Kinetics of Cd²⁺ and Cr³⁺ Sorption from Aqueous Solutions Using Mercaptoacetic Acid Modified and Unmodified Oil Palm Fruit Fibre(*Elaeis guineensis*) Adsorbents

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Abstract: The kinetics of the sorption of Cd²⁺ and Cr³⁺ from aqueous solutions by mercaptoacetic acid modified and unmodified oil palm fruit fibre adsorbents were investigated. The results indicate that sorption equilibrium was reached within 60 min for both metals. Also, the removal efficiency of the three adsorbents was observed to increase for both metals with stronger treatments with mercaptoacetic acid. This may be attributed to the influence of the thiolation of the adsorbents. Furthermore, Cr³⁺ had higher removal percentages than Cd²⁺ for all the adsorbents. The sorption mechanism based on the intraparticle diffusion model shows that Cd²⁺ sorption is better described than Cr³⁺. The intraparticle diffusion rate constants, K_{id}, for Cd²⁺ are 62.04 min⁻¹ (untreated), 67.01 min⁻¹ (treated with 0.5 mol/L mercaptoacetic acid), and 71.43 min⁻¹ (treated with 1.0 mol/L mercaptocacetic acid) while those for Cr³⁺ are 63.41 min⁻¹ (untreated), 65.79 min⁻¹ (0.5 mol/L acid treated), and 66.25 min⁻¹ (1.0 mol/L acid treated).

Key words: kinetics; adsorbent; agricultural by-products; oil palm fruit fibre; heavy metals

Introduction

Heavy metal pollution poses serious problems in the environment. Cadmium, which is a widely used metal and extremely toxic in relatively low concentrations, is one of the heavy metals responsible for causing kidney damage, renal disorder, high blood pressure, bone fragility, and destruction of red blood cells[1]. Trivalent chromium interferes with essential body metabolism, acts as a gastric irritant and causes skin ulcers, bronchitis, and dermatitis[2]. The main anthropogenic pathway through which Cd²⁺ and Cr³⁺ enter water bodies is via wastes and run off from industrial processes such as electroplating, plastic manufacturing, metallurgical processes, pigment production, and Cd/Ni battery production[3].

Due to the toxicity and bioaccumulation of these metals, different treatment techniques have been developed to remove both dissolved and suspended heavy metal ions from industrial and municipal wastewater. Conventional treatment techniques for heavy metal removal include precipitation or neutralization, ultra-filtration, electrode-position, solvent extraction, cementation, and evaporation[4].

However, the high cost of these methods and the disposal problems associated with them have limited the process applications and put them out of reach of small industries.

In recent years, considerable attention has been devoted to develop unconventional materials like agricultural by-products for the removal of heavy metals from wastewater. Since these plant-based by-products represent unused resources, they are widely available and environmentally friendly[5].

Thus, in the quest to explore the effectiveness of agricultural by-products as adsorbents, several plant

based materials have been used to treat heavy metals in aqueous solutions and wastewater. The removal of lead and copper ions from aqueous solutions by sago waste was reported by Quek et al.[6] Also a range of other agricultural by-products used for metal removal include banana pith[7], tree fern[8], and hop (*Humulus lumpus*)[9].

In addition, studies have also shown that chemical modification of agricultural by-products significantly enhances their ion-binding properties, thereby providing greater flexibility in their applications to a wide range of heavy metal ions[10]. In this direction, the sorption of cadmium and lead ions on chemically modified groundnut (*Arachis hypogea*) husks has been reported[11]. Similarly, Cd^{2+}, Cu^{2+}, and Zn^{2+} have been removed from aqueous solutions by the use of chemically modified and unmodified cassava waste[12]. Copper ions have also been removed from aqueous solutions using dye-treated oil palm fibres[13].

However, only a limited number of studies have so far been focused on the use of oil palm fruit fibres for the removal of heavy metal ions from aqueous solutions. The purpose of this work is to investigate the removal of cadmium (II) and chromium (III) from aqueous solutions using unmodified and mercaptoacetic acid modified oil palm (*Elaeis guineensis*) fruit fibres with a focus on the sorption kinetics of both metals.

1   Materials and Methods

All the reagents used for the study were of analytical reagent grade. Distilled deionized water was used for the preparation of all sample solutions. 1000 mg/L stock solutions of cadmium (II) from $CdCl_2 \cdot 2.5H_2O$ and chromium (III) from $Cr(NO_3)_3 \cdot 9H_2O$ were prepared. 50 mg/L working solutions of the two metals were prepared from the stock solutions by serial dilution with distilled-deionized water.

1.1   Adsorbent preparation

The oil palm fruit fibre waste was obtained from an oil palm mill in a village near Uyo, Akwa Ibom State, Nigeria. The oil palm fibre was deoiled by soaking in hot deionized water with detergent for 24 h. It was then rinsed in hot deionized water to remove all debris and air dried. The air dried oil palm fruit fibre was ground using an electric blender (National). The fibre was screened through a set of sieves (250 μm, 150 μm, and 106 μm). The fibre that passed through the 106 μm sieve was then used for the sorption studies.

1.2   Activation of adsorbent

The screened fine adsorbent was further soaked in excess 0.3 mol/L HNO_3 for 24 h. The adsorbent was then filtered through Whatman No.41 filter paper and rinsed with deionized water. The rinsed adsorbent was later air dried for 12 h. The treatment of the adsorbent with 0.3 mol/L HNO_3 aids the removal of any debris or soluble biomolecules that might interact with the metal ions during the sorption. This process is called chemical activation of the oil palm fruit fibre.

1.3   Chemical modification of the absorbent

The air dried activated oil palm fruit fibre was weighed and divided into 3 parts. 100 g of the first part labeled "1" was left untreated and was labeled the "unmodified oil palm fruit fibre (UOPF). 100 g of the second part labeled "2" was acid treated by dissolving it in excess 0.5 mol/L mercaptoacetic acid ($HSCH_2COOH$) solution. The suspension was stirred for 30 min and left to stand for 24 h at 28℃ and was labeled "0.5 mol/L modified oil palm fruit fibre (0.5 MOPF)". 100 g of the third part labeled "3" was also acid treated by dissolving it in excess 1.0 mol/L mercaptoacetic acid solution. The resulting suspension was stirred for 30 min and left to stand for 24 h at 28℃ and was labeled the "1.0 mol/L modified oil palm fruit fibre (1.0 MOPF)".

After 24 h, the mixtures labeled 0.5 MOPF and 1.0 MOPF were filtered using Whatman No. 41 filter paper. The residue in each filter paper was then soaked in 1.0 mol/L hydroxylamine (NH_2OH) for 1 h. They were then filtered again using Whatman No. 41 filter paper and rinsed with deionized water. The washed residue of the 0.5 MOPF and 1.0 MOPF samples were then air-dried. The three working adsorbents were then stored in airtight plastic containers.

1.4   Adsorbent characterization

The three adsorbents, UOPF, 0.5 MOPF, and 1.0 MOPF, were characterized based on the following surface properties: percentage of thiol content (SH), specific surface area (S_{AA}), and pH point of zero charge (pH_{pzc}).

1.4.1 Determination of thiol percentage

The extent to which the mercaptoacetic acid incorporated the thiol (SH) group into the 0.5 MOPF and 1.0 MOPF adsorbents was determined by the method described by Okieimen et al.[14] 0.5 g of 0.5 MOPF and 1.0 MOPF adsorbents were weighed into two 250-cm³ Erlenmeyer flasks. 20 cm³ of 0.5 mol/L iodine solution was added to each flask at pH 7.2. The flasks were agitated on a shaker (EFLI-mk-3 model) for 10 min and then allowed to settle. The unreacted iodine was back titrated with 0.1 mol/L sodium thiosulphate until the color of the solution turned yellow. Then 2 cm³ of starch solution was added and the solution turned blue. The titration with sodium thiosulphate was continued until the solution finally became colourless indicating the end point. The titre values were recorded and used to calculate the thiolation percentage.

1.4.2 Determination of specific surface area

The specific surface area of the three adsorbents (UOPF, 0.5 MOPF, and 1.0 MOPF) were determined using the methylene blue absorption test (MBT) method described by Santamarina et al.[15] 2.0 g of each adsorbent was dissolved in 200 cm³ of deionized water. 10 ppm of methylene blue solution was added to the adsorbent suspension which was then agitated in a shaker for 2 h. The solution was kept for 24 h to reach equilibrium. A 10-cm³ aliquot was then taken and centrifuged using a Sigma 301-centrifuge. The centrifuged aliquot was then analyzed in a UNICAM-8700 UV/visible spectrophotometer to determine the amount of methylene blue absorbed.

Thereafter, 20 ppm, 30 ppm, 40 ppm, 50 ppm, 60 ppm, and 70 ppm solutions of methylene blue were then added sequentially and the previous steps repeated. For the 1.0 MOPF adsorbent, 80 ppm solution of methylene blue was also used. A graph of the concentration of methylene blue added versus the amount of absorbed methylene blue was used to identify the point of complete cation replacement. The specific surface area was calculated from the amount of absorbed methylene blue at the optimum point as

$$\text{Specific surface area} = \frac{m_{MB} A_v A_{MB}}{319.89} \times \frac{1}{M_s} \quad (1)$$

where m_{MB} is the amount of methylene blue absorbed at the point of complete cation replacement; M_s is the mass of the adsorbents; A_v is Avogadro's number, 6.02×10^{23}; A_{MB} is the area covered by one methylene blue molecule (typically assumed to be 13 nm).

1.4.3 Determination of pH$_{pzc}$

The pH point of zero charge (pH$_{pzc}$) of each of the adsorbents (UOPF, 0.5 MOPF, and 1.0 MOPF) was determined as described in Onyango et al.[16] 50 cm³ of 0.01 mol/L NaCl solution was measured into different closed Erlenmeyer flasks. The pH of each solution in each flask was adjusted to values of 2, 4, 6, 8, 10, and 12 by adding 0.1 mol/L HCl or 0.1 mol/L NaOH solutions. Then 0.5 g of each adsorbent was added and agitated in a shaker for 1 h and then allowed to settle for 48 h to reach equilibrium at 28℃. The zeta potential (mV) of each solution was then determined for all the adsorbents. A graph of zeta potential (mV) versus initial pH was used to determine the pH$_{pzc}$ of each adsorbent.

2 Kinetics of Metal Sorption

The kinetics of Cd²⁺ and Cr³⁺ sorption were studied for each of the three adsorbents (UOPF, 0.5 MOPF, and 1.0 MOPF) at 28℃ and an initial metal concentration of 50 mg/L. The pH and ionic strength of the solutions were adjusted to 6.2 and 0.01 mol/L NaCl, respectively. 100 cm³ of each metal solution was transferred into different 250-cm³ Erlenmeyer flasks, corked and labeled accordingly. 0.5 g of each adsorbent (UOPF, 0.5 MOPF, and 1.0 MOPF) was weighed into the appropriate flask and agitated in a shaker for various contact times (10, 15, 20, 30, 45, 60, 90, and 120 min).

The content of each flask was then filtered using Whatman No. 41 filter paper after the agitation. The residual concentration of each metal was then analyzed using 20 cm³ of the filtrate using a UNICAM 919 solar atomic absorption spectrophotometer.

2.1 Data analysis

The amount of each metal adsorbed (a_t) in mg/L at time t was computed as

$$a_t = C_0 - C_t \quad (2)$$

where C_0 is the initial metal ion concentration (mg $\cdot$ L⁻¹), and C_t is the metal ion concentration at time t (mg $\cdot$ L⁻¹).

The metal removal percentage was then computed as

$$R_{EM} = \frac{C_0 - C_t}{C_0} \times 100\% \quad (3)$$

2.2 Sorption dynamics

The metal ion sorption kinetics on the various adsorbents were analyzed using the intraparticle diffusion model[17-19] as

$$R = K_{id}(t)^a \tag{4}$$

Equation (4) can be written in a linearized form as

$$\log R = \log K_{id} + a \log t \tag{5}$$

where R is the percent of metal adsorbed, t is the contact time, a is the slope on a logarithmic plot which depicts the adsorption mechanism, and K_{id} is the intraparticle diffusion rate constant.

If the sorption can be represented by the model, a plot of $\log R$ vs. $\log t$ should yield a linear relationship with a slope a, and an intercept $\log K_{id}$.

3 Results and Discussion

3.1 Adsorbent characterization

The three adsorbents used for the sorption studies, UOPF, 0.5 MOPF, and 1.0 MOPF, were characterized using the surface properties: SH, pH_{pzc}, and S_{AA}.

The results obtained from the surface characterization of the three adsorbents are presented in Table 1.

Table 1   Adsorbent characteristics

	$S_{AA}/(m^2 \cdot g^{-1})$	SH/%	pH_{pzc}
UOPF	248.42	—	7.1
0.5 MOPF	289.83	1.35	6.4
1.0 MOPF	331.23	2.83	6.0

3.1.1   Extent of thiolation of adsorbents

The SH on the chemically modified adsorbents indicates the efficiency of the thiolation process, which is the degree to which the adsorbent were modified with mercapotacetic acid [$CH_2(SH)COOH$] by the introduction of the thiol (SH) group into the adsorbent matrix.

The major functional group on the oil palm fibres is the polar hydroxyl group, with carboxylic and phenolic groups presented in Low et al.[13] These functional groups are possible sites for metal sorption. Thus, chemical modification of the adsorbents with mercaptoacetic acid altered the chemical properties of the adsorbent. The process exchanges the hydroxyl group to the sulphydryl group from the acid. The exchange mechanism as proposed by Horsfall et al.[20] is

$$B\text{-}CH_2OH + HSCH_2COOH \xrightarrow{\ H^+\ }$$
$$B\text{-}CH_2SHCH_2COOH + H_2O \tag{5}$$
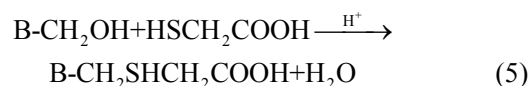
Hence, the chemical modification of the adsorbents incorporates a sulphydryl group into the adsorbent surface in addition to the other functional groups, thereby increasing the number of metal binding sites on the chemically modified adsorbents. The results in Table 1 show that the increase in the concentration of the chemically modifying acid from 0.5 mol/L to 1.0 mol/L increased the thiol percentage incorporated onto the adsorbent from 1.35% to 2.83%. It has been reported by Abia et al.[12] that the incorporation of thiol groups on an adsorbent surface enhances the binding ability of the sorbent by increasing the number of binding sites.

3.1.2   Specific surface area of adsorbent

S_{AA} of an adsorbent is the ratio of its surface area to its mass[15]. The results in Table 1 show that the S_{AA} of the adsorbents was increased by the chemical modification. Also, the increased acid concentration had a significant effect, increasing S_{AA} from 289.83 m^2/g for 0.5 MOPF to 331.23 m^2/g for 1.0 MOPF. The increased adsorbent surface area tends to increase the adsorbent removal efficiency[21].

3.1.3 pH_{pzc} of adsorbents

The pH_{pzc} is the pH of the adsorbent suspension at which the surface acidic (or basic) functional groups of an adsorbent no longer contribute to the pH of the suspension[22]. The plot of the initial pH against the zeta potential shown in Fig. 1 was used to determine pH_{pzc} for each adsorbent. The plot shows that each adsorbent (UOPF, 0.5 MOPF, and 1.0 MOPF) was positively charged over the pH range of 2-5. The pH_{pzc} of 1.0 MOPF was found to be 6.0, that of 0.5 MOPF was 6.4 and that of UOPF was 7.1.
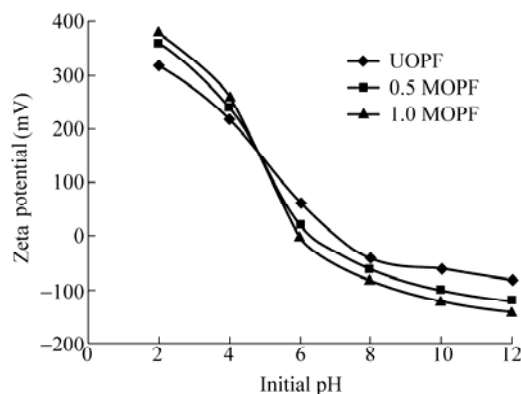

Fig. 1 pH_{pzc} of the three oil palm adsorbents

At pH values above the pH$_{pzc}$ for each adsorbent, the surface possesses a negative charge. Below that pH, the surface has a positive charge. The surface acidity of the 0.5 MOPF and 1.0 MOPF solutions leads to a reduction in the pH$_{pzc}$ due to the introduction of the thiol (SH) functional group onto the adsorbent surface. A similar result was obtained for the pH$_{pzc}$ of sulphurised carbon[23].

3.2 Adsorption dynamics

Studies on the kinetics of metal sorption by various adsorbents are important for designing an adsorption system. The rate at which sorption occurs is very important when designing batch sorption systems. The time dependency of such systems must also be established for accurate process designs[8].

The required contact time for the sorption process to be completed gives insight into the sorption process. This also provides information on the minimum time required for significant adsorption to take place and on the possible diffusion control mechanism between the metal ion as it moves towards the adsorption surface.

Modeling kinetic data is fundamental for industrial applications of sorption processes since such data enables comparisons among different biomaterials for different operational conditions to design and optimize operating procedures[24]. The percentages of Cd^{2+} and Cr^{3+} adsorbed as a function of contact time are shown in Figs. 2 and 3. The results indicate that the sorption reached equilibrium within 60 min for both metals.

Figures 4-6 show the percentages of metals removed by the three adsorbents, UOPF, 0.5 MOPF, and 1.0 MOPF. The results in Figs. 4-6 show that the removal percentages for each metal increased according to the trend UOPF < 0.5 MOPF < 1.0 MOPF.

Hence, the chemically modified adsorbents had increased metal removal percentages due to the increased sorption sites. This is consistent with the results of previous studies[11, 12, 25].

Furthermore, Cr^{3+} had a higher removal percentage than Cd^{2+} for all three adsorbents. This trend can be explained by considering that Cr^{3+} has an ionic radius of 0.069 nm while that of Cd^{2+} is 0.097 nm. Since Cr^{3+} has a smaller ionic radius, it tends to diffuse to the potential adsorption sites easier than Cd^{2+}. In addition,
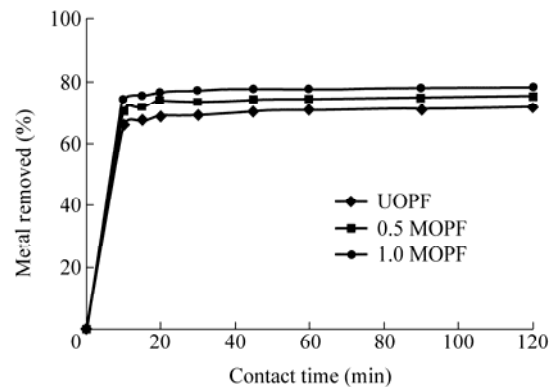

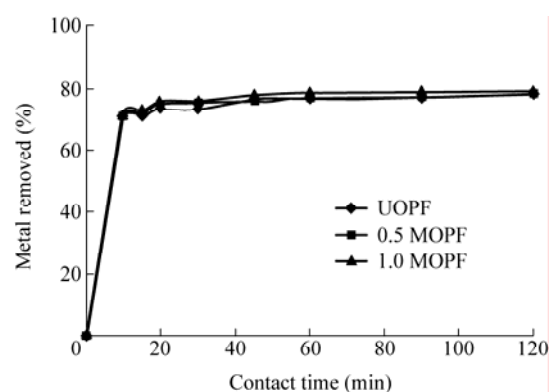Fig. 2   Metal removed over time for Cd^{2+}

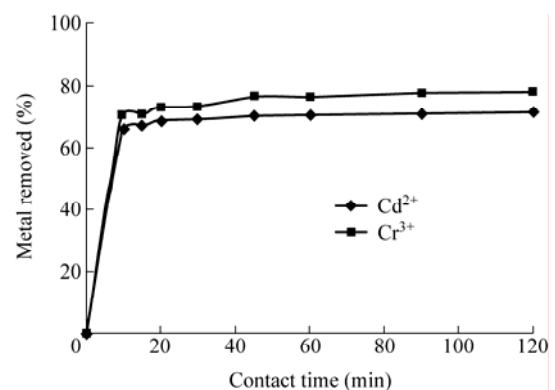Fig. 3   Metal removed over time for Cr^{3+}

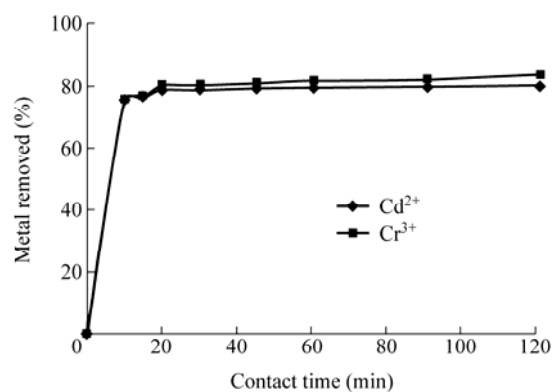Fig. 4   Metal removal percentages for UOPF

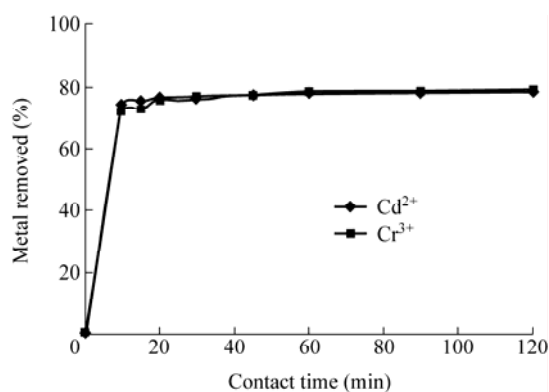Fig. 5   Metal removal percentages for 0.5 MOPF

Fig. 6 Metal removal percentages for 1.0 MOPF

Atkinson et al.[26] reported that when there are interactions between various metal ions and an adsorbent, ions with smaller ionic radii and higher ionic charge are more strongly attracted to the adsorbent sites. Chromium has a charge of +3 while cadmium is of +2; hence, a larger percentage of chromium is removed.

The kinetic transport mechanism for the sorption of Cd^{2+} and Cr^{3+} on the three adsorbents was based on the intraparticle diffusion model[17,18]. Kinetic results based on the intraparticle diffusion model for Cd^{2+} are illustrated in Fig. 7, while those of Cr^{3+} are shown in Fig. 8.
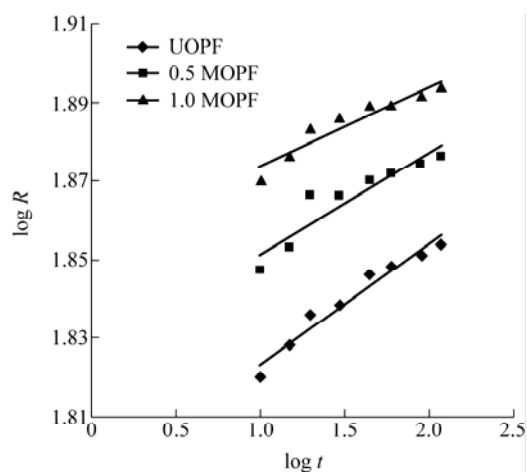

Fig. 7 Intraparticle diffusion kinetic model results for Cd^{2+}
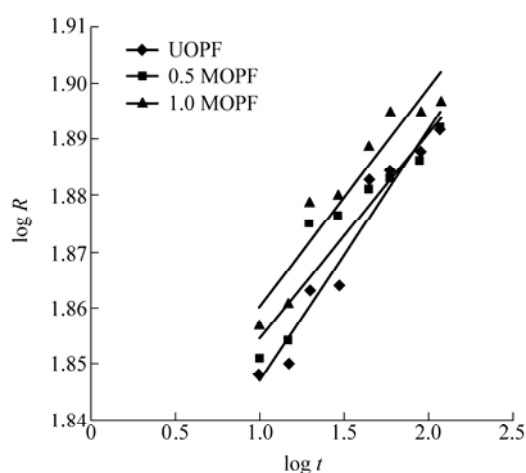

Fig. 8 Intraparticel diffusion kinetic model results for Cr^{3+}

Table 2 presents the kinetic rate constants and parameters based on the intraparticle diffusion model. The intraparticle diffusion rate constant (K_{id}) was increased by the chemical modification with K_{id} of 62.044 min^{-1} for UOPF, 67.019 min^{-1} for 0.5 MOPF, and 71.433 min^{-1} for 1.0 MOPF for Cd^{2+}. The results for Cr^{3+} were similar.

However, analysis of the determination coefficient (r^2) for the sorption of the two metals by the three adsorbents indicates that the Cd^{2+} sorption is better described by the intraparticle diffusion model than the Cr^{3+} sorption.

Thus, for sorption of cadmium onto the three adsorbents, the cadmium ions are transported from the liquid phase to the solid phase by diffusion and the intraparticle transport is the rate controlling step.

However, the deviation of the lines for the two metals from the origin indicates that the intraparticle transport may not be the only mechanism that determines the metal ion transport onto the adsorbent[21]. The metal ion transport mechanism onto an adsorbent surface proposed by Hadjar et al.[27] includes the following steps.

Table 2 K_{id}, a, and r^2 for Cd^{2+} and Cr^{3+} on UOPF, 0.5 MOPF, and 1.0 MOPF

Adsorbent	K_{id}/min^{-1}		a		r^2	
	Cd^{2+}	Cr^{3+}	Cd^{2+}	Cr^{3+}	Cd^{2+}	Cr^{3+}
UOPF	62.044	63.416	0.030	0.044	0.960	0.948
0.5 MOPF	67.019	65.796	0.025	0.036	0.920	0.877
1.0 MOPF	71.433	66.252	0.019	0.039	0.944	0.904

(1) Transfer of metal ions from the solution towards the boundary layer surrounding the particle.

(2) Transfer through the boundary layer towards the adsorbent surface as external film diffusion.

(3) Transfer of the surface metal ions towards the adsorbent sites as intraparticle diffusion.

(4) Adsorption and complexation of metal ions onto the binding sites on the adsorbent pores.

These transport mechanisms may act in series or in parallel to affect the sorption of Cd^{2+} ad Cr^{3+} onto the three adsorbents.

4   Conclusions

The kinetics of the sorption of Cd^{2+} and Cr^{3+} ions were examined using three different adsorbents. The metal removal percentages increased with strong treatments with mercaptoacetic acid. The sorption pattern for each metal can be described by a fast removal rate stage followed by a second slower removal rate stage until equilibrium. Cr^{3+} had a higher removal percentage than Cd^{2+} due to the influence of ionic radii and ionic charge of the metals on the uptake rate.

Analysis of the intraparticle diffusion kinetic model shows that the Cd^{2+} ion transport is better described by this model than the Cr^{3+} transport. Future studies will examine other kinetic models to compare the applicability of such models. The results show that the low cost adsorbents used in this study have great potential for the removal of Cd^{2+} and Cr^{3+} ions from polluted aquatic systems.

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MOU Signed Between the University of Wisconsin at Madison and Tsinghua University

A Memorandum of Understanding was signed between Tsinghua University and the University of Wisconsin at Madison on May 24, 2007, during the visit of Chancellor John D. Wiley, the University of Wisconsin at Madison.

The purpose of the MOU was to promote friendly relations through the development of educational and research collaboration between the two universities. Tsinghua President Gu Binglin had a discussion with Chancellor Wiley prior to the signing ceremony. The two exchanged ideas on university development, student exchange, and joint research.

After the signing ceremony, the delegation members also had group discussions with the faculty of several departments of Tsinghua, including the Department of Automobile Engineering, the School of Humanities and Social Sciences, the Academy of Arts and Design, the Department of Accounting, the Department of Industrial Engineering, and the Department of Biological Sciences and Biotechnology.

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