solutions with a pH of 5.5 for Cu²⁺.

Adsorption isotherms of copper ions and phosphate ions

The data equilibrium isotherms of adsorption were conducted in 298 K, five initial concentrations of copper ions with the solutions' pH 5.5 (50, 75, 100, 125, and 150 mg L⁻¹), and those of phosphate ions with the solutions' pH 3.0 (400, 500, 600, 700, and 800 mg L⁻¹). The Langmuir and Freundlich equations [26,27] were applied to experimental data to examine the relationship between sorption ion concentration at equilibrium. The Langmuir equation could be expressed as follows (Equation (2)):

$$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{Q_m k_L C_e} \quad (2)$$

where Q_e and Q_m are the equilibrium and maximum adsorption capacities of copper ion/phosphate on the adsorbent (mg g⁻¹), C_e, the equilibrium concentration of copper ion/phosphate in solution (mg L⁻¹), and k_L, the Langmuir adsorption constant (L mg⁻¹). The linear form of the Freundlich equation can be represented as follows (Equation (3)):

$$\log Q_e = \log k_F + \frac{1}{n} \log C_e \quad (3)$$

where k_F is the Freundlich constant (L mg⁻¹), and n is the heterogeneity factor. The values of q_m and k_L are determined from the slope and intercept of the linear plots of C_e/Q_e versus C_e, and the values of k_F and 1/n are determined from the slope and intercept of the linear plot of lnQ_e versus lnC_e, as shown in Table 2. The correlation coefficient of the Langmuir isotherms was found to be 0.9999 for the copper ions and 0.9918 for phosphate. However, those of the Freundlich isotherms for copper and phosphate ions were 0.9844 and 0.9872, respectively. Obviously, the data were fitted better by the Langmuir equation than by the Freundlich equation for both copper and phosphate. Furthermore, fitting of the Langmuir isotherm indicates a monolayer coverage for both Cu²⁺ and phosphate on the EDA/MMA/OA/Fe₃O₄ surface during adsorption. Moreover, the maximum monolayer phosphate uptake of 34.507 mg g⁻¹ was significantly higher than the maximum monolayer copper uptake of 7.096 mg g⁻¹ (Figure 3).

Adsorption kinetics

The effects of a contact time on the adsorption of Cu²⁺ and phosphate by EDA/MMA/OA/Fe₃O₄ at various temperatures (10, 25, and 40°C) were also evaluated, as shown in Table 3. The adsorption kinetics were analyzed using the pseudo-first-order and pseudo-second-order kinetic models, expressed in their linearized forms as Equation (4) and (5), respectively [28]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

Treatments	Langmuir			Freundlich		
	Q _m (mg g ⁻¹)	K _L (Lmg ⁻¹)	R ²	n	K _F	R ²
Phosphate-ion	34.507	0.0044	0.9918	2.6371	2.2393	0.9872
Copper ion	7.096	0.0245	0.9999	1.728	0.668	0.9844

Table 2: Parameter values of different types of adsorption isotherm models fitting the experimental results for copper ions and phosphate adsorption, respectively on the EDA/MMA/OA/Fe₃O₄ adsorbents.

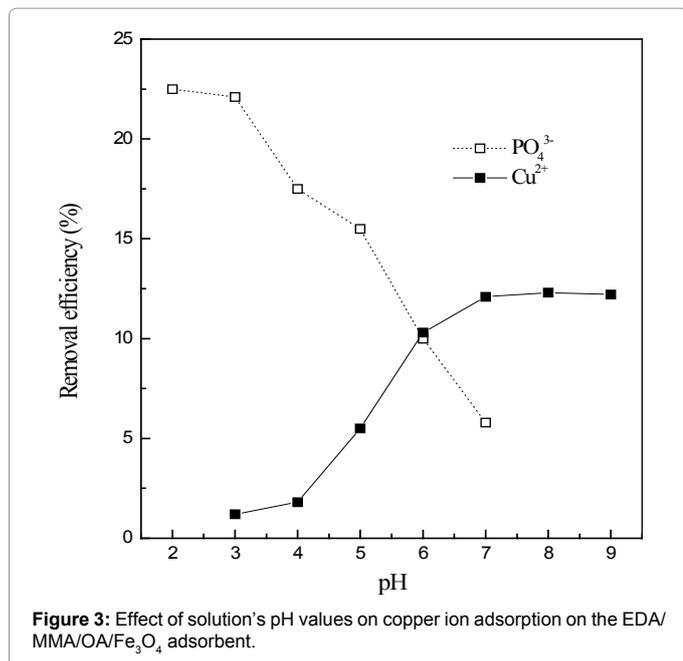


Figure 3: Effect of solution's pH values on copper ion adsorption on the EDA/MMA/OA/Fe₃O₄ adsorbent.

Treatments	Temperature	R ²		Rate Constants	Activated Energy
		1 st order	2 nd order	k ₂ (g mg ⁻¹ min ⁻¹)	Ea(kJ mole ⁻¹)
Phosphate-ion	10°C	0.062	0.997	0.093	7.344
	25°C	0.096	0.999	0.107	
	40°C	0.186	0.999	0.125	
Copper ion	10°C	0.784	0.998	0.2214	13.356
	25°C	0.754	0.999	0.2981	
	40°C	0.757	0.999	0.3804	

Table 3: Parameter values of the kinetics models fitting the experimental results for copper ions and phosphate adsorption on the EDA/MMA/OA/Fe₃O₄ adsorbent.

where, q_t (mg g⁻¹) is the adsorption uptake at time t (min); q_e (mg g⁻¹) is the adsorption capacity at adsorption equilibrium; and k_1 (min⁻¹) and k_2 (g(mg·min)⁻¹) are the kinetics rate constants for the pseudo-first-order and the pseudo-second-order models, respectively. The results distinctly revealed that the adsorption kinetics for copper ions and phosphate closely follow the pseudo-second-order kinetic model rather than the pseudo-first-order kinetic model, which suggested that the adsorption process was quite rapid and was probably dominated by a chemical adsorption phenomenon.

Moreover, the temperature dependence of the kinetic parameter k_2 could be described by the Arrhenius equation (Equation (6)):

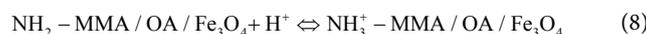
$$\ln k = \ln A - E_a/RT \quad (6)$$

where A , E_a , T and R are the frequency factor, activation energy, temperature (K), and gas constant, respectively. By plotting $\ln k_2$ against $1/T$ (K⁻¹), the determined E_a of the copper ion and phosphate were 13.356 kJ mol⁻¹ and 7.344 kJ mol⁻¹, respectively.

Desorption

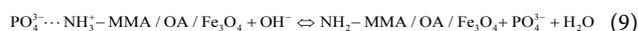
HNO₃ and NaOH solutions with different concentrations at the loading of EDA/MMA/OA/Fe₃O₄ = 5 g L⁻¹, reaction time = 24 h, and $T = 298$ K were examined in a desorption study, as listed in Table 4. It is interesting to note that the maximum desorption efficiency of copper ions was achieved at a concentration of 0.1 M HNO₃, and any

higher or lower HNO₃ concentrations resulted in lower desorption efficiencies. Thus, one may assume that the reactions taking place in acidic desorption solutions can be given by the following equations [29]:



At an HNO₃ concentration > 0.1 M in an aqueous solution, the high concentration of H⁺ will shift both Equation (7) and (8) toward the right-hand side and more MMA/OA/Fe₃O₄NH₃⁺ will be generated. However, the generation of MMA/OA/Fe₃O₄-NH₃⁺ will favor the reverse reaction of Equation (7) to the left-hand side and simultaneously hinder the desorption of copper ions from the adsorbent. Therefore, when the concentration of HNO₃ in the desorption solution exceeded 0.1 M, the results revealed that the desorption efficiency was reduced. On the other hand, at an HNO₃ concentration < 0.1 M in an aqueous solution, the low concentration of H⁺ may be insufficient to drive the reaction in Equation (7) to the right-hand side for the desorption of copper ions. Therefore, the results observed show that the desorption efficiencies were lower than those at a 0.1M HNO₃ concentration.

The results of the phosphate ion desorption is also interesting to note since maximum desorption efficiency was achieved at an NaOH concentration greater than 0.05 M and the desorption efficiencies were lower at lower NaOH concentrations. The reason for this is similar to the former explanation of Cu₂₊ desorption from a magnetic adsorbent. In order to explain this trend, one may assume that the reactions taking place in basic desorption solutions are represented by the following equations:



The added OH^- will shift the balance in both Equation 9 and 10 toward the right-hand side and a higher amount of MMA/OA/Fe₃O₄NH⁻ will be generated. Furthermore, the generation of MMA/OA/Fe₃O₄NH⁻ will facilitate phosphate desorption from the magnetic adsorbent. It was found that an NaOH concentration of 0.05 M was sufficient to achieve desorption of the phosphate. Corresponding to the experimental results of adsorptions at various p^H values, the EDA/MMA/OA/Fe₃O₄ adsorbent did not significantly adsorb phosphate ions with the increasing p^H value, which suggests that the adsorbed phosphate ion could possibly be desorbed in a solution with an increasing p^H value.

Conclusions

A dual functional adsorbent (EDA/MMA/OA/Fe₃O₄) was developed as a porous adsorbent for the adsorption of copper ions and phosphate. In a batch system, the optimal p^H values for copper ions and phosphate adsorptions were 5.5 and 3, respectively. The adsorption equilibrium data were better fitted by the Langmuir equation than by the Freundlich equation for both copper ions and phosphate. Moreover,

Concentration of HNO ₃ or NaOH (M)	Copper ion desorption (%)	Phosphate desorption (%)
0.01	82.6	86.1
0.05	85.2	90.7
0.1	90.4	90.3
0.5	84.1	89.5
1.0	84.6	88.9

Table 4: Desorption efficiency of copper ions and phosphates from the EDA/MMA/OA/Fe₃O₄ adsorbent in solutions with different HNO₃ (for Cu²⁺)/NaOH (for phosphate) concentrations.

the maximum monolayer's phosphate uptake of 34.507 mg g⁻¹ was significantly higher than the maximum monolayer's copper uptake of 7.096 mg g⁻¹. The adsorption kinetics for copper ions and phosphate closely follow the pseudo-second-order kinetic model rather than the pseudo-first-order kinetic model. The derived activation energies of EDA/MMA/OA/Fe₃O₄, with the adsorption reaction of copper ions and phosphate were 13.356 kJ mol⁻¹ and 7.344 kJ mol⁻¹, respectively. The optimum conditions to desorb cationic and anionic adsorbates from the dual functional adsorbents were 0.1 M HNO₃ for the copper ions and 0.05 M NaOH for phosphate, respectively. As expected, the prepared amino group magnetite (EDA/MMA/OA/Fe₃O₄) exhibited improved capacities for copper ions and especially phosphate, which opened a novel field to water treatment.

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