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A novel rectorite-based composite adsorbent for removing heavy metal ions and PAHs

Tang Yu-bin*, Chen Fang-yan, Ye Wei, Jiang Duo-duo

School of Environmental and Chemical Engineering, Jiangsu University of Science and Technology, Zhenjiang, Jiangsu, China

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ABSTRACT

To control the combined pollutions of Heavy Metal Ions and PAHs, a novel rectorite-based adsorbent, composite of rectorite/sodium polyacrylate/humic acid, was prepared. The adsorption of heavy metal ions (Pb^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}) and PAHs (phenanthrene, pyrene) on the adsorbent was investigated. The results revealed that sodium polyacrylate is incorporated into the interlayer of rectorite by intercalation mode and linked with each other by hydrogen bond, resulting in increase of rectorite's interlayer spacing from 2.69 to 6.79 nm, to form intercalation-type polymer/clay composites. The maximum adsorptive capacity attained is 1666.7, 666.7, 303.0, 454.6, 18.45 and 3.3 mg/g for Pb^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, phenanthrene and pyrene, respectively. The adsorption of the heavy metals ions and PAHs on the adsorbent can all be described by Langmuir, Freundlich and D-R models. The PAHs adsorption even more conforms to Henry model. The heavy metals ions are adsorbed by ion exchange or complexation. The adsorption mechanism of the PAHs is due to partition action. No obvious competitive adsorption was found between Pb^{2+} and phenanthrene in coexistence system of the two. The adsorbent can simultaneously remove heavy metal ions and PAHs, indicating that the adsorbent has a good application prospect in controlling combined pollution of heavy metals and PAHs.

Key words: Adsorbent, preparation, heavy metals, PAHs, combined pollutions

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INTRODUCTION

Heavy metals in the environment come mainly from some production processes, such as mining, non-ferrous metal processing, electroplating, paper making, pesticide, medicine, dye, paint, and so on [1]. The heavy metals in environment are nonbiodegradable. They can enter human body via food chain and cause severe health risk, such as mental retardation, nervous illness or cancer [2]. Just like heavy metals, PAHs is a kind of refractory pollutants, which is difficult to be biodegraded due to their steady structure. Because some PAHs have carcinogenic, teratogenic and mutagenic properties, they have been blacklisted as priority pollutants in many countries [3]. At present, Water, soil and air are all polluted by PAHs to varying degrees all over the world. Usually, heavy metal and PAHs exist in the same wastewater or environment simultaneously. The combined pollution resulting from the interaction between heavy metal and PAHs can cause more complicated environmental effect than that of simplex heavy metals or simplex PAHs [4-6]. So far, water and soil are polluted by PAHs and heavy metals, to some extent. For this reason, it is necessary to pay more attentions to the problem of combined pollution caused by heavy metals and PAHs.

A variety of techniques such as adsorption, ion exchange, membrane separation, chemical precipitation and oxidation-reduction have been used to remove heavy metals from wastewater [7, 8]. And PAHs in wastewater are usually removed by biodegradation [9], adsorption [10-12], photocatalysis oxidation [13]. Adsorption is considered to be a most effective and promising technique for removing heavy metal and PAHs due to its quick adsorption rate and high adsorption capacity. Commercial activated carbon and macromolecular adsorption resins are commonly used as adsorbents to remove heavy metals and PAHs. But, unfortunately, the high cost limits their wide application.

Therefore, many researchers have attempted to seek low-cost and effective substitutes. However, the previous works on developing novel adsorbent just aimed at adsorption of simplex heavy metal or PAHs. It is not found that the adsorbent to remove heavy metals and PAHs from water simultaneously was developed. Recently, preparation and application of organic-inorganic composite material has attracted increasing interest. Organics and clay minerals were chosen to prepare low-cost and effective composite adsorbent, such as polyacrylamide/bentonite composite adsorbent [14, 15], polyacrylic acid/ bentonite composite adsorbent [16] and chitosan/ bentonite composite adsobent [17], and so forth. These polymers/clay composite adsorbent are mainly utilized in adsorption of hydrophilic heavy metals and cationic dyes. None of them were used as adsorbent to remove hydrophobic organic pollutants such as PAHs. Rectorite is a sort of regularly interstratified clay mineral with dioctahedral mica-like layer and dioctahedral smectite-like layer existing in 1:1 ratio, which possesses high adsorption and ion exchange capacity due to its swelling property in perpendicular slice and large surface area in exterior and interior [18]. The intercalation of sodium polyacrylate into rectorite interlayer can improve adsorption properties of rectorite [19-21]. Humic acid is one of major components of humic substances in environment, which contains both hydrophilic groups and hydrophobic groups, such as carboxyl, phenolic hydroxyl group, carbonyl group, as well as loosened “sponginess-like” structure with large surface area, contributing to its high adsorption capacity for heavy metals and organics. Up to now, there has been no report on preparation of rectorite/ humic acid/ sodium polyacrylate composite adsorbent. In this research, rectorite/ humic acid/ sodium polyacrylate composite adsorbent was prepared by polymerization of sodium acrylate into the interlayer of CTAB-modified rectorite along with loading of humic acid, and the adsorption capability for heavy metals and hydrophobic PAHs were also investigated.

EXPERIMENTAL SECTION

Materials and instruments employed

Acrylic acid, N, N’-methylene bisacrylamide (MBA) (C.P., Shanghai Co., Ltd. of Chemical Reagents); Cetrimonium bromide (CTAB), hydrochloric acid, potassium persulfate and sodium hydroxide (A.R., Shanghai Co., Ltd. of Chemical Reagents); Lead, copper, zinc, cyclohexane, phenanthrene, pyrene (chromatographic pure, Shanghai Co., Ltd. of Chemical Reagents); Rectorite was supplied by Hubei Zhongxiang Rectorite Corporation, China. Humic acid was obtained from Hebei Guoxing Turf Factory, China.

AA-6300 atomic absorption spectrophotometer（SHIMADZU Instruments Co. Ltd. Japan）; GC-2014 gas chromatograph（SHIMADZU Instruments Co. Ltd. Japan）; DKZ-2 electrothermal homoeothermic oscillation sink(Shanghai Precision Instruments Co., Ltd); micromeritics ASAP 2020 V3.04H adsorption–desorption instrument (American Micromeritics Corporation); GSM-6480 scanning electron microscope (GSM-6480, Japanese Corporation of Electron); D8 ADVANCE polycrystalline X-ray diffractometer（Bruker AXS Germany）; TENSOR 27 Fourier transform infrared spectrometer (Germany Bruker Corporation).

Preparation of adsorbent

Preparation of organic rectorite:

The organic rectorite was prepared by a cation exchange between Ca^{2+}-rectorite galleries and CTAB in an aqueous solution. Rectorite (10 g) was dispersed in 100 mL of distilled water to obtain clay suspensions using a stirrer, and placed standing for 24 h after vigorous stirring for 60 min. CTAB (1 g) was dissolved in water, and then added slowly into the rectorite suspensions. The mixture was then transferred into a three-neck flask and stirred for 24 h at 70℃ in water-bath. The product was washed several times with distilled water and filtered to ensure a complete removal of bromide ions, which were detected with $AgNO_3$ until no AgBr precipitate was found. The resulting product was dried at 120℃ and sieved to a uniform particle size with 200 mesh sieve to yield organic rectorite.

Preparation of composite adsorbent

0.35 g of acrylic acid was weighed into a beaker (500 mL capacity), and 100 mL of deionized water was added into the beaker to ensure acrylic acid dissolved. Then, under the conditions of ice-water bath, added NaOH aqueous solution into the beaker to neutralize the acrylic acid solution for 5min in the molar ratio of NaOH and acrylic acid 1:0.75. Subsequently, the neutralizing product (monomer) was transferred into a four-necked flask. Then, 0.5 g of organic rectorite and 0.15 g of humic acid were added into the monomer solution under nitrogen (99.99%) protection, stirred for 10 min in order to prevent precipitation and agglomeration. The crosslinker N, N’-methylene bisacrylamide (MBA) and initiator potassium persulfate (The mass ratio of N, N '- methylene bisacrylamide and acrylic acid is 0.5%; the mass ratio of potassium persulfate and acrylic acid was 2.5%) were in turn dropwise added into the mixture solution under nitrogen atmosphere, heated to 40℃, and stirred for 30 min to polymerize, then heated to 70℃, stirred for additional 3 h. The resulting product was transferred into a beaker and washed with ethanol for several times, finally dried at 80℃, grinded and sieved to a uniform particle size with 200 mesh sieve. Namely, a novel rectorite-based adsorbent (sodium polyacrylate/humic acid/rectorite composite) was prepared.

Characterization of the adsorbent

The specific surface area of adsorbent sample was obtained by nitrogen adsorption–desorption isotherm determined by micromeritics ASAP-2020 V3.04 H instrument (American Micromeritics Corporation) at 77 K.

Polycrystalline X-ray diffraction patterns were recorded to analyze the adsorbent sample by XRD (D8 Advance, Bruker AXS Germany).

The functional groups on the surface of adsorbent sample were identified by FTIR technique (TENSOR 27, Germanic Bruker Corporation).

The surface topography of the adsorbent prepared was observed by scanning electron microscope (GSM-6480, Japanese Corporation of Electron).

Adsorption procedure

Adsorption of heavy metals

Samples of the various adsorbates (Pb^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+} ions) were prepared at various concentrations in aqueous solution (10~400 mg/L). 0.01 g of the dried adsorbent prepared was then weighed into each of a series of conical flasks (250 mL capacity) and 100 mL of a particular concentration of a heavy metal ion solution was added to each flask. At 25℃, after shaking for 4 h at the rate of 200 r/min, the samples were centrifugalized and the concentration of heavy metal remaining in the supernatant was determined by atomic absorption method (each sample was measured 3 times, and took the average). The adsorptive capacity of heavy metal on to the adsorbent prepared was calculated by eqn. (1).

$$q=\frac{V_0(C_0-C_e)}{1000m} \qquad (1)$$

Where, q is the amount of metal ions adsorbed onto unit amount of the adsorbent (mg/g); C_0 and C_e are the initial and equilibrium concentrations of the metal ions, respectively (mg/L); V_0 is the aqueous solution volume (mL), and m is the mass of adsorbent (g).

Adsorption of PAHs

The stock solution of 1000 mg/L of phenanthrene and pyrene was prepared, respectively, by dissolving a known quantity of phenanthrene and pyrene into methanol solutions. And the various working solution with the concentration ranging from 200 to 1000 μg/L was obtained by diluting with distilled water.

0.01 g of the dried adsorbent prepared was then weighed into each of a series of conical flasks (250 mL capacity) and 150 mL of various working solution added to each flask. At 25℃, after shaking for 4 h at the rate of 200 r/min, the samples were centrifugalized, then the supernatant was extracted with cyclohexane immediately. And the concentration of phenanthrene and pyrene remaining in the extract was determined by gas chromatography (each sample was measured 3 times, and took the average). The amount of phenanthrene and pyrene adsorbed onto the adsorbents was also calculated by eqn. (1).

Adsorption was carried out in darkness. No volatilization and photolysis of phenanthrene and pyrene were observed in the preliminary experiment.

Co-adsorption of heavy metal and PAH

The adsorption of Pb^{2+} under the conditions of coexistence of phenanthrene:

The mixed solution containing 50 mg/L of Pb^{2+} ions and 1.0 mg/L of phenanthrene was prepared. 0.01 g of the dried adsorbent prepared was then weighed into each of a series of conical flasks (250 mL capacity) and 100 mL of the mixed solution was added to each flask. At 25℃, after shaking for a known time （1, 3, 5, 10, 15, 30, 60, 120, 180 min）at the rate of 200 r/min, respectively, the samples were centrifugalized and the concentration of Pb^{2+} remaining in the supernatant was determined by atomic absorption method (each sample was measured 3 times, and took the average).

The adsorption of phenanthrene under the conditions of coexistence of Pb^{2+}

The procedure is same as that of adsorption of Pb^{2+} under the conditions of coexistence of phenanthrene except for the sampling time. The sampling time for this procedure was 10, 30, 60, 120, 150, 180, 240, 360, 480 min, respectively. The concentration of phenanthrene remaining in the supernatant was determined by gas chromatography.

RESULTS AND DISCUSSION

Characterization and analysis of the adsorbent

XRD analysis of adsorbent

XRD spectra of raw rectorite and composite adsorbent prepared were shown in Fig. 1. From Fig.1, we can see, there exist two diffraction peaks 001and 002 for raw rectorite located at 2θ = 3.28° and 7.14°, respectively, and only one peaks 001 for the composite adsorbent at 2θ=1.30°. Compared with raw rectorite, the peaks 001 of composite adsorbent was shifted to a lower angle and peak 002 disappeared, indicating that sodium polyacrylate has been intercalated into the interlayer of rectorite to lead to interlayer spacing of rectorite increased, and form the polymer / clay composites.

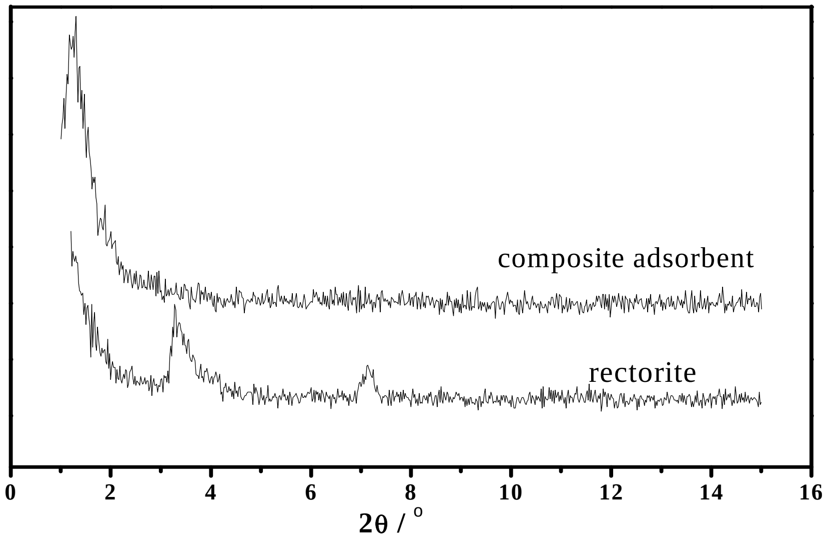

Fig.1 XRD spectra of rectorite and composite adsorbent

This also indicates that the composite adsorbent prepared was intercalated. That is to say, the rectorite modified by CTAB was intercalated by chains of sodium polyacrylate [19]. The d-spacing of the clays can be calculated from their degree 2θ of diffraction peak 001 based on Bragg equation. [22].

$$d = \frac{\lambda}{2\sin\theta} \tag{2}$$

Where, λ is X-ray wavelength, d is layer gap, and 2θ is degree 2θ of diffraction peak 001.

The d-spacing of raw rectorite and composite adsorbent prepared is calculated to be 2.69 nm and 6.79 nm, respectively. Obvious increase in d-spacing of composite adsorbent prepared suggested that layer gap was expanded due to cationic exchange reaction between rectorite and CTAB in the galleries of the rectorite. The larger d-spacing of the modified rectorite was propitious for polymerization of sodium acrylate in the interlayer of rectorite.

FTIR analysis of the adsorbent prepared

The FT-IR spectra of rectorite, sodium polyacrylate and composite adsorbent prepared were shown in Fig. 2.

From Fig. 2(b) we can see, the absorption band of sodium polyacrylate at 3446 cm^{-1} is due to –OH stretching vibration, the band at 1714 cm^{-1} is attributed to C=O in –COOH group stretching vibration, and the bands at 1564 cm^{-1} ,1455 cm^{-1} and 1410 cm^{-1} is ascribed to asymmetric stretching and symmetric stretching in -COO^{-} group, respectively. These absorption bands all appeared in the spectra of composite adsorbent prepared, indicating the existence of sodium polyacrylate in the composite adsorbent (see Fig. 2(a)). The absorption band of raw rectorite at 3342 cm^{-1} represents stretching vibration of –OH, the band at 1637 cm^{-1} is due to bending vibration of Si-OH, the band at 1092 cm^{-1} is ascribed to stretching vibration of Si-O (See Fig. 2(c)). The Si-OH bending vibration band in composite adsorbent was weaker than that in raw rectorite, indicating that the amount of Si-OH in composite adsorbent prepared was decreased. The Si-O stretching vibration band at 1092 cm^{-1} shifted to a lower wave number of 1084 cm^{-1} and was weakened. This phenomenon suggested that group Si-O in rectorite have probably participated the reaction or a certain bonding force exist between Si-O and other groups. Moreover, The band of the C=O stretching vibration at 1714 cm^{-1} in composite adsorbent prepared was weaker than that in sodium polyacrylate and the -OH stretching vibration band shifted from 3446 cm^{-1} to a lower wave number of 3432 cm^{-1}, suggesting that there may be exist hydrogen bonding between rectorite and sodium polyacrylate [23].

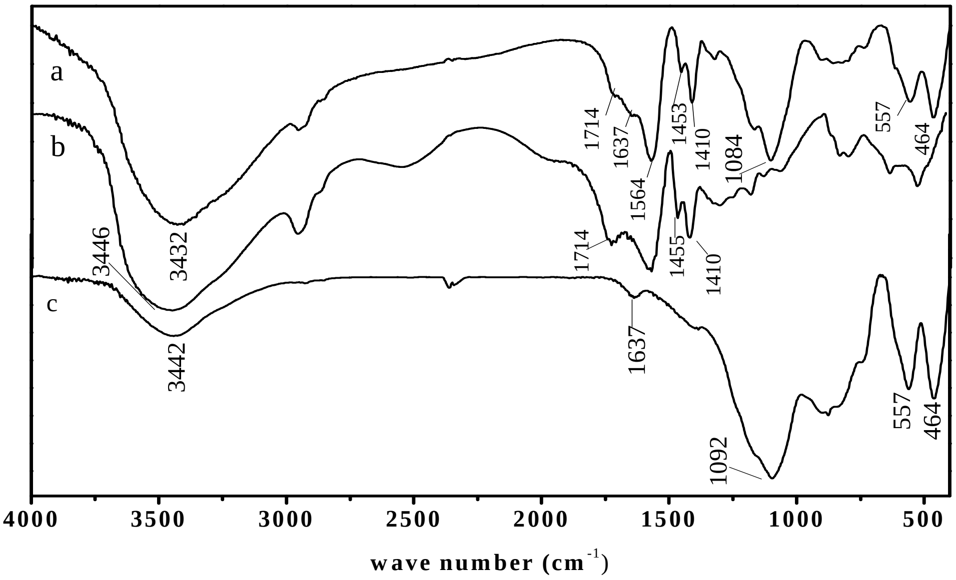

Fig. 2 FTIR spectra of adsorbent(a), sodium polyacrylate(b) and rectorite(c)

The analysis given above indicate that polymerization of sodium acrylate was carried out in the interlayer of rectorite to form the polymer/lay composite via hydrogen bonding between rectorite and sodium polyacrylate.

Surface morphology of the adsorbent

Fig. 3 shows the surface morphology of rectorite and composite adsorbent prepared under the optimizing conditions examined by SEM.

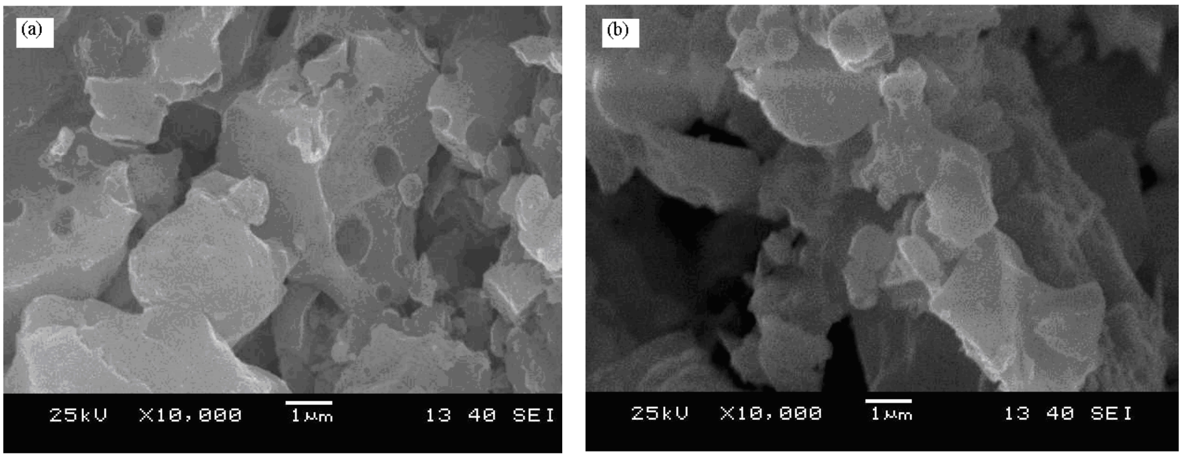

Fig.3 SEM photomicrograph of rectorite (a) and composite adsorbent (b)

As can be seen from Fig. 3, rectorite exhibited a smooth and comparatively dense surface with lamellar structures, while the composite adsorbent prepared showed a coarse and protuberant surface without obvious lamellar structures. Pores of the composite adsorbent prepared can be observed to be evidently larger than that of rectorite. The specific surface area of rectorite and the composite adsorbent determined by N_2 adsorption-desorption method was 7.474 m^2/ g and 13.769 m^2/ g, respectively. The significant increase in specific surface area of the composite adsorbent is due to the coarse surface and pores, which was more favorable to adsorption of heavy metals ion and PAHs.

Isothermal Adsorption of heavy metal ions

In this research, Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isothermal adsorption model were applied to fit the adsorption equilibrium data. Langmuir model is valid for monolayer adsorption onto surface, which can be expressed in linear form:

$$\frac{C_e}{q_e}=\frac{1}{q^0 b}+\frac{C_e}{q^0} \tag{2}$$

Freundlich model is empirical equation describing adsorption onto heterogeneous surface. The linear form of Freundlich model is presented as:

$$\lg q_e = \lg k + \frac{1}{n}\lg Ce \tag{3}$$

Where, q is the adsorption capacity (mg/g). C_e is the equilibrium concentration of adsorbates (mg/L). q^0 is the maximum amount of adsorbate at complete monolayer coverage (mg/g). b is Langmuir equilibrium constant related to the energy/intensity of adsorption (L/mg). The Freundlich constants k and $1/n$ are related to the adsorption capacity and heterogeneity factor, respectively.

The D-R model is expressed as：

$$q_e = q_m \exp(-\beta\varepsilon^2) \tag{4}$$

$$\varepsilon = RT \ln(1+\frac{1}{C_e}) \tag{5}$$

Equation (4) can be expressed in linear form:

$$\ln q = \ln q_m - \beta[RT(1+\frac{1}{C_e})]^2 \tag{6}$$

Where, q_m is D-R constant related to theoretical saturation capacity. β is a constant related to mean adsorption energy （mol^2/kJ^2） ; R is the ideal gas constant (8.3145J/mol·K). T is the absolute temperature in Kelvin (K).

E (kJ/mol) is defined as the free energy change required transferring 1 mol adsorbate from solution to the solid surface, which is calculated from

$$E=\frac{1}{\sqrt{2\beta}} \tag{7}$$

The value of E is used to estimate the type of adsorption reaction. In the case of E<8kJ/mol, adsorption may be affected by physical force. When E is in the range of 8-16 kJ/mol, the adsorption was governed by chemical adsorption or ion-exchange. On the other hand, adsorption may be dominated by particle diffusion if E>16 kJ/mol [25].

The linear adsorptive isotherm of heavy metals Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} ions onto the composite adsorbent fitted by Langmuir, Freundlich and D-R was shown in Fig. 4. The fitted results obtained via the three models are listed in Table 1. As shown in Fig.4 (a) to Fig. 4(c), it’s clear that the adsorption process conformed to Langmuir, Freundlich and D-R models. The adsorption fits best with the Langmuir model (the linear correlation coefficients are all greater than 0.99, see Fig.4a), indicating the monolayer coverage of the heavy metal ions on the surface of the composite adsorbent. As can be seen from table 1, q^0 obtained from Pb^{2+} adsorption was much higher than that obtained from Cd^{2+}, Cu^{2+} and Zn^{2+}. The adsorption capacity of the four heavy metal ions on the adsorbent decreased in the order $Pb^{2+} > Cd^{2+} > Zn^{2+} > Cu^{2+}$.

Freundlich constants 1/n is a function of strength of adsorption in the adsorption process. The smaller value of 1/*n*, the stronger is the adsorption affinity. The values of 1/*n* were found to lie in the range 0 to 1.0, is a measure of favorable adsorption. Values of 1/*n* below 1.0 represent favorable.

Table 1 isotherm parameters for the adsorption of heavy metal ions onto the adsorbent

Ions	Langmuir		Freundlich		D-R		
	b(L·mg^{-1})	q^0(mg·g^{-1})	1/n	k	q_m(mmol·g^{-1})	β(mol^2·kJ^{-2})	E(kJ·mol^{-1})
Pb^{2+}	0.111	1667	0.318	325.8	18.30	0.0027	13.61
Cd^{2+}	0.121	667	0.297	155.9	12.97	0.0028	13.36
Cu^{2+}	0.035	303	0.293	2.33	11.61	0.0030	12.91
Zn^{2+}	0.053	455	0.117	89.3	6.83	0.0027	13.61

The values of 1/*n* shown in Table 1 are all less than 0.5, indicating that Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} ions are all favorably adsorbed by the composite adsorbent.

E value obtained from D-R model were found to be in the range of 8-16 kJ/mol, indicating that the adsorption is dominated by chemiadsorption involving ion exchange or complexation between the heavy metal ions and the composite adsorbent.

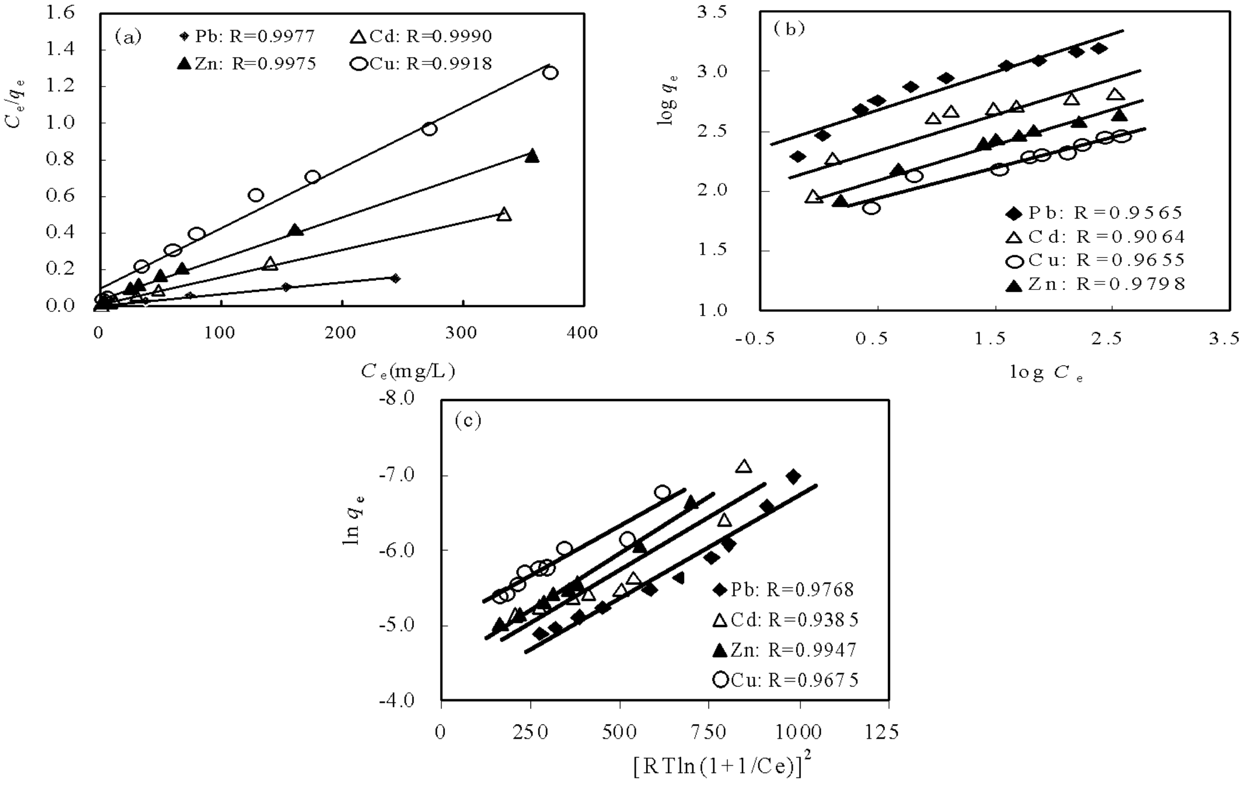

Fig. 4 Linear Langmuir isotherm (a), Freundlich isotherm (b) and D-R isotherm (c) for heavy metal ions

Isothermal Adsorption of PAHs

The adsorption isotherms of phenanthrene and pyrene on the composite adsorbent at 25℃ are depicted in Figure 5 as plots of the adsorption capacity, q_e, versus equilibrium concentration of phenanthrene or pyrene, C_e.

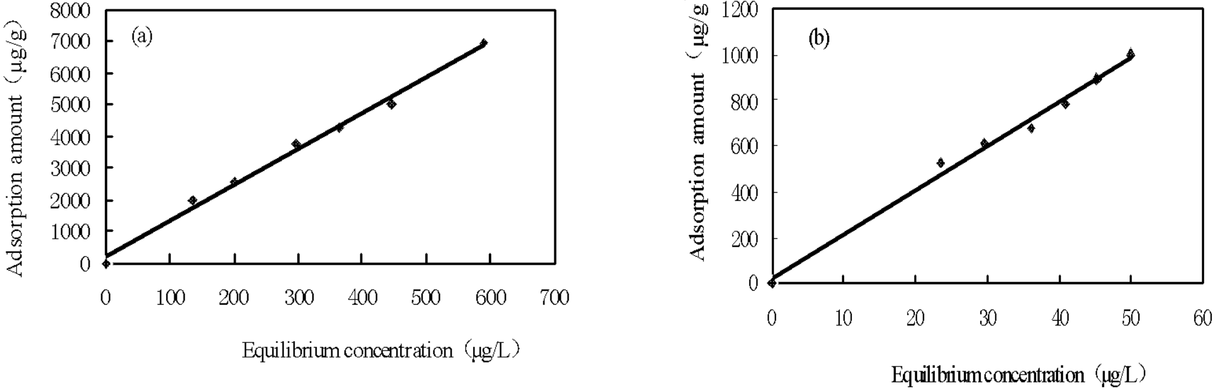

Fig. 5 Adsorption isotherm for phenanthrene (a) and pyrene (b)

From Figure 5 we can see, the adsorption isotherms appear linear, indicating that the adsorption may be conform to Henry model. Henry model was linear equation widely used to describe the adsorption of the organics on solid surface, which can be expressed as:

$$q_e = K_d\, C_e \qquad (10)$$

Where, K_d is partition coefficient.
Here, the data obtained from the adsorption equilibrium experiments for phenanthrene and pyrene may also be fitted to the Langmuir, Freundlich, D-R and Henry models.

The fitted results obtained via the four models mentioned above are listed in Table 2. From Table 2 we can see, the correlation coefficient are all more than 0.98, indicating that the adsorption process of phenanthrene or pyrene can well be described by Langmuir, Freundlich, D-R models and Henry models. From the fitted results to Henry model, we can conclude that the adsorption of phenanthrene or pyrene on the composite adsorbent is partition adsorption.

Table 2 Isotherm parameters of polycyclic aromatic hydrocarbons

Adsorbate	Langmuir			Freundlich			Henry		D-R		
	q^0 (mg/g)	b (L/mg)	R	k	$1/n$	R	K_d	R	β (mol²/kJ²)	E (kJ/mol)	R
phenanthrene	18.45	0.9	0.9939	29.91	0.846	0.9959	10.80	0.9962	0.0084	7.72	0.9877
pyrene	3.33	7.6	0.9804	34.87	0.847	0.9830	17.96	0.9859	0.0092	7.37	0.9871

The values of E for adsorption of phenanthrene and pyrene derived from D-R model were all less than 8.0 kJ/mol, indicating that adsorption of PAHs on the composite adsorbent was mainly governed by physical adsorption, that is to say, by partition action.

Co-adsorption of heavy metal and PAH

The co-adsorption experiment was conducted at 25℃ employing the method described in the Experimental section above. The results obtained are depicted graphically in Figure 6.

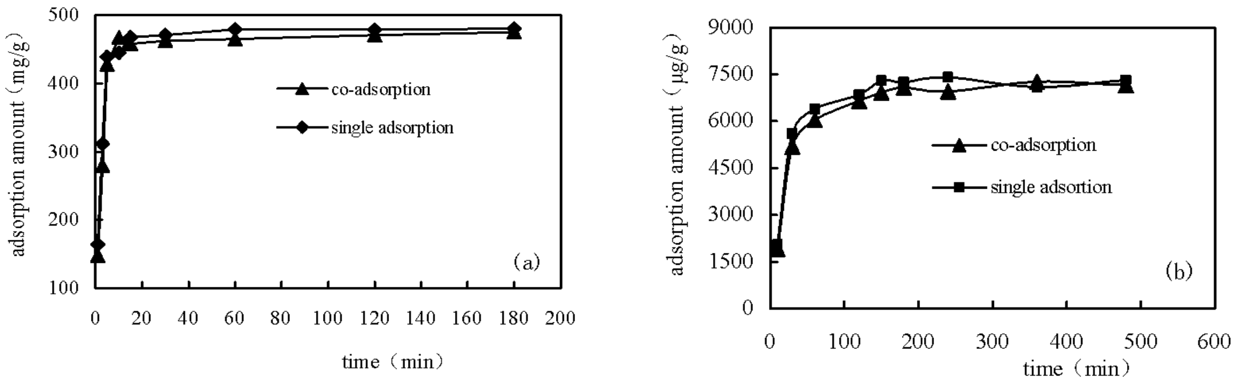

Fig. 6 Adsorption of Pb(II) with coexistence of phenanthrene (a) and Adsorption of phenanthrene with coexistence of Pb (II) (b)

As shown in Fig.6 (a), the adsorption rate curve of Pb^{2+} in co-adsorption system was almost overlapped with standalone adsorption rate curve of Pb^{2+}, indicating that no obvious influence was exerted on adsorption rate and adsorption capacity of Pb^{2+} on to composite adsorbent under the coexistence of phenanthrene.

Similarly, it can be seen from Fig. 6 (b) that no evident change in rate and capacity of phenanthrene adsorption occurs in co-adsorption system compared with those of solitary adsorption of phenanthrene. That is to say, coexistence of Pb^{2+} in the solution had no obvious effects on adsorptive properties of phenanthrene onto the composite adsorbent.

Undoubtedly, it is concluded that there is no obvious competitive adsorption between Pb^{2+} and phenanthrene, which is mainly attributed to the difference in the adsorption mechanism of Pb^{2+} and phenanthrene each other.

Adsorption of phenanthrene was primarily carried out by hydrophobic partition on hydrophobic sites of interlayer of the composite adsorbent, while adsorption of Pb^{2+} was mainly accomplished by electrostatic interaction or complexation on hydrophilic sites of the composite adsorbent. Thus, it is believed that the composite adsorbents can remove heavy metal ions and PAHs simultaneously from water and has a good application prospect in controlling the combined pollution of heavy metals and PAHs.

CONCLUSION

A novel rectorite-based adsorbent, the composite of rectorite/sodium polyacrylate/humic acid/ was successfully prepared by polymerization of sodium acrylate in the interlayer of CTAB-modified rectorite followed by loading of humic acid. Sodium polyacrylate is incorporated into rectorite interlamination by intercalation mode and linked with rectorite by hydrogen bond, resulting in increase of rectorite's interlayer spacing from 2.69 nm to 6.79 nm, to form intercalation-type polymer/clay composites. The surface of the composite adsorbent is asperous and polyporous, and its structure is favorable to the adsorption of heavy metal ions and PAHs.

The adsorption of Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} on to the composite adsorbent prepared may be classified as being of the monomolecular layer type which can be well described by the Langmuir, Freundlich and D-R adsorption models. The values of Freundlich constants $1/n$ are less than 0.5, indicating that all four kinds of heavy metal cations were readily adsorbed by the composite adsorbent prepared. The maximum amount of Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} adsorbed on the composite adsorbent with complete monolayer coverage is 1666.7, 666.7, 303.0 and 454.6 mg/g, respectively. The sequence of adsorptive capacities attained for Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} ions on the composite adsorbent was found to be $Pb^{2+} > Cd^{2+} > Zn^{2+} > Cu^{2+}$.

The values of free energy change E calculated from D-R model were all found to be in the range of 8~16 kJ/mol, suggesting that the adsorption is dominated by chemiadsorption involving ion exchange or complexation between heavy metal ions and composite adsorbent.

The adsorptive isotherms of phenanthrene and pyrene appear linear, which can be well described by Langmuir, Freundlich, D-R and Henry models. The values of E derived from D-R model were less than 8.0 kJ/mol. Adsorption for PAHs was governed by physical adsorption by partition action.

No obvious competitive adsorption between Pb^{2+} and phenanthrene in co-adsorption system containing Pb^{2+} and phenanthrene was found. We concluded that the composite adsorbents can effectively remove heavy metal ions and PAHs simultaneously from water, and the adsorbent will play an important role in controlling combined pollution of heavy metals and PAHs.

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