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Competition and complexation of heavy metal ions and humic acid on zeolitic MCM-22 and activated carbon

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Abstract

Zeolitic MCM-22 and activated carbon have been used as adsorbents for removal of heavy metals (Cu^{2+} and Pb^{2+}) and humic acid from aqueous solution. The adsorption behaviour has been investigated in single- and binary-adsorbate systems and the effect of humic acid on metal adsorption was obtained. It is found that the MCM-22 and activated carbon are effective in metal ion and humic acid adsorption. In single component system, the MCM-22 presents the adsorption capacities of Cu^{2+}, Pb^{2+}, and humic acid at 33, 94, and 78 mg/g, respectively, while the activated carbon exhibits the adsorption capacities of Cu^{2+}, Pb^{2+}, and humic acid at 12, 61, and 74 mg/g, respectively, lower than those on the MCM-22. Solution pH will significantly influence the adsorption. Cu^{2+} and Pb^{2+} adsorption will increase with increasing pH while humic acid shows a decreasing trend as pH is increased. In binary-adsorbate system, metal–humic acid interaction will affect the adsorption of metal and humic acid on the MCM-22 and activated carbon. On the MCM-22, Cu^{2+}, Pb^{2+} will present competitive adsorption with humic acid. On the activated carbon, Pb^{2+} and humic acid also exhibit competitive adsorption, while Cu^{2+} and humic acid will have a complexation effect, resulting in an increase of Cu^{2+} adsorption on the activated.

Keywords: Heavy metals; Humic acids; Zeolite MCM-22; Activated carbon; Competitive adsorption

1. Introduction

Heavy metal ions in waters are toxic or poisonous to human health and aquatic animals even at low concentrations. Among the heavy metals, Cu^{2+} and Pb^{2+} are the two important polluting ions. Removal of heavy metal ions from contaminated water or wastewater is very important for water cleaning. Among various techniques, adsorption is one of the most effective methods for the removal of heavy metals from the environments.

Humic acids (HAs) are generally part of humic substances. The presence of HA is very harmful in water treatment processes. The most serious health hazard caused by HA originates from the formation of chloroform during chlorination in water treatment. In addition, the capability of HA complexation with heavy metals can increase the migration of heavy metal ions in water, which is also an important issue in water treatment. Removal of HA can be achieved by adsorption using activated carbon [1–4].

In the past decades, zeolites have been used as effective adsorbents for heavy metal removal in water treatment because of their strong ion-exchange ability [5–9]. However, few investigations have been reported on zeolite application for HA removal [10,11]. To our knowledge, no work has been reported on the effect of humic acid on heavy metal removal using zeolite.

Synthetic zeolite MCM-22 is a new developed microporous material. In our previous investigations, it has been found that zeolite MCM-22 exhibits higher adsorption capacity for organic dyes than natural zeolite and its regeneration is also effective than natural zeolite [12–14]. In this report, we tested MCM-22 for heavy metal ion and humic acid adsorption in single and binary component systems and compare the adsorptive behaviour with a commercial activated carbon.

2. Experimental

2.1. Chemicals and materials characterisation

An activated carbon (AC) was obtained from Calgon, USA. The particle size is 100–150 μm. Zeolite MCM-22 was lab-synthesised with a ratio of Si/Al at 30 [14]. An organic mixture

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solution (denoted by L) produced by catalytic hydrogenation of caprolactam and composed of hexamethylenimine and caprolactam was used as a template. A certain amount of sodium aluminium, sodium hydroxide, L, silica, and deionised water were added into a vessel in that order under vigorous stirring for 20 min. The chemical composition of the gel was as follows: $SiO_2/Al_2O_3 = 30$, $OH/SiO_2 = 0.20$, $R/SiO_2 = 0.32$ (R representing organic mixture in L), and $H_2O/SiO_2 = 43$. Then, the reaction mixtures were introduced into a stainless-steel autoclave, heated to 150 °C and kept for a given time until crystallisation was completed. After the autoclave was quenched in cold water, the crystalline products were filtered, washed with water and dried at 110 °C overnight. Then the sample was calcined in a muffle furnace at 540 °C for 3 h. The average particle size of MCM-22 is 100 μm. Lead nitrate, cupric nitrate, sodium hydroxide, and nitric acid were supplied by Ajax Chemicals. All chemicals were used without further purification. HA in sodium form was supplied by Aldrich Chemical Company. HA was dissolved in water and filtrated to remove undissolved matters. Aldrich humic acid has been widely used as a representative humic substance in many investigations. At the beginning, stock solutions of heavy metals and HA were prepared. Then the sample solutions for all adsorption tests were prepared by diluting the stock solution with distilled water to achieve the desired concentrations.

The surface area, total pore volume, and pore size distribution of all samples were determined by N_2 adsorption under −196 °C using Autosorb (Quantachrome Corp.). All samples were degassed at 200 °C for 4 h, prior to the adsorption experiments. The BET surface area was obtained by applying the BET equation to the adsorption data. The micropore volume was obtained by t-plot. The pore size distribution was obtained using the BJH method.

The chemical phases of the samples were determined by X-ray diffraction (XRD) analyses with a Rigaku miniflex diffractometer with Co Kα radiation generated at 30 kV, 15 mA. Scattering patterns were collected from 1.5° to 80° with a scan time of 1 min per two steps.

The pH of samples was measured as follows: 0.1 g of samples were mixed with 10 ml of distilled water and shaken for 24 h at 30 °C. After filtration, the pH of solution was determined by a pH meter (Radiometer PHM250 Ion Analyser).

2.2. Adsorption experiments

The tests of HA and heavy metal adsorption onto the MCM-22 and AC were conducted in batch experiments. In single-adsorbate systems, 200 ml of Cu^{2+}, Pb^{2+}, or HA solution with varying initial concentrations was mixed with the adsorbents at a fixed loading of 250 mg/l in 250 ml bottles. These flasks were then placed in a shaker and shaken for varying time at 30 °C to reach equilibrium. After an appropriate time, some of solution samples were taken out, separated by centrifugation and examined to obtain the concentration of Cu^{2+}, Pb^{2+}, or HA. The concentrations of Cu^{2+} and Pb^{2+} were measured by a flame atomic adsorption spectrometer (AAS, Varian) using air/acetylene flame. The analytical wavelengths of Cu^{2+} and Pb^{2+} are 324.8 and 217 nm, respectively. A SP-8001 UV–vis spectrophotometer (Metertech Inc.) was used for the determination of HA concentration at 254 nm. An expandable ion analyser EA940 (Linbrook Company) was used for all pH measurements and an orbital shaker incubator with temperature control (Thermoline Scientific) was used for adsorption. In most of experiments, two samples were prepared and tested and the average values are reported. The errors are within 10%.

The effect of pH on metal ion and HA adsorption was also investigated in batch mode. The solutions were first prepared by diluting the stock solution using distilled water and the pH was adjusted using 0.1 M HNO_3 or NaOH. After that the adsorbent was added in the solutions. The amount of adsorbents, the concentration of adsorbate and the solutions temperature were fixed at 250 mg/l, 50 mg/l, and 30 °C, while the solution pH was varied in a range of 3–7.

In experiments of the effect of HA concentration for binary-adsorbate system, the solutions were also prepared by diluting the stock solutions of HA and metals with distilled water. The initial copper or lead concentrations and the amount of adsorbents were fixed at 10 and 250 mg/l, respectively. The HA concentration was varied from 10 to 50 mg/l. The solution pH was fixed at 5 by using 0.1 M HNO_3 and NaOH solutions. The analysis of Cu^{2+}, Pb^{2+}, or HA was conducted as described above.

In the effect of metal concentration experiments for binary-adsorbate system, the solutions were prepared similarly as described above. The HA concentration and the amount of adsorbents were fixed at 50 and 250 mg/l, respectively. The Cu^{2+}or Pb^{2+} concentrations were 10–30 mg/l and solution pH was fixed at 5.

3. Results and discussion

3.1. Adsorbent characterisation

Fig. 1 presents the N_2 adsorption isotherm of MCM-22 and activated carbon. The textural properties of the two adsorbents are given in Table 1. From the N_2 adsorption, it is seen that the activated carbon exhibits a typical isotherm of microporous structure. MCM-22 shows a macroporous structure. BET surface

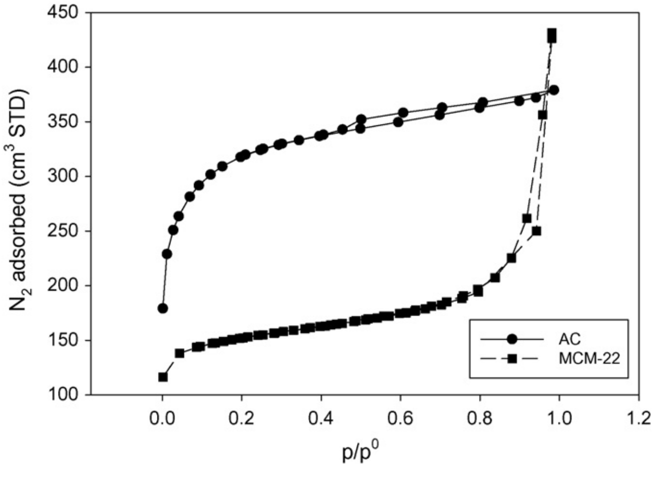

Fig. 1. N_2 adsorption isotherm on MCM-22 and activated carbon.

Table 1
Characteristics of MCM-22 and activated carbon

Adsorbent	S_{BET} (m^2/g)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	pH
MCM-22	490	0.387	0.184	0.203	5.7
AC	972	0.525	0.495	0.030	8.7

areas of the MCM-22 and AC are 490 and 970 m^2/g, respectively. AC has much high microporous volume while MCM-22 exhibits higher mesoporous volume. From Table 1, it is shown that slurry pH of the two solids is different. MCM-22 presents acidic around 6 while AC is basic close to 9, which suggests that the surface charge of MCM-22 is positive but the AC is negatively charged.

The pore size distribution of MCM-22 and AC is presented in Fig. 2. As seen that AC has a sharp peak around 13 Å while MCM-22 presents two strong peaks. One is centred at 37 Å and the other is at 370 Å. This is due to the two pore systems of MCM-22 [15].

3.2. Adsorption of single component

Fig. 3 presents dynamic adsorption of Cu^{2+}, Pb^{2+}, and HA in single-adsorbate system on MCM-22 and AC. As shown, the adsorption of Cu^{2+}, Pb^{2+}, and HA will reach equilibrium after 24 h. The equilibrium adsorption of Cu^{2+}, Pb^{2+}, and HA on two adsorbents follows the same order of $Pb^{2+} > HA > Cu^{2+}$. For heavy metal ions, Cu^{2+} and Pb^{2+}, MCM-22 will exhibit higher adsorption than AC. But for HA, the adsorption on AC and MCM-22 is similar.

The adsorption isotherms of Cu^{2+}, Pb^{2+}, and HA on MCM-22 and AC are illustrated in Fig. 4. These isothermal data are fitted using two models, the Langmuir and Freundlich isotherms, which are listed in Eqs. (1) and (2):

$$\frac{q_e}{Q_m} = \frac{K_L C_e}{1 + K_L C_e} \tag{1}$$

$$q_e = K_F C_e^{1/n} \tag{2}$$

where Q_m and K_L are the Langmuir parameters, indicative of the maximum adsorption capacity (mg/g) and adsorption equilibrium constant (l/g). K_F and n are the Freundlich parameters, showing adsorption capacity and adsorption intensity.

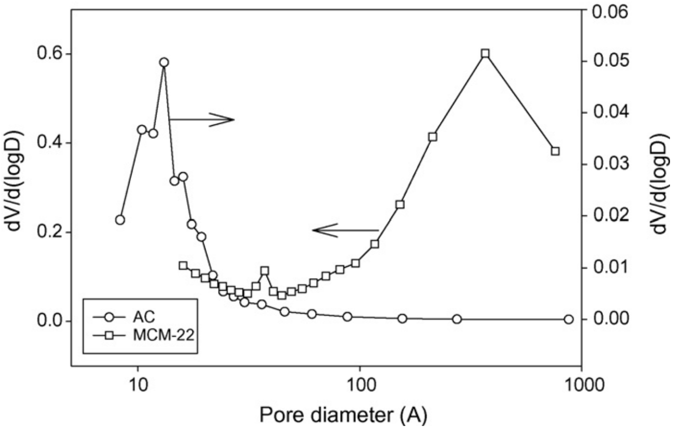

Fig. 2. Pore size distribution of MCM-22 and activated carbon.

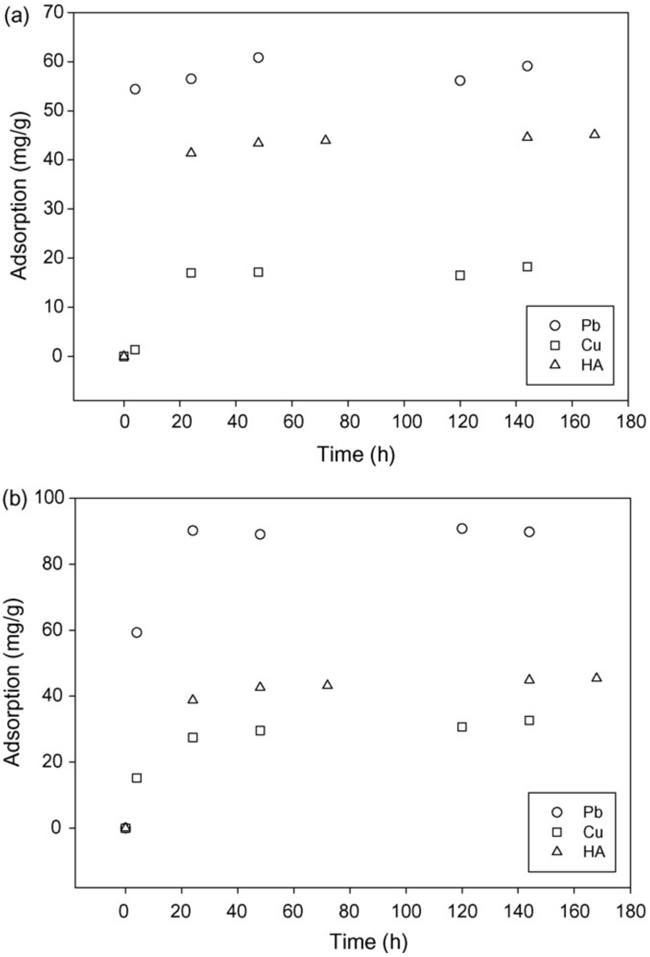

Fig. 3. Dynamic adsorption of Cu^{2+}, Pb^{2+}, and HA on MCM-22 and AC. (a) AC and (b) MCM-22, adsorption conditions: 30 mg/l, pH 5, 30 °C.

Table 2 gives the calculated parameters of the above two isotherms. As seen that the two-adsorption isotherms will describe the experimental data very well and the Freundlich isotherm presents slightly better correlation coefficients. The adsorption capacity presents an order of $Pb^{2+} > HA > Cu^{2+}$ for two adsorbents. The K_L values in the Langmuir isotherm also show the order of $Pb^{2+} > Cu^{2+} > HA$ for two adsorbents, which suggests that the affinity of Pb^{2+} to MCM-22 and AC is the strongest.

Fig. 5 illustrates the effect of solution pH on Cu^{2+}, Pb^{2+}, and HA adsorption on MCM-22 and AC. It is seen that pH has different effects on metal ion and HA adsorption. Cu^{2+} and Pb^{2+} adsorption on MCM-22 and AC will increase with the increasing pH while HA adsorption will decrease as pH is increased. At pH 7, $Cu^{2+}$and Pb^{2+} adsorption shows a significant increase. For heavy metal adsorption, the increased adsorption at higher pH is due to the increase of hydroxyl concentration in solution, which produces surface precipitation of Cu^{2+} and Pb^{2+} on adsorbent. For HA adsorption, many investigation have shown the similar observation as found in this work [4,16–18]. It was reported that the HA from Aldrich has a negative zeta poten-

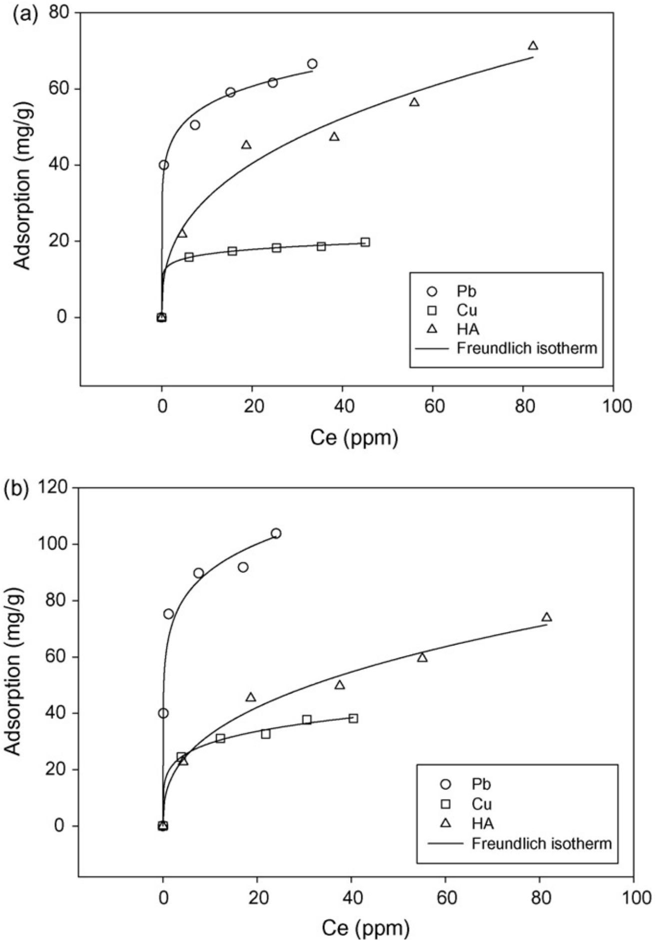

Fig. 4. Adsorption isotherms of Cu^{2+}, Pb^{2+}, and HA on MCM-22 and AC. (a) AC and (b) MCM-22.

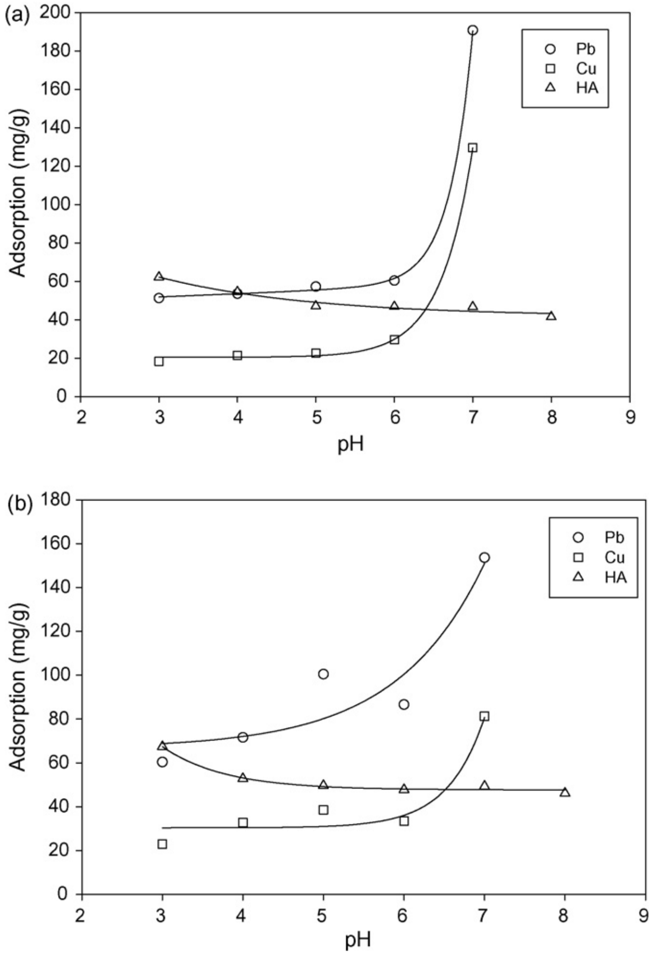

Fig. 5. Effect of pH on Cu^{2+}, Pb^{2+}, and HA adsorption on MCM-22 and AC. (a) AC and (b) MCM-22.

tial at pH > 1.6 and a positive zeta potential at pH < 1.6 [19]. At low pH, the HA macromolecules exist as partly or fully undissociated/protonated forms while MCM-22 and activated carbon present positive charge, which favours the HA adsorption due to the electrostatic abstraction. At high pH, the inter- and intramolecular electrostatic repulsive interactions become more important among the HA macromolecules and the HA becomes less hydrophobic [16]. The surface of MCM-22 and activated carbon also becomes increasingly negatively charged as the pH is increased. Thus, less HA adsorption is observed.

The effect of temperature on HA adsorption on MCM-22 and activated carbon was also investigated. Fig. 6 demonstrates the results. As shown, temperature has a remarkable influence on HA adsorption on MCM-22 while little changes can be observed on AC. HA adsorption decreases with increasing temperature on MCM-22, suggesting the exothermal nature of the adsorption.

3.3. Adsorption in binary-adsorbate system

The dynamic adsorption of heavy metal ions and HA on AC in single and binary systems is compared in Fig. 7. One can see, Cu^{2+}, Pb^{2+}, and HA adsorption in binary systems will take a longer time (around 72 h) to reach equilibrium. For Cu–HA/AC,

Table 2
Isothermal parameters of Cu^{2+}, Pb^{2+}, and HA adsorption on MCM-22 and AC

Adsorbent	Adsorbate	Langmuir isotherm			Freundlich isotherm		
		Q_m (mg/g)	K_L (l/g)	R^2	K_F	$1/n$	R^2
AC	Cu^{2+}	12.2	1.61	0.9965	13.0	0.105	0.9992
	Pb^{2+}	60.8	3.59	0.9638	41.9	0.124	0.9944
	HA	74.4	0.0736	0.9573	13.3	0.371	0.9790
MCM-22	Cu^{2+}	32.3	0.384	0.9879	18.8	0.193	0.9960
	Pb^{2+}	94.4	6.30	0.9756	65.1	0.143	0.9753
	HA	78.4	0.0705	0.9628	13.7	0.376	0.9877

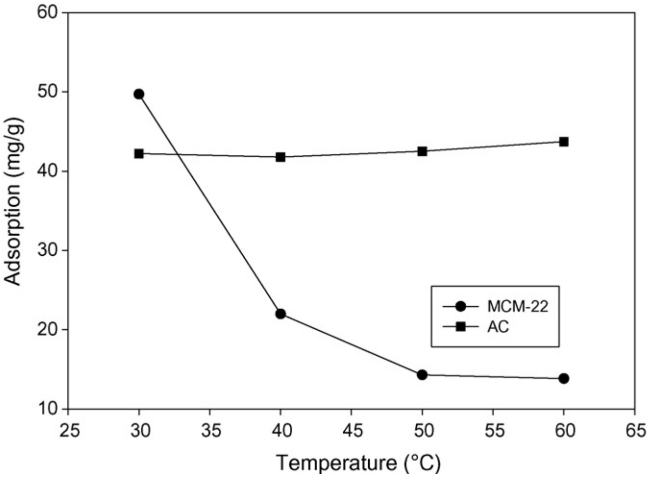

Fig. 6. Effect of temperature on HA adsorption on MCM-22 and AC.

Cu^{2+} adsorption is increased at the presence of humic acid while HA adsorption is decreased. For Pb–HA/AC, Pb^{2+} and HA adsorptions are all decreased compared with the single system.

Fig. 8 presents the dynamic adsorption of heavy metal ions and HA on MCM-22 in single and binary systems. For Cu–HA/MCM-22, Cu^{2+} and HA adsorption is decreased, unlike the case in Cu–HA/AC system. For Pb–HA/MCM-22, Pb^{2+} and HA adsorption is also decreased compared with single-adsorbate system.

The effects of Cu^{2+} and Pb^{2+} initial concentration in binary-adsorbate system on HA adsorption on MCM-22 and AC are presented in Fig. 9. One can see that HA adsorption decreases with the increasing metal initial concentration. Reduction in

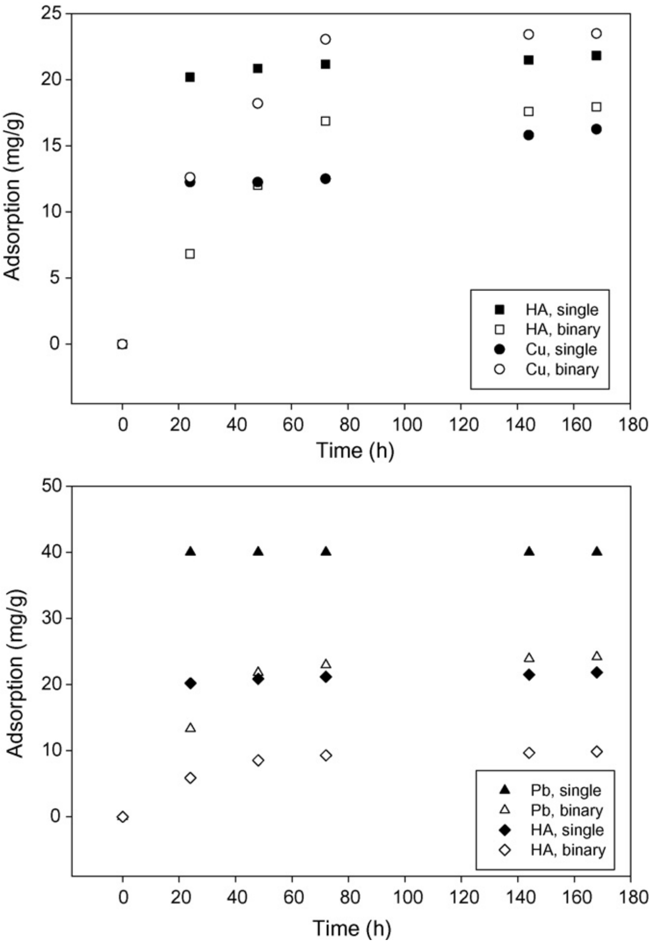

Fig. 7. Dynamic adsorption of heavy metals and HA on AC in single and binary component systems: [Pb^{2+}], [Cu^{2+}] = 30 mg/l, [HA] = 50 mg/l, pH 5, 30 °C.

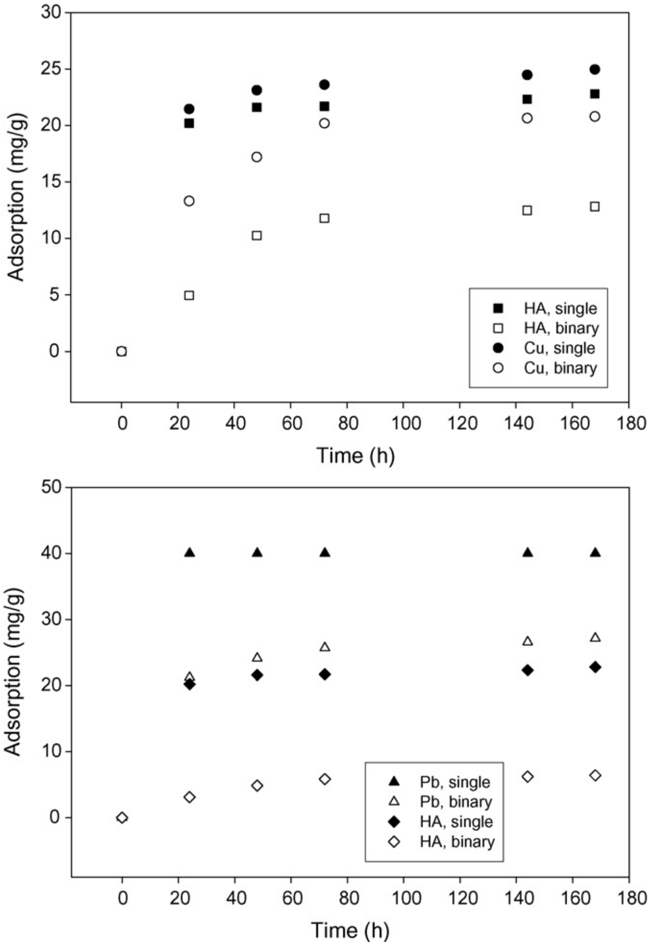

Fig. 8. Dynamic adsorption of heavy metals and HA on AC in single and binary component systems.

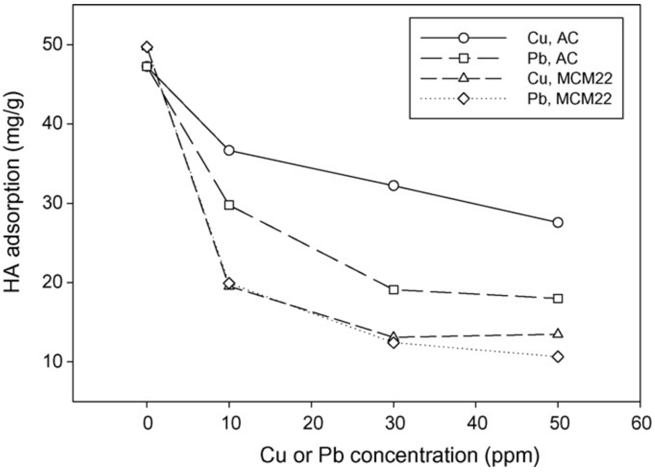

Fig. 9. Effect of heavy metals on HA adsorption on MCM-22 and AC.

HA adsorption is greater on MCM-22 than on AC. For AC, the presence of Pb^{2+} ion produces stronger effect than Cu^{2+} ion on HA adsorption. At 50 ppm Pb^{2+} or Cu^{2+}, HA adsorption reduces from 47 mg/g to 28 and 18 mg/g, respectively. For MCM-22, the presence of Pb^{2+} and Cu^{2+} ions shows similar effect and the HA adsorption shows a slight lower value at the presence of Pb^{2+} ion. At 50 ppm Pb^{2+} or Cu^{2+}, HA adsorption decreases from 50 mg/g to 10 and 13 mg/g, respectively.

In the past, few investigations have been reported on the effect of heavy metals on HA adsorption on adsorbents. Ferro-Garcia et al. [20] studied the adsorption of different compounds such as gallic (GA), tannic (TA), and humic acids on an activated carbon in the presence of Cr^{3+}. The capacity of the carbon to adsorb GA and TA in the presence of Cr^{3+} is slightly higher than that in the absence of this metal. Liu and Gonzalez [21] investigated the metal adsorption/desorption in a system consisting of humic acid, metal ions, and clay minerals and found that humic acid adsorption decreased with increasing ionic strength. A slight increase in humic acid adsorption on montmorillonite was observed when there were bivalent metals (Pb^{2+}, Cu^{2+}, and Cd^{2+}) present in the system.

In this investigation, it has been found that humic acid adsorption will be decreased in the presence of heavy metal ions (Pb^{2+} and Cu^{2+}). This suggests that the active sites for metal ions and HA are similar and that the competitive adsorption between metal ions and HA makes the HA adsorption reduced.

Fig. 10 shows the effect of presence of HA on heavy metal adsorption on MCM-22 and AC. As shown, Cu^{2+} adsorption is increased when HA concentration is increased in Cu–HA/AC system. Pb^{2+} adsorption is decreased at the presence of HA but the adsorption is almost the same at HA concentration between 10 and 30 ppm. When HA concentration is increased to 50 ppm, Pb^{2+} adsorption shows slightly increased. For Cu–HA/MCM-22 system, Cu^{2+} adsorption exhibits a decrease with increasing HA concentration. For Pb–HA/MCM-22, Pb^{2+} adsorption decreases at lower HA concentration and then shows a slight increase at HA concentration of 50 ppm, which is similar to the case of Pb–HA/AC.

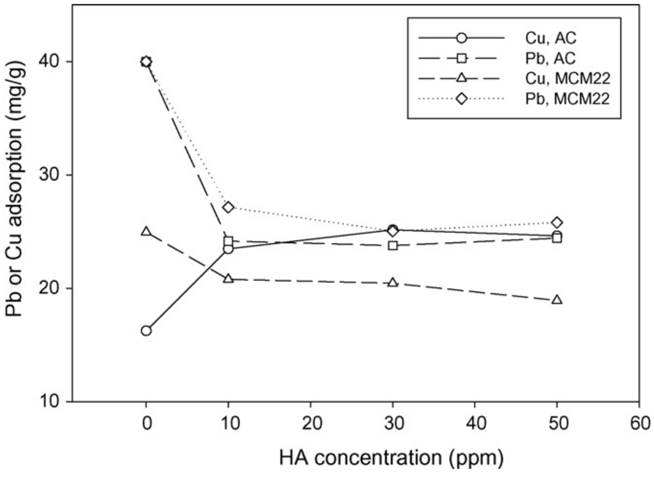

Fig. 10. Effect of HA on heavy metals adsorption on MCM-22 and AC.

The effect of HA on metal ion adsorption could mainly be explained by the reaction occurring at the surface of the adsorbent. The adsorption of HA on the surfaces of adsorbents may affect heavy metal adsorption throughout the following mechanisms: (1) HA binds to the same sites on adsorbent surface as heavy metal ions; (2) HA attaches to an adsorbent surface through a mechanism different from metal ions, and the total sites available for subsequent heavy metal adsorption remain the same, but a layer of HA adsorbed on the surface of an adsorbent may produce a barrier for heavy metals to connect to the available adsorption sites [22]. In the meantime time, adsorption of HA on adsorbent causes an increase in the surface negative charges, which may favour the heavy metal adsorption.

Bautista-Toledo et al. [23] studied the adsorption process of Cr^{3+} ions on activated carbons in the presence of humic acid in solutions and found that the Cr^{3+} uptake decreases mainly when humic acid is in low concentrations, which was due to a blockage effect of the adsorbed humic acid on the surface of the carbon. Chen and Wu [16] investigated simultaneous adsorption of copper ions and humic acid from Aldrich onto an activated carbon. They found that there exists a critical concentration (CC) of HA for copper adsorption. At HA concentrations < CC, a decrease in copper adsorption is observed: however, the HA improves the adsorption at HA concentrations > CC. Petrovic et al. [24] investigated the sorption of metal ions (Pb^{2+}, Zn^{2+}, and Cu^{2+}) and soil humic acids (HA) from aqueous solutions onto mineral particles (sand, calcite, and clay). Results showed that the presence of humic acids, dissolved or bound onto mineral surfaces, considerably influenced the fixation of heavy metals in three-component system and the effect was dependent on mineral type, humic concentration and specific metal-ion. Sorption of Cu^{2+} ions on all minerals studied rapidly increased as the concentration of dissolved HA increased. The amount of Pb^{2+} ions sorbed on sand slightly decreased. Sorption of Zn^{2+} ions on all minerals studied decreased at pH 4.

In this investigation, it is seen that Cu^{2+} adsorption is increased on AC at the presence of HA while Pb^{2+} adsorption is decreased in the presence of HA at lower concentration. These results suggest that Cu^{2+} and Pb^{2+} adsorption on activated carbon is different. In single component system, it has been shown that the adsorption of Cu^{2+}, Pb^{2+} and HA follows the order of $Pb^{2+} > HA > Cu^{2+}$. Thus, in Cu–HA/AC system, HA would be favourable to be adsorbed on the carbon surface and produces more organic functional groups in the HA–carbon surface, which causes an enhancement in the copper adsorption. On the contrary, in Pb–HA/AC system, relative similar adsorption of Pb^{2+} and HA onto carbon surface produces a blockage of some active sites by HA, resulting in the decrease of Pb^{2+} adsorption. At higher HA concentration, complexation of Pb^{2+} with HA then increases the adsorption of Pb^{2+} on activated carbon. This is similar to the above reports. For metal–HA/MCM-22 system, the decrease in Pb^{2+} and Cu^{2+} adsorption was due to the blockage of HA. At higher HA concentration, complexation of Pb with HA makes a slight increase in Pb^{2+} adsorption.

Fig. 11 presents the adsorption isotherms of Pb^{2+}, Cu^{2+}, and HA adsorption in metal–HA/AC system. As shown, adsorption of Pb^{2+} and Cu^{2+} increases with increasing Pb^{2+} and Cu^{2+} equi-

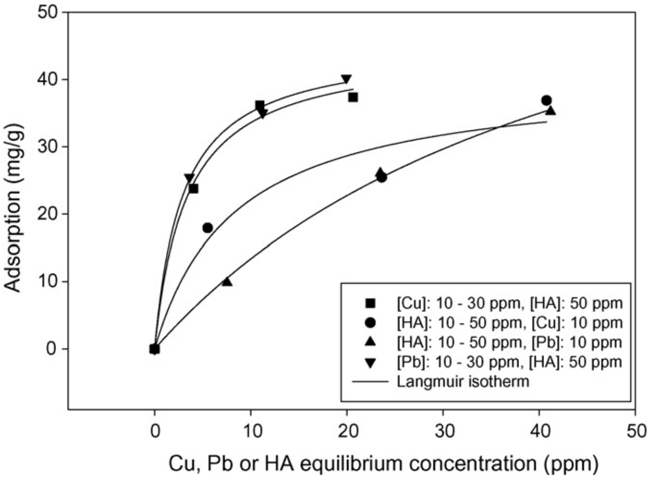

Fig. 11. Adsorption isotherms of heavy metals and HA on AC in binary component system.

librium concentration in the presence of HA. The amount of adsorption of Pb^{2+} and Cu^{2+} is similar. At equilibrium concentration of 20 ppm, Pb^{2+} and Cu^{2+} adsorption will reach about 40 mg/g. HA adsorption is also increased with increasing HA equilibrium concentration at the presence of Pb^{2+} or Cu^{2+}. The amount of adsorption of HA is lower than heavy metals.

For metal–HA/MCM-22 system, the adsorption isotherm of Pb^{2+}, Cu^{2+}, and HA adsorption is illustrated in Fig. 12. Pb^{2+} adsorption is higher than Cu^{2+} at the presence of HA and Cu^{2+} adsorption approaches equilibrium at 20 ppm with the adsorption around 39 mg/g. HA adsorption is slightly higher at the presence of Cu^{2+} than that at the presence of Pb^{2+}, but lower than metal ion adsorption, which is similar to the case of metal–HA/AC system.

The Langmuir isotherm was employed to fit the adsorption data and the results are presented in Table 3. As seen, the Langmuir isotherm fits the experimental data well with higher regression coefficients. For AC or MCM-22, Cu shows much improved adsorption capacity compared with that in single-adsorbate system while HA exhibits decreased adsorption capacity. In the binary-adsorbate system, Pb^{2+} and Cu^{2+} exhibit higher adsorption constant than HA.

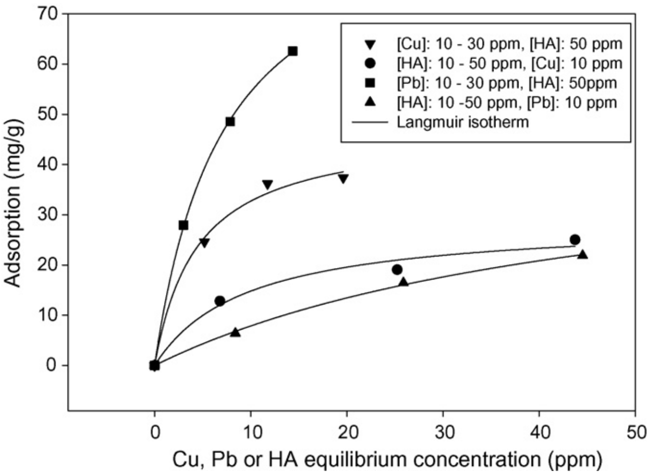

Fig. 12. Adsorption isotherms of heavy metals and HA on MCM-22 in binary component system.

Table 3
The parameters of the Langmuir isotherm in binary-adsorbate systems

Adsorbent	Adsorbate	Langmuir isotherm		
		Q_m (mg/g)	K_L (L/g)	R^2
AC	Cu in Cu–HA	44.8	0.301	0.9940
	HA in Cu–HA	40.6	0.120	0.9528
	Pb in Pb–HA	45.4	0.343	0.9984
	HA in Pb–HA	75.6	0.0214	0.9986
MCM-22	Cu in Cu–HA	47.3	0.225	0.9938
	HA in Cu–HA	28.9	0.105	0.9825
	Pb in Pb–HA	93.5	0.140	0.9999
	HA in Pb–HA	46.3	0.0205	0.9988

4. Conclusion

Cu^{2+}, Pb^{2+}, and HA in aqueous solution shows different affinity to solid surface with an order of $Pb^{2+} > Cu^{2+} >$ HA. MCM-22 and AC are effective adsorbents for removal of Cu^{2+}, Pb^{2+}, and HA from aqueous solution in both single-component and binary-component systems. MCM-22 exhibits much higher adsorption of Cu^{2+}, Pb^{2+} than AC due to higher ion exchange capacity. MCM-22 also exhibit similar HA adsorption as AC. For single component system, higher solution pH will increase metal adsorption due to surface precipitation while HA adsorption on MCM-22 and AC is reduced ascribed to electrostatic repulsive interaction between adsorbent surface charge and HA. In the binary-adsorbate systems (Cu^{2+}–HA, Pb^{2+}–HA), competitive adsorption will occur on MCM-22, resulting in lower adsorption of both heavy metal and HA. For AC, complexation of Cu^{2+} and HA will increase Cu^{2+} adsorption but competitive adsorption between Pb^{2+} and HA results in the decrease in Pb^{2+} and HA adsorption on AC.

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