Amino groups functionalized Kaolin was facilely prepared via mussel inspired chemistry. The modified Kaolin exhibited much enhanced adsorption capability toward heavy metal ions.

Mussel inspired preparation of amine-functionalized Kaolin for effective removal of heavy metal ions

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Abstract

Adsorption has been well regarded as a promising and efficient method for the removal of low concentration heavy metal ions in aqueous solutions. And kaolin has been considered as a kind of low cost and environment-friendly adsorbent for its abundant in nature. But the low adsorption capacity to heavy metal ions and severe aggregation in solution restrains its application. In this work, an environment-friendly adsorbent (denoted as Kaolin-PDA-PEI) was prepared based on mussel inspired chemistry and Michael addition reaction between high reaction activity of polydopamine (PDA) and polyethyleneimine (PEI), which possesses a number of amine groups. The amine groups have displayed strong adsorption affinity towards copper ions. The successful modification of Kaolin by PDA and PEI was confirmed by a series of analyses, such as Fourier transform infrared spectroscopy, transmission electron microscopy, thermal gravimetry analysis and X-ray photoelectron spectroscopy. The effects of various parameters such as contact time, pH, initial concentrations of copper ions and temperature on copper ion adsorption by Kaolin-PDA-PEI were investigated. Kaolin-PDA-PEI shows higher adsorption capacity as compared with the raw Kaolin. The kinetic adsorption data were analyzed using pseudo-first-order, pseudo-second-order and intraparticle diffusion model. The Langmuir isotherm and Freundlich isotherm equilibrium model were applied to adsorption isotherm data to find the better fit isotherm. The results showed that adsorption process was well fitted by Langmuir isotherm model. The values of thermodynamics constants such as entropy change (ΔS^0), enthalpy change (ΔH^0) and Gibbs free energy (ΔG^0) were also calculated. The results indicated that the adsorption process of Kaolin-PDA-PEI were endothermic and spontaneous.

1. Introduction

Water, the base of life, has long been the requirement of human survival and economic development[1]. As the increasing development of economy, the demand of water increasing and the problem of water pollution has become more serious. Heavy metal pollution, defined as a kind of environment pollutions resulting from heavy metals or their compounds, is one of the most serious water pollutions.[2] Due to its bioaccumulation and toxicity, heavy metal pollution has made seriously effect on ecosystems and human beings [3, 4]. Among them, copper ions are one of the most commonly contained heavy metal ions in waste water. On the other hand, copper ions are one of the essential elements for human and play critical roles of human life process. However, the copper ions in high concentrations have toxic and adverse effects to living organism. Recent research shows that long-term drinking with high concentration copper (> 1 mg/L) is associated with hemolytic anemia, hepatic failure, shock and death [5]. However, the concentration of copper ions in water generally increased with increasing industrial activities, which has become a potential threat to public health. Therefore, it is extremely urgent to explore corresponding solutions to reduce the copper ions in solution to keep the hygienic safety of drinking water [6, 7].

To date, several technologies, including coagulation, flocculation, membrane filtration, biological treatment, organic material and adsorption, have been developed and implemented for the purpose of removing heavy metal ions in solution. Adsorption has been considered as an efficient method to remove heavy metal ions from waste water because of its low cost and easy operation.[8] Currently, many adsorbents such as activated carbon [9, 10], sawdust [11], fly ash [12, 13], zeolite [14], chitosan in prawn shell [15], lignin [16], rubber leaf [17], manganese oxide coated sand [18], green algae [19], carbon nanotubes [20-24], graphene related materials [25, 26] and Kaolin [27] have been reported for removal of copper ions. Among them, Kaolin is considered as low cost natural clay that has been widely used in heavy metal ion removal. The physicochemical properties of Kaolin included small size, large specific surface area, and weak interlayer binding force are beneficial to the adsorption of heavy metal in solution. However, its severe agglomeration and low adsorption capacity in solution limits its applications severely. For example, its adsorption capacity to copper ions is only 0.67 mg/g [28]. Tavani EL et al [29] have investigated the amount of adsorbed chromium ions from tannery wastewater by natural Kaolin clay is only 0.108 mg/g. Thus, numerous modification strategies, including high-temperature, coupling modification, surface grafting [30], radiation modification [31] and so on, have been developed to the modification of Kaolin to improve its dispersibility and adsorption capacity towards heavy metal ions. But many methods mentioned above suffer from defects such as high energy consumption, high cost, and high risk operation etc. Consequently, it is necessary to develop a facile, simple and effective strategy for Kaolin modification.

Mussel inspired chemistry is an emerging surface modification tool that has drawn greater attention in recent years.[32] It started originally by Herbert Waite's[33] research of marine mussel adhesion in 1980s. Subsequently, Lee et al [34, 35] carried out the further experimental research about dopamine self polymerization in an alkaline environment. They also demonstrated that mussel-inspired chemistry can be used as a universal and promising strategy for surface modification of various inorganic and organic materials.[34] Fei et al [36] have successfully synthesized varied thickness PDA coated carbon nanotubes based on

dopamine self-polymerization and polymerization time-controlled. Yang et al[37] have developed a method to prepare a layer of protective shell on the surface of yeast cell combined with covalent conjugate and dopamine self-polymerization. Zhao et al[38] have prepared two-dimensional PDA/graphene oxide by self-assembly of dopamine monomers on graphene oxide surface for removal of radioactive element uranium. Zhang et al[39-51] have fabricated well-dispersed carbon nanotubes by surface modification with 3-mercaptopropyl sulfonic acid sodium salt, normal dodecanethiol, polyethylene glycol and polymers through combination of mussel inspired chemistry and Michael addition reaction. On the other hand, the formation of PDA coating has also investigated by some groups.[52, 53] A lot of parameters such as pH, temperature and oxygen might influence the self polymerization of PDA. However, the detailed mechanism is still not clear for the complexity of self polymerization procedure.

In this study, we prepared an environment-friendly adsorbent combined with mussel inspiration and Michael addition reaction (**Scheme 1**). Kaolin was first coated with a thin layer of PDA coating via the self-polymerization of dopamine, and then PEI was conjugated with PDA coating through Michael addition reaction. The successful preparation of amine functionalized Kaolin was confirmed by a series of analyses. This prepared adsorbent was used to the removal of copper ions from waste water and the effect of contact time, pH, contact temperature, and initial concentration of copper ions were studied. The adsorption kinetics and thermodynamics of the adsorption process were also investigated.

Scheme.1 Schematic diagram shows the preparation of Kaolin-PDA-PEI via combination of mussel inspired chemistry and Michael addition reaction.

2. Experimental procedure

2.1. Materials and methods

2.1.1. Materials

Kaolin ($\text{Al}_2\text{Si}_2\text{O}_9\text{H}_4$) was purchased from Aladdin Industrial Co., Ltd. Polyethyleneimine (PEI) (molecular weight of 800 Da), copper nitrate trihydrate (>99.99%) and bis-(cyclohexanone)-oxalyldihydrazone (98.0%) used in this study were purchased from Aladdin Industrial Co., Shanghai, China. The dopamine hydrochloride (>98%) was purchased from Sangon Co. and tris-(hydroxymethyl)-aminethane (Tris) (>99%) was purchased from Tianjin Heowns Biochem.LLC.Co.

2.1.2. Preparation of Kaolin-PDA-PEI

The surface functionalization of Kaolin with amine groups was performed according to previous study[54]. Briefly, 500 mg Kaolin and 500 mg dopamine were dispersed into 100 mL alkaline buffer solution (10 mM Tris) in a flask. The mixture was constantly stirred at room temperature for 8 h. After that, the mixture was centrifuged under 8000 r/s for 5 min and washed 3 times with deionized water. The product (named as Kaolin-PDA) was obtained via dried under vacuum at 353 K. Then 500 mg Kaolin-PDA and 500 mg PEI were added into a flask with 100 mL 10 mM Tris buffer solution and then dispersed by ultrasonicator for 10 mi and stirred at room temperature for 8 h. The obtained mixture was centrifuged under 8000 r/s for 5 min, washed several times by deionized water and dried at 353 K for 4 h.

2.1.3. Characterization of Kaolin, Kaolin-PDA and Kaolin-PDA-PEI

The chemical structural information of Kaolin and functionalized Kaolin were measured by Fourier transform infrared spectroscopy (Perkin-Elmer Spectrum 100 spectrometer) in the wave number range of 400-4500 cm^{-1} with a resolution of 1 cm^{-1} . The elements of Kaolin were characterized by X-ray photoelectron spectroscopy by using VGESCALAB 220-IXL with Al $K\alpha$ X-ray source (1486.6 eV). The particle size and morphology characteristics of Kaolin were detected with a 100 KV transmission electron microscopy (TEM, Hitachi-7650B). The thermo gravimetric analysis (TGA) was performed on a SDTQ600 thermo gravimetric analyzer at 20 K/min under 100 mL/min nitrogen flow.

2.2. Adsorption studies

The adsorption performance of amine functionalized Kaolin was evaluated in the batch adsorption of copper ions. Adsorption kinetic experiments were conducted by a 50 mL sample tube containing 10 mg/L of copper ions and 10 mg of adsorbents to determine the adsorption equilibration time at room temperature. The sample tube was placed on a vapor-bathing constant temperature vibrator and about 4 mL suspensions were taken from it at different time intervals of the adsorption reaction. The concentrations of copper ions after the adsorption was measured by the ultraviolet and visible spectrophotometer (purchased from Beijing Purkinje General Instrument Co.). Adsorption thermodynamics batch experiments were carried out at different temperature (293, 303, 313, 323 and 333K) with same concentration, pH and contact time to study the effect of temperature on the adsorption. The adsorption isotherm experiments were conducted by adjusting the initial concentrations of copper ions in the range of 10-400 mg/L. The effects of pH on the adsorption capacity of amine functionalized Kaolin for copper ions were evaluated in the pH range of 2-12. The solution pH was adjusted to certain pH values by adding 0.1 M HCl and 0.1 M NaOH solution.

The amount of copper ions adsorbed by amine functionalized Kaolin was calculated using following mass balance equation:

$$Q_e = \frac{C_0 - C_e}{m} \times V$$

Where Q_e (mg/g) is the amount of heavy metal ions adsorbed per gram dry weight of the adsorbent at adsorption equilibrium time, C_0 (mg/L) is the initial concentrations of copper ions and C_e (mg/L) is the equilibrium concentrations of copper ions, m (g)

is the mass of adsorbent in the adsorption medium and V (L) is the volume of adsorption medium.

$$Q_t = \frac{C_0 - C_t}{m} \times V$$

Where Q_t (mg/g) is the amount of adsorbed heavy metal ions adsorbed per gram dry weight of the adsorbent at the time t (min), C_0 (mg/L) is the initial heavy metal ion concentration and C_t (mg/L) is the heavy metal ion concentration at time t (min), m (g) is the mass of adsorbent in the adsorption medium and V (L) is the volume of adsorption medium.

3. Results and discussion

3.1. Characterizations of Kaolin and functionalized Kaolin

The particle size and morphological characteristics of Kaolin, Kaolin-PDA and Kaolin-PDA-PEI were obtained by TEM (shown in **Fig. 1**). It is clear to see that raw Kaolin (**Fig. 1A**) consists of large particles and compact clearance with plate like structure. The size of these particles is rather unhemogeneous with size about several hundred nanometers. On the other hand, these small particles are piled up into larger aggregates with size about several micrometers. After Kaolin particles were coated with PDA, their structure has not been obviously changed (**Fig. 1B**). While the color of Kaolin samples was tuned from light grey to khaki grey (insets of **Fig. 1A** and **Fig. 1B**). Further immobilization of PEI onto Kaolin-PDA, the color of Kaolin-PDA-PEI was changed to tawny (Inset of **Fig. 1C** and **Fig. 1D**). Moreover, we can see that the structure of Kaolin-PDA-PEI has no difference with raw Kaolin, but a thin layer of polymer is covered on the surface of the Kaolin particles (**Fig. 1C** and **Fig. 1D**). Based on the above results, we can **preliminarily speculate** that Kaolin is modified by PDA and PEI through self polymerization of dopamine and subsequently Michael addition reaction.

Fig. 1 TEM images of Kaolin (A), Kaolin-PDA (B) and Kaolin-PDA-PEI (C and D). Scale bar = 2 μm (A-C) and scale bar = 1 μm (D). The color change of Kaolin samples implied that PDA and PEI have immobilized on Kaolin through mussel inspired chemistry and Michael addition reaction.

The FT-IR spectra of raw Kaolin and modified Kaolin are shown in **Fig. 2A**. From the FT-IR spectrum of Kaolin, the band assignments are: the peaks at 3695.9 and 3622.3 cm^{-1} can be assigned to external hydroxyl and internal hydroxyl of Kaolin respectively. Si-O in-plane vibration at 1008.9 cm^{-1} ; Al-OH vibration at 914.3 cm^{-1} and Si-O-Al bending vibration at 538.5 cm^{-1} were also observed. After surface modified with PDA and PEI, new peak appears at 2974.7 cm^{-1} was found in Kaolin-PDA-PEI. It can be attributed to stretching vibration of $-\text{CH}_2$. Furthermore, new peaks at 1644.3 cm^{-1} and 1595.1 cm^{-1} can be ascribed to $-\text{NH}_2$ deformation vibration and stretching vibration of aromatic rings of PDA and PEI. The comparison implied that the PEI and PDA have successfully immobilized onto raw Kaolin through facile mussel inspired strategy.

Fig. 2 (A) FT-IR spectra of Kaolin, Kaolin-PDA and Kaolin-PDA-PEI; (B) TGA curves of Kaolin, Kaolin-PDA and Kaolin-PDA-PEI.

TGA is used to study the thermo-stability of raw Kaolin, Kaolin-PDA, and Kaolin-PDA-PEI and to estimate the amount of PEI on the surface of Kaolin. As shown in **Fig. 2B**, the decomposition temperature of Kaolin is around 670 K. When the temperature was increased to 870 K, the weight loss percentage was reached to about 11.89%. After being modified, the decomposition temperature was decreased. For example the T5 values for kaolin, kaolin modified PDA, and kaolin PDA-PEI are 780, 745, and 720 K, respectively. The weight loss of modified Kaolin below 750 K is estimated at about 4% and 7% corresponding to the decomposition of PDA and PEI, respectively. There is a significant weight loss from 750 to 880 K, which is ascribed to the decomposition of Kaolin. From the change of weight percentage in the TGA curves, it can be calculated that the amount of PDA and PEI is about 4.38 % and 3.57 %, respectively, which indicates that the properties of modified Kaolin are preserved. The TGA results clearly showed that the organic films have been introduced on Kaolin through self polymerization of dopamine and further Michael addition reaction between Kaolin-PDA and PEI.

Fig. 3 XPS spectra for Kaolin and Kaolin-PDA-PEI. (A): survey XPS scans from 0 to 1200 eV; (B-F): high resolution XPS scans of C1s, N1s, O1s, Si2p, Al2p.

The chemical compositions of raw Kaolin and Kaolin-PDA-PEI are investigated by X-ray photoelectron spectroscopy (XPS). From **Fig. 3**, it can be seen that the elements including C, N, O, Si and Al are present in the samples of Kaolin and Kaolin-PDA-PEI (**Fig. 3A**), and the binding energy peaks of C1s, N1s, O1s, Si2p and Al2p of Kaolin are located at 284.8, 402.51, 532.21, 102.86 and 74.37 eV, respectively. After being modified, there are a bit of changes in the location of those elements binding energy peaks. For instance, the peaks of binding energy of C1s, N1s, O1s, Si2p and Al2p of Kaolin-PDA-PEI are relocated at 284.84, 399.12, 531.59, 102.37 and 73.84 eV, respectively. According to **Fig. 3B-F**, it is clear to see that the percentage of C is increased from 11.8 % to 49.54 %. More importantly, there is a significant change in the N percentage, which was increased from 0.44 % to 7.11 %. Meanwhile, the percentages of O, Si and Al are decreased from 60.78 %, 14.0 %, and 12.98 % to 31.49 %, 6.23 % and 5.63 %, respectively. These results further confirmed that PEI was incorporated into Kaolin-PDA-PEI. Based on the XPS results in **Table 1**, the weight percentage of Kaolin to PDA and PEI can be calculated. We found that the weight percentage of Kaolin is 44.5% and the weight percentage of PDA and PEI is about 55.5%. The results

implied that PDA and PEI could effectively coated on Kaolin.

Table 1 Element contents (%) of Kaolin nanoparticles based on XPS analysis

Sample	Atom percentage (%)				
	C1s	N1s	O1s	Si2p	Al2p
Kaolin	11.80	0.44	60.78	14.00	12.98
Kaolin-PDA-PEI	49.54	7.11	31.49	6.23	5.63

3.2 Adsorption experiment studies

3.2.1 The effect of contact time and adsorption kinetics

The adsorption equilibration time is a significance parameter in the adsorption process. **Fig. 4A** shows the effect of contact time on the adsorption of copper ions by Kaolin and Kaolin-PDA-PEI. It can be seen that the rapid adsorption of Kaolin-PDA-PEI to copper ions in solution takes place within 20 min, while the adsorption equilibration time of raw Kaolin to copper ions in solution require more than 60 min. The maximum adsorbed copper ions amount at adsorption equilibration time of Kaolin-PDA-PEI is about 20.54 mg/g, which is higher than the maximum amount of adsorbed copper ions by raw Kaolin (about 13.01 mg/g). These results indicate that the amine groups modified Kaolin is in favor of the adsorption to copper ions in solution.

The adsorption kinetics is one of the essential parameters to describe the copper ions uptake rate and control the residue time of the adsorbent at the solid-solution interface, from which the efficiency of the copper ions adsorption by Kaolin-PDA-PEI can be determined [55]. In order to predict the favor adsorption kinetic model, the pseudo-first-order, pseudo-second-order and intraparticle diffusion models are used to fit the experiment data in this study (**Fig. 4B**).

Fig. 4 (A) The adsorption amount of Kaolin-PDA-PEI to 10 mg/L copper ions at room temperature, initial pH 7.1, and adsorbent dose 10 mg. **(B)** The experiment data are fitted by pseudo-first-order, pseudo-second-order and intraparticle diffusion models.

The non-linear form of the pseudo-first-order kinetic model can be expressed as follows:

$$Q_t = Q_e(1 - e^{-k_1 t})$$

Where Q_e (mg/g) and Q_t (mg/g) are the amount of adsorbed copper ions on the surface of Kaolin-PDA-PEI at equilibrium and at time t (min), respectively. k_1 (min^{-1}) is the rate constant of the pseudo-first-order equation, the values of those parameters are listed in **Table 2**. It is clear to see that the calculated value of Q_e from this model is about 20.25 mg/g, which is very close to the value (20.54 mg/g) of Q_e from the adsorption experiment. The value of correlation coefficient (R^2) of this equation is 0.9848 and the value of rate constant k_1 is about 0.1486 min^{-1} .

The pseudo-second-order kinetic model which is based on the assumption that chemisorption is the rate determining step can be described by follow equation [56]:

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t}$$

$$h = k_2 Q_e^2$$

Where k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$) is the pseudo-second-order rate constant, and Q_e (mg/g) and Q_t (mg/g) are the amount of adsorbed copper ions on the surface of Kaolin-PDA-PEI at equilibrium and at time t (min), respectively, h (mg/g min) represents the initial adsorption rate. According to the **Table 2**, the value of parameter h is about 5.053 mg/g min and pseudo-second-order rate constant k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$) is 0.01041. The Q_e value of Kaolin-PDA-PEI obtained from the pseudo-second-order equation is about 22.03 mg/g, which also correspond with the experiment data but does not fit well. The lower correlation coefficient ($R^2 = 0.9591$) of pseudo-second-order at the side of the pseudo-first-order correlation coefficient also suggest that experimental kinetic data for Kaolin-PDA-PEI to copper ions in solution follow the pseudo-first-order better more than the pseudo-second-order rate model.

The intra-particle diffusion equation is given as:

$$Q_t = k_p t^{0.5} + C$$

Where k_p ($\text{mg g}^{-1} \text{ min}^{-1/2}$), the intra-particle diffusion rate constant, is listed in Table 2. The value of k_p and constant C are 0.8554 and 12.80, respectively. The plot of Q_t vs. $t^{0.5}$ using the initial experiment kinetic data up to 140 min gives correlation coefficient value of 0.4462 for the adsorption process. The very low R^2 value indicates that this adsorption process is not suitable for intra-particle diffusion.

According to those results mentioned above, this adsorption process better fits to the pseudo-first-order model compared to pseudo-second-order kinetic order, the chemisorption plays a significant role in this adsorption process; and the values of correlation coefficient from pseudo-first-order and pseudo-second-order both are over 0.9, which indicates that the chemisorption is accompanied by physisorption in the adsorption process of Kaolin-PDA-PEI to copper ions in solution.

Table 2 Data of Pseudo-first-order, Pseudo-second-order and Intraparticle diffusion models parameters at 292 K

Models	Parameters	Initial concentration (mg/L)
		10
Pseudo-first-order equation	$Q_{e(cal)} (mg/g)$	20.25
	$k_1 (min^{-1})$	0.1486
	R^2	0.9848
Pseudo-second-order equation	$Q_{e(cal)} (mg/g)$	22.03
	$k_2 (g\ mg^{-1}\ min^{-1})$	0.01041
	$h (mg\ g^{-1}\ min^{-1})$	5.053
	R^2	0.9591
Intraparticle diffusion	$k_p (mg\ g^{-1}\ min^{-0.5})$	0.8454
	C	12.80
	R^2	0.4462

3.2.2 Adsorption isotherms

In this study, adsorption isotherm is used to describe the adsorption equilibrium of copper ions at the surface of Kaolin-PDA-PEI, the adsorption equilibrium models could provide some useful information about the adsorption mechanism, the surface properties and the affinity of adsorbent [57]. In order to understand the adsorption mechanism, the experiment data is simulated by Langmuir and Freundlich isotherms models (**Fig. 5**).

The Langmuir isotherm model is based on the assumption that the adsorption process occurs in a monolayer, homogeneous and finite mode on the absorbent, and there is no interaction between the adsorbed molecules. The Langmuir isotherm mode is represented by following non-linear equation:

$$Q_e = \frac{K_L Q_m C_e}{1 + K_L C_e}$$

Where C_e (mg/L) is the equilibrium concentration of copper ions, Q_e (mg/g) is the amount of adsorbed copper ions by Kaolin-PDA-PEI at equilibrium time, Q_m (mg/g) is related to the maximum adsorption capacity of the absorbent and K_L (L/mg) is the Langmuir adsorption constant related to the energy of adsorption. The value of Q_m (mg/g) and K_L (L/mg) are calculated from the equation of Langmuir isotherm model and shown in **Table 3**. In this paper, the calculated maximum value of Q_m (mg/g) is 60.99 and the K_L (L/mg) is 0.06354. The essential characteristics of Langmuir isotherm could be described as a dimensionless equilibrium parameter (R_L) and is defined as followed equation:

$$R_L = \frac{1}{1 + K_L C_0}$$

Where C_0 (mg/L) is the initial concentration of copper ions and K_L (L/mg) is the Langmuir constant. The value of R_L indicates that the type of isotherm is irreversible when $R_L = 0$, while the isotherm type is favorable as $0 < R_L < 1$, the isotherm type is linear as $R_L = 1$ and unfavorable as $R_L > 1$, the data of R_L is shown in **Table 3**.

Fig. 5 The adsorption isotherms of Cu^{2+} ions by Kaolin-PDA-PEI at initial heavy metal ions concentration from 10 to 400 mg/L, absorbent dose 10mg, and room temperature for 60 min, the data from the experiment have been fitted by Langmuir and Freundlich models.

The Freundlich adsorption isotherm equation is applied to monolayer adsorption as well as heterogeneous adsorption and describes the adsorption mechanism on the heterogeneous surface in low concentration system. The non-linear form of Freundlich isotherm model can be represented as following:

$$Q_e = K_F C_e^{1/n}$$

Where Q_e (mg/g) is the amount of adsorbed copper ions per unit mass of Kaolin-PDA-PEI at equilibrium, C_e (mg/L) is the equilibrium concentration of copper ions. And K_F [(mg/g) (L/mg)^{1/n}] is the adsorption equilibrium constant of Freundlich isotherm model, represents the adsorption capacity of Kaolin-PDA-PEI. n is the Freundlich constant and represents the degree of dependence of adsorption on the equilibrium concentration. Generally speaking, the value of n^{-1} in the range of 0–1 illustrates that the adsorption process is favorable; while the value of n^{-1} in the range of 0.1–0.5 represent that adsorbate is much favorably adsorbed on adsorbent. On the contrary, while the value of n^{-1} is beyond 2. It means that the adsorbates are unfavorably adsorbed by adsorbents. The values of K_F and n are calculated from the equation of the Freundlich isotherm model and listed in **Table 3**. It

can be observed that the value of K_F and n are 18.13 (mg/g) (L/mg)^{1/n} and 4.704, respectively.

As seen from the **Fig. 5**, the equilibrium uptake increased with the increasing of equilibrium copper ions concentration at the range of experimental concentration. This is a result of the increase in the driving force from the concentration gradient [58], the active sites of Kaolin-PDA-PEI are surrounded by much more copper ions as the copper ion concentration increased. The more copper ions are adsorbed. Thus the value of Q_e (mg/g) increased with the increasing of equilibrium copper ion concentrations. From the **Table 3**, it is clear to see that the experimental data are better fitted by Langmuir isotherm model ($R^2 = 0.9672$) than Freundlich isotherm model ($R^2 = 0.8668$). The above results indicate that chemisorption plays an essential role in the adsorption process. Furthermore, the value of R_L is found to be 0.6114. This confirms that Kaolin-PDA-PEI is favorable for adsorption of copper ions in solution under the conditions used in this study. The calculated value of n^{-1} is 0.2126, indicating that copper ions is very favorably adsorbed by the Kaolin-PDA-PEI. This also suggests the formation of a heterogeneous surface.

Table 3 Data of adsorption isotherms of Langmuir and Freundlich models for the adsorption on Kaolin-PDA-PEI at 303 K.

Isotherms	Parameters	Temperature (K)
		303
Langmuir	Q_m (mg/g)	60.99
	K_L (L/mg)	0.06354
	R_L	0.03786-0.6114
	R^2	0.9672
Freundlich	K_F [(mg/g)(L/mg) ^{1/n}]	18.13
	n	4.704
	R^2	0.8668

3.2.3 The effect of solution pH on copper ions uptake

The solution pH plays a significant role in the adsorption process of adsorbates onto adsorbents [59]. In order to study the effect of solution pH on the surface of Kaolin-PDA-PEI, the batch experiment is carried out at different solution pH range from 2 to 12 at room temperature at a fixed copper ion concentration of 10 mg/L. **Fig. 6** shows the variations in the removal of copper ions at various solution initial pH. It is evident that the maximum removal of copper ions is observed at pH of 11.1. With the increasing of pH from 2 to 12, the amount of adsorbed copper ions increases from 1.8 to 45.1 mg/g at initial pH of 11.1, and then decreases to 40.9 mg/g with further increase pH values. This may be the result of competitive adsorption effect and the protonation of amine groups. A high concentration of H⁺ at acidic pH leads to the protonation of amine groups. Therefore, copper ions are difficult to be adsorbed by active sites on the surface of Kaolin-PDA-PEI. The increase in pH from initial pH 2 to 11.1 during adsorption

indicates the decrease in hydrogen ions concentration in the solution [60] and increase of copper ion removal efficiency. The significant change of adsorption capacity of Kaolin-PDA-PEI is observed at pH 6 to 8. The reason may be the effect of formation of copper hydroxide precipitation. No significant change of adsorption capacity of Kaolin-PDA-PEI at pH 9.9 to 11.1 was found. The decrease of amount of adsorbed copper ions at pH 12 suggests that protonation of amine groups is not effective in low concentration of free hydrogen ions solution. In a word, the increase of solution pH is beneficial to the adsorption of copper ions on the surface of Kaolin-PDA-PEI.

Fig. 6 The effect of initial pH of copper ions solution on adsorption of the Cu^{2+} onto Kaolin-PDA-PEI. Experimental condition: 10 mg/L, T = room temperature.

3.2.4 The effect of temperature and adsorption thermodynamics

Temperature is one of most important factor for adsorption process of Kaolin-PDA-PEI. In order to study the effect of temperature, the batch experiment is carried out for the initial concentration of copper ions at 10 mg/L and five different temperatures, i.e., 293.15, 303.15, 313.15, 323.15 and 333.15 K, at pH 7.1. **Fig. 7A** shows the amount of copper ions adsorbed by Kaolin-PDA-PEI at equilibrium time at different temperature. It can be seen that the amount of copper ions adsorbed by Kaolin-PDA-PEI was increased from 18.1 to 30.9 mg/g with the increase of temperature from 293 to 333 K, suggesting that the adsorption reaction is an endothermic process. The reason may be that the physical bonding between copper ions and the active sites of Kaolin-PDA-PEI weakened and the move ability of adsorbent increased as the temperature increased. Thus the value of Q_e (mg/g) increased with the increasing of temperature.

In order to estimate the effect of temperature on the adsorption of copper ions onto Kaolin-PDA-PEI, the three basic

thermodynamic parameters, entropy (ΔS^0), enthalpy (ΔH^0) and Gibbs free energy (ΔG^0) are calculated from the temperature dependent adsorption data. The standard entropy change, enthalpy change and Gibbs free energy change can be calculated from the following equations:

$$\ln K\alpha = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R \cdot T}$$

$$K\alpha = \frac{Q_e}{C_e}$$

$$\Delta G^0 = -RT \ln K\alpha$$

Where $K\alpha$ is the adsorption equilibrium constant and the R is the gas constant (8.314 J/mol·K). T is the temperature of the solution (K), Q_e is the amount of adsorbed cooper ions at equilibrium (mg/g) and the C_e is the equilibrium concentration of copper ions. Considering the relation between the Gibbs free energy change (ΔG^0) and $K\alpha$, the enthalpy change (ΔH^0) and entropy change (ΔS^0) are determined from the slope and intercept of the Van't Hoff plots of $\ln K\alpha$ versus of $1/T$ (**Fig. 7B**). The value of ΔS^0 , ΔG^0 , ΔH^0 , and other thermodynamic parameters at various temperatures are listed in **Table 4**.

Fig. 7 (A) Effect of temperature on the adsorption of Cu^{2+} by Kaolin-PDA-PEI. Experimental condition: $C_{\text{Cu}^{2+}} = 10 \text{ mg/L}$, $\text{pH} = 7.1$, $t = 60 \text{ min}$. (B) Van't Hoff plot for the adsorption for the Cu^{2+} onto Kaolin-PDA-PEI.

According to the result from **Table 4**, it can be found that the value of Gibbs free energy change in various temperature is negative. The equilibrium constant $K\alpha$, was decreased from -2.573 to -5.706 kJ/mol, which indicates that the adsorption reaction is a spontaneous and irreversible process. The decrease of the value of Gibbs free energy change suggests that the adsorption process of copper ions onto Kaolin-PDA-PEI becomes more favorable at higher temperature. The value of entropy change and enthalpy change calculated from the plots of $\ln K\alpha$ versus of $1/T$ are given as 0.09203 kJ/mol K and 24.39 kJ/mol, respectively. The positive value of ΔH^0 suggests that the adsorption on the surface of Kaolin-PDA-PEI is an endothermic process. The ΔS^0 positive value indicates that the randomness increased at the solid-liquid interface during the adsorption process of copper ions on

Kaolin-PDA-PEI. More importantly, the amount of functional groups (e.g. amine groups) can be adjusted by change the experimental conditions. It can be expected that the adsorption capability of Kaolin-PDA-PEI towards copper ions will increased when the amount of PEI was increased. Furthermore, other surface modification strategies relied on mussel inspired chemistry, which combined with free radical polymerization, single electron transfer living radical polymerization or reversible addition fragmentation chain transfer polymerization can be also developed for preparation of a large number of functionalized adsorbents.[61-64] The properties of these adsorbents can be well designed according to the demand. It is therefore, the mussel inspired strategy described in this work should be a general tool for fabrication of many multifunctional composites for different environmental applications.

Table 4 Data of the thermodynamic parameters for the adsorption of copper ions onto Kaolin-PDA-PEI

T (K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol K)
293.15	-2.573	24.39	0.09203
303.15	-3.470		
313.15	-4.340		
323.15	-5.706		
333.15	-6.038		

4. Conclusions

The amine functionalized Kaolin is prepared via mussel inspired and Michael addition reaction. A series of characterization analyses including FT-IR, TEM, TGA, and XPS evidence the successful modification of Kaolin with PDA and PEI. The present study confirms the promotion in the capability and effectiveness of Kaolin-PDA-PEI as an environmental adsorbent for the copper ions removal in solution. Adsorption behavior of copper ions onto Kaolin-PDA-PEI was affected by experimental parameters such as solution pH, contact time, temperature and initial concentrations of copper ions. It can be found that the adsorption process of copper ions on Kaolin-PDA-PEI is favored at high solution pH. The experimental data are found to be better fitted by pseudo-first-order and the adsorption isotherms are better described by the Langmuir isotherm model in this study. The thermodynamic experiment indicates that the adsorption of copper ions on Kaolin-PDA-PEI is spontaneous, irreversible and endothermic process. Thus, mussel inspiration strategy described in this work could be a promising method for surface modification and enhancement adsorption capacity of different materials for its universality.

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