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Adsorption of lead ions from aqueous solutions by citric acid-modified celluloses

Chao-Yin Kuo[a], Chung-Hsin Wu[b,*], Meng-Jia Chen[c]

[a] *Department of Environmental and Safety Engineering, National Yunlin University of Science and Technology, Yunlin, Taiwan, Tel. +886 5 5347311; email: kuocyr@ms35.hinet.net*
[b] *Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Sciences, 415 Chien Kung Road, Kaohsiung 807, Taiwan, Tel. +886 7 3814526, ext. 5158; Fax: +886 7 3830674; email: wuch@kuas.edu.tw*
[c] *Department of Environmental Engineering, Da-Yeh University, Da-Tsuen, Chang-Hua, Taiwan, Tel. +886 983161092; email: f9405251@hotmail.com*

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ABSTRACT

In this study, citric acid was utilized to modify the surface of cellulose and the citric acid-modified cellulose (CAMC) was then used to remove Pb^{2+} from aquatic solutions. The surface characteristics of CAMC were determined by Fourier-transform infrared spectroscopy and zeta potential analyses. The exact effects of CAMC dosage, pH, and temperature on the adsorption of Pb^{2+} by CAMC were determined. After 180 min of reaction, the adsorption percentages of Pb^{2+} at 0.5, 1.5, and 2.5 g/L CAMC were 66, 87, and 94%, respectively. The Pb^{2+} removal efficiency of CAMC increased with CAMC dosage, pH, and temperature. Experimental results reveal that the pseudo-second-order model best represents the adsorption kinetics. The Freundlich model fits the experimental isotherms better than does the Langmuir model. ΔH° and ΔS° were 43.34 kJ/mol and 224.4 J/mol K, respectively. The value of ΔH° suggested that the Pb^{2+} was adsorbed onto CAMC via physisorption.

Keywords: Adsorption; Citric acid; Cellulose; Lead ions; Isotherm; Kinetics; Thermodynamics

1. Introduction

Some industrial uses of metals and domestic processes have introduced considerable amounts of potentially toxic heavy metals into the aquatic environment. Lead, an element that has been utilized by industry for many years, is a long-term environmental contaminant. Numerous methods for removing lead ions from aqueous solutions exist. These include precipitation, electrochemical treatment, ionic exchange, reverse osmosis, and adsorption. The adsorption process is highly efficient for the removal of heavy metals; moreover, it is simple and insensitive to toxic substances. Activated carbon is the adsorbent that is most frequently used in wastewater treatment. However, the cost of activated carbon is high. Accordingly, researchers are encouraged to develop other types of adsorbent that cheaply and effectively removes heavy metals.

Several investigations have been published on the features and advantages of unconventional methods of removing lead ions, such as biosorption and the use of low-cost agricultural by-products. Wood pulp [1,2], corncobs [3], rice husk ash [4], rice husk [5,6], sawdust [7,8], peanut hulls [9], tea leaves [10], grape stalks [11],

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*Corresponding author.

and bamboo fibers [12] have all been used as adsorbents to remove Pb^{2+} from aquatic solutions. The main component of all of these agricultural by-products is cellulose. Cellulose is cheap, renewable, biodegradable, and the most abundant organic original material in the world; hence, it is a suitable basis for a new adsorbent. However, most relevant research has focused on the use of agricultural by-products but little is known about the adsorption kinetics, equilibrium, and thermodynamics of the binding of Pb^{2+} with cellulose. Low et al. [1] modified wood pulp using citric acid for the sorption of Pb^{2+} from aqueous solutions and found that esterification increases the carboxylic acid content of the wood at its surface, increasing the sorption of Pb^{2+}. Accordingly, in this study, citric acid was used to modify the surface of original cellulose. The citric acid-modified cellulose (CAMC) was used to remove Pb^{2+} from aqueous solutions. The adsorption rates were evaluated and compared with those obtained using the pseudo-second-order and intraparticle diffusion models. The Langmuir and Freundlich isotherms were used to fit adsorption equilibrium data. The objectives of this study were: (i) to determine the effects of CAMC dosage and pH on the adsorption of Pb^{2+} by CAMC, (ii) to evaluate adsorption rates using pseudo-second-order and intraparticle diffusion models, (iii) to measure the coefficients of the Langmuir and Freundlich isotherms, and (iv) to derive changes in the thermodynamic parameters enthalpy (ΔH°) and entropy (ΔS°) during adsorption.

2. Materials and methods

2.1. Materials

Cellulose (C6413) was purchased from Sigma-Aldrich. Lead(II) nitrate, citric acid, nitric acid, and sodium hydroxide were obtained from Merck. The pH of solutions was adjusted by adding nitric acid and sodium hydroxide. All compounds except cellulose were used as received without purification.

2.2. Experimental methods

2.2.1. Cellulose modification

To prepare CAMC, 20 g of original cellulose was combined in a beaker with 400 mL 1.2 M citric acid and stirred for 2 h. The mixture was filtered and the residue was dried in an oven at 50℃ for 24 h. Finally, the obtained particles were heated at 150℃ for 180 min. The CAMC thus formed was washed using distilled water until its pH was neutral before it was used in subsequent adsorption experiments.

2.2.2. Characterization

A Zeta-Meter 3.0 (Zeta-Meter, Inc., USA) was used to determine the zeta potential of CAMC. The functional groups of original cellulose and CAMC were identified by Fourier-transform infrared spectroscopy (FTIR) using a Spectrum One and Autoimagic system (Perkin–Elmer, USA) with the KBr pressed disc method.

2.2.3. Metal ions adsorption

All adsorption experiments were performed in a closed 250 mL glass pyramid bottle. The bottle, which contained an appropriate amount of CAMC and 200 mL Pb^{2+} (20 mg/L) solution, was placed in a water bath and shaken at 100 rpm. To determine the effect of the CAMC dosage, CAMC doses of 0.5, 1.5, and 2.5 g/L were used; to identify the effect of pH, the initial solution pH was adjusted to 3 and 5. The initial pH was 5.0 in all experiments except those to determine the effects of pH. Kinetic and equilibrium experiments were conducted for 3 and 24 h, respectively, at a controlled temperature of 25 and 15–45℃ in the kinetic and equilibrium experiments, respectively. Suspended particles were separated by filtering them through a 0.22 μm filter (Millipore). The Pb^{2+} concentrations before and after adsorption were measured using an atomic absorption spectrophotometer (Perkin–Elmer 3300, USA). All adsorption experiments were conducted in triplicate and the values shown are averages.

3. Results and discussion

3.1. Surface characteristics of original cellulose and CAMC

.The FTIR spectra of the original cellulose and CAMC samples were recorded in the range 400–4,000 cm^{-1} (Fig. 1). Original cellulose and CAMC both yielded peaks at 893, 1,047, 1,113, 1,161, 1,522, 1,647, 2,901, 2,978, and

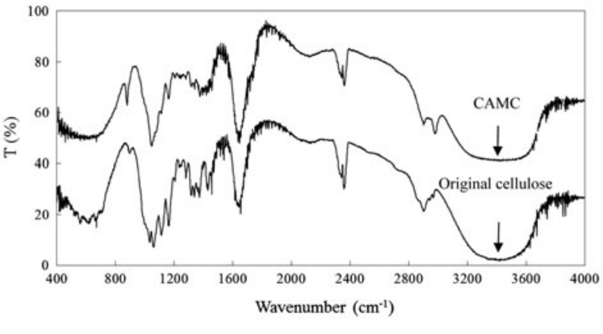
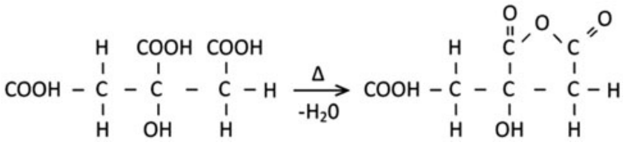
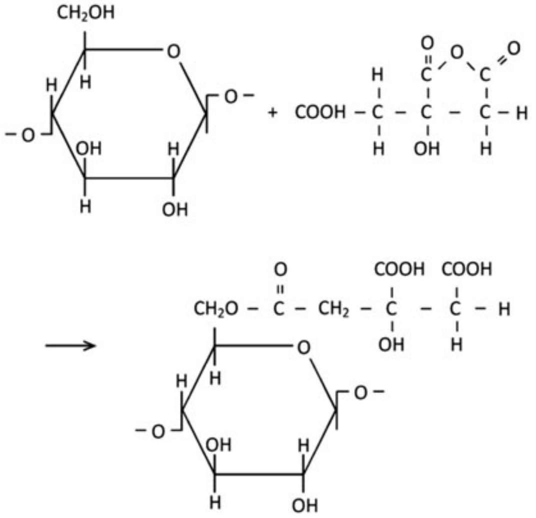


Fig. 1. FTIR spectra of original cellulose and CAMC.

3,200–3,600 cm^{-1}. The peak at 893 cm^{-1} is associated with COC, CCO, and CCH deformation and stretching [13]. The peaks at 1,000–1,300 cm^{-1} are associated with C–O stretching in acids, alcohols, phenols, ethers, and esters [14]. Ma and Ouyang [15] indicated that the peaks at approximately 1,100 cm^{-1} are attributable to C–O vibration. The peaks at 1,300–1,530 cm^{-1} are related to the vibration of C=C in the aromatic rings and methyl [15]. The peaks at 1,640–1,660 cm^{-1} are associated with the C=O stretching vibration [16]. The peaks at 2,800–3,000 cm^{-1} are associated with C–H vibration [15,17]. The peaks at 3,200–3,600 cm^{-1} are associated with the OH stretching vibration of carboxylic acids, alcohols, and phenols [17]. The peaks generated by C–O, C=O, and –OH vibrations were attributed to the presence of a carboxyl group on the surface of cellulose. The citric acid was heated to form citric acid anhydride (Eq. (1)). The reactive citric acid anhydride combined with cellulosic hydroxyl groups, forming an ester linkage and introduced carboxyl groups (Eq. (2)). [18]. At pH 5, the zeta potentials of the original cellulose and CAMC were 12 and −41 mV, respectively. The addition of carboxyl functions on CAMC formed a negatively charged surface and increased the extent of binding with the positively charged Pb^{2+}.





3.2. Analyses of kinetic adsorption

Fig. 2 plots the kinetics of the adsorption of Pb^{2+} onto CAMC. Pseudo-second-order [19,20] and intraparticle diffusion [21] models were tested against the experimental data and used to elucidate the adsorption process kinetics (Table 1). After 180 min reaction, the Pb^{2+} removal percentage by original cellulose (1.5 g/L) was less than 10%. The adsorption percentages of Pb^{2+} at 0.5, 1.5, and 2.5 g/L CAMC were 66, 87, and 94%, respectively. Citric acid modification significantly enhanced the adsorption ability of cellulose for Pb^{2+}. When 1.5 g/L CAMC was added, the pH declined from 5 to 3.6 during 180 min of reaction. This change was attributed to the bonding of Pb^{2+} to the functional groups of CAMC, such as COOH and OH, and the release of H^+ ions. The adsorption rate was rapid in the first 60 min and then slowed (Fig. 2). Initially, all surface sites on the adsorbent were vacant and the Pb^{2+} concentration gradient was relatively high, so the initial adsorption rate was high. This initial phase might be explained by passive uptake through physical adsorption or ion exchange at the surface [15,22]. Increasing the CAMC dosage increased the adsorption of Pb^{2+}, mainly by increasing the adsorptive surface area and availability of additional adsorption sites on CAMC. However, the mass of Pb^{2+} adsorbed per unit mass of CAMC declined as

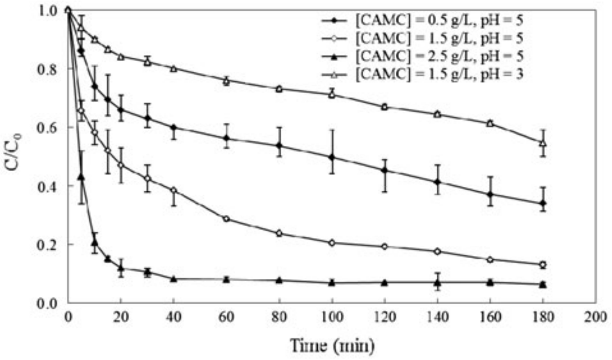


Fig. 2. Kinetic analyses of Pb^{2+} adsorption onto CAMC ($[Pb^{2+}]$ = 20 mg/L).

Table 1
Equations of kinetic model, equilibrium isotherm, and thermodynamic expression

Kinetic models	
Pseudo-second-order model	$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$
Intraparticle diffusion model	$q = k_i t^{1/2} + C$
Equilibrium isotherms	
Langmuir isotherm	$q_e = \frac{q_m K_L C_e}{(1 + K_L C_e)}$
Freundlich isotherm	$q_e = K_F C_e^{1/n}$
Thermodynamic expressions	
Van't Hoff equation	$\Delta G^\circ = -RT\ln(K_L)$ $\ln(K_L) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$

the CAMC dose increased (Table 2). The decrease in unit adsorption as the CAMC dose increased results from the fact that the adsorption sites remain unsaturated during the adsorption process and possibly the fact that adsorption sites may overlap each other owing to CAMC particle overcrowding. Franca et al. [23] also determined that unit adsorption capacity decreased as the adsorbent dosage increased.

Solution pH is an important adsorption parameter because pH depends on complex reactions and electrostatic interactions in physisorption processes that occur at the adsorption surface. Reducing pH decreased adsorption (Fig. 2). At higher pH, the CAMC surface attracts more negative charges, and so attracts more Pb^{2+}. A positively charged surface site on CAMC did not favor the adsorption of Pb^{2+} owing to electrostatic repulsion.

Figs. 3(a) and 3(b) show the regressions of pseudo-second-order model and intraparticle diffusion model, respectively. Table 2 presents the kinetic parameters of the removal of Pb^{2+} by CAMC. The correlation coefficient (R^2) of the pseudo-second-order model exceeded 0.97; moreover, the q values ($q_{e,\ \mathrm{cal}}$) that were derived from the pseudo-second-order model were consistent with experimental q values ($q_{e,\ \mathrm{exp}}$). Therefore, the pseudo-second-order model best represented the adsorption kinetics. A similar phenomenon has been observed in the adsorption of Acid Blue 93 by natural sepiolite [24], and of Acid Red 57 by surfactant-modified sepiolite [25]. The regression of intraparticle diffusion model exhibited two stages of adsorption process (Fig. 3(b)). The first linear section was attributed to the process in which lead ions diffuse to the CAMC surface; hence, the fastest sorption stage. The second section was ascribed to intraparticle diffusion, a delayed process [26,27]. When the regression of q versus $t^{1/2}$ is linear and passes through the origin, intraparticle diffusion is the sole rate-limiting step [25]. Although the regression was linear herein, the plot did not pass through the origin (Table 2), suggesting that adsorption involved intraparticle diffusion; however, intraparticle diffusion was not the only rate-limiting step. Other kinetic mechanisms probably controlled the adsorption rate, which finding is similar to that of other adsorption study [24]. Akkaya et al. [28] demonstrated that pore diffusion and surface diffusion occur simultaneously in an adsorbent particle. Since, the BET surface area of CAMC is very small ($0.47\,m^2/g$), this study suggests that the adsorption kinetics are dominated by surface diffusion.

3.3. Analyses of equilibrium adsorption

Fig. 4 displays analyses of the adsorption isotherms of Pb^{2+} on CAMC. Langmuir [29] and Freundlich [30] isotherms were utilized herein to specify equilibrium adsorption (Table 1). The Langmuir isotherm assumes monolayer coverage of the adsorption surface and no subsequent interaction among adsorbed molecules. The Freundlich isotherm is used to model multilayer adsorption and adsorption on heterogeneous surfaces. Table 3 presents isotherm parameters at various temperatures. The R^2 values reveal that the Freundlich model fits the experimental isotherms better than does the Langmuir model, suggesting that a heterogeneous surface exists for the adsorption of Pb^{2+} onto CAMC. Stephen et al. [31] also indicated that the adsorption interactions between heavy metals and adsorbents were best described by the Freundlich model. Notably, K_L, K_F, and q_m increased with temperature, suggesting that the adsorption of Pb^{2+} on CAMC increased with temperature (Table 3). These experimental results indicate that the affinity of binding sites for Pb^{2+} increased with temperature, suggesting that the adsorption of Pb^{2+} onto CAMC is endothermic.

Changes to ΔH° and ΔS° upon adsorption were calculated. The Langmuir isotherm was applied to calculate thermodynamic parameters using the Van't Hoff equation (Table 1). Fig. 5 shows the Van't Hoff plot. The ΔH° and ΔS° were 43.34 kJ/mol and 224.4 J/mol K, respectively. The negative values of ΔG° at all temperatures indicate that the adsorption of Pb^{2+} onto CAMC

Table 2
Kinetic parameters for the removal of Pb^{2+} by CAMC ($[Pb^{2+}] = 20$ mg/L, pH = 5)

Pseudo-second-order model	$q_{e,\ \mathrm{exp}}$ (mg/g)	k_2 (g/mg min)	$q_{e,\ \mathrm{cal}}$ (mg/g)	R^2
[CAMC] = 0.5 g/L	26.4	1.4×10^{-3}	28.1	0.977
[CAMC] = 1.5 g/L	11.6	5.5×10^{-3}	12.3	0.997
[CAMC] = 2.5 g/L	7.5	7.1×10^{-2}	7.6	0.999

Intraparticle diffusion model	k_i (mg/g min$^{0.5}$)	C (mg/g)	R^2
[CAMC] = 0.5 g/L	1.568	5.18	0.964
[CAMC] = 1.5 g/L	0.606	4.09	0.956
[CAMC] = 2.5 g/L	0.289	5.59	0.888

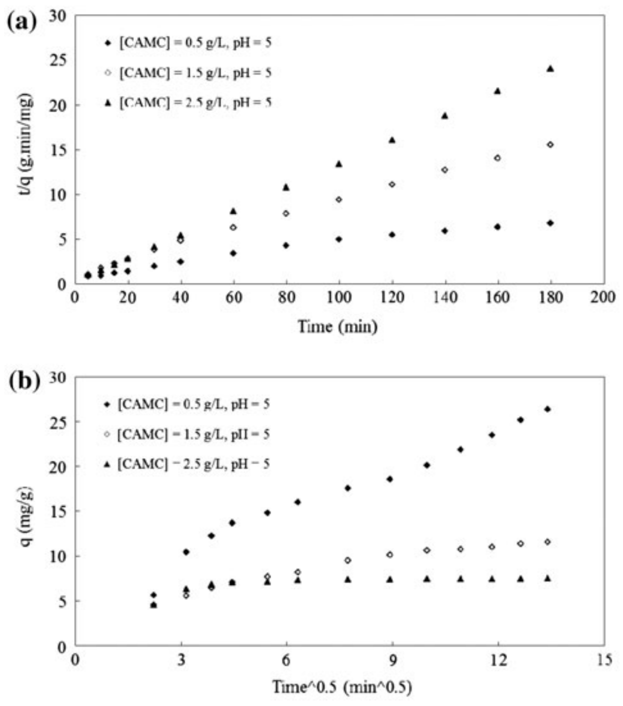


Fig. 3. Regressions of kinetics model. (a) Pseudo-second-order model. (b) Intraparticle diffusion model.

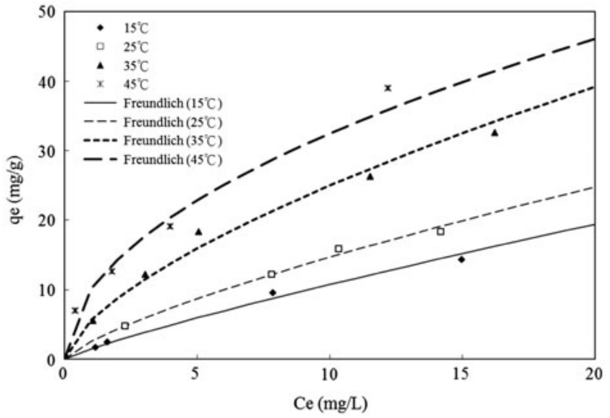


Fig. 4. Adsorption isotherm analyses of Pb^{2+} on CAMC.

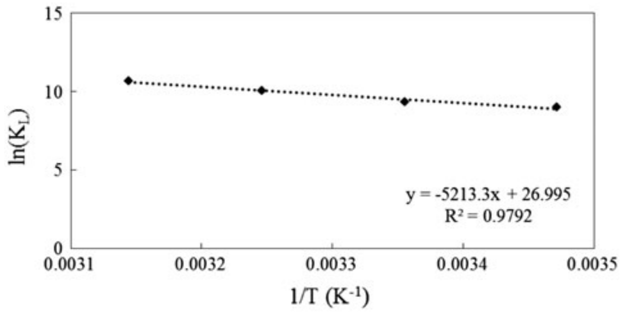


Fig. 5. Regression of Van’t Hoff plots.

was spontaneous. The positive ΔH° indicates that the adsorption process was endothermic. The positive value of ΔS° suggests that randomness increased at the solid–liquid interface during adsorption. To a certain level, the type of interaction can be classified by the magnitude of enthalpy change. Physical sorption, such as hydrogen bonding, is generally lower than 35 kJ/mol [32]. Physisorption processes, such as Van der Waals interactions, are usually lower than 20 kJ/mol. Electrostatic interactions range from 20 to 80 kJ/mol; this kind of interaction is frequently classified as physisorption. Chemisorption bond strengths can be in the range of 80–450 kJ/mol [33]. Hence, the ΔH° value herein suggests that the adsorption of Pb^{2+} onto CAMC was driven by a physisorption process. In the desorption experiments, 1.5 g of Pb^{2+}-loaded CAMC was placed in a bottle that contained 200 mL of 0.5 M HNO_3, which was shaken at 100 rpm for 3 h. The Pb^{2+} concentrations that were removed by CAMC and released by Pb^{2+}-loaded CAMC were 17.4 and 16.9 mg/L after 3 h of reaction, respectively. The Pb^{2+}-loaded CAMC was easily desorbed, confirming that the adsorption was physisorption. Table 4 summarizes the adsorption capacity of Pb^{2+} in various adsorbents. Modification by acid improved the Pb^{2+} adsorption capacity of the adsorbent. Based on a comparison of CAMC with other agricultural by-products (Table 4), this study suggests that CAMC is an effective adsorbent for removing Pb^{2+}.

Table 3
Isotherm parameters for the removal of Pb^{2+} by CAMC

Pb^{2+}	Langmuir			Freundlich		
Temp (˚C).	q_m (mg/g)	K_L (L/mg)	R^2	K_F	n	R^2
15	39.22	0.0388	0.971	1.5111	1.1734	0.995
25	41.67	0.0560	0.973	2.5852	1.3257	0.996
35	49.02	0.1118	0.987	5.6118	1.5418	0.985
45	52.08	0.2069	0.893	10.1344	1.9775	0.986

Table 4
Adsorption capacity of Pb^{2+} in various adsorbents

	Adsorption capacity (mg/g)	Modification agent	Refs.
Cellulose	41.67	Citric acid	This study
Wood pulp	7.71	–	Low et al. [1]
	82.64	Citric acid	Low et al. [1]
	7.04	–	Abdel-Aal et al. [2]
Corncobs	8.28	–	Vaughan et al. [3]
	91.08	Citric acid	
Rice husk ash	12.61	–	Feng et al. [4]
Rice hulls	8.07	–	Low et al. [5]
Saw dust	3	–	Shukla et al. [7]
	55.9	Acrylic acid	Güçlü et al. [8]
Peanut hulls	30.02	–	Brown et al. [9]
Tea leaves	2.1	–	Ahluwalia and Goyal [10]
Grape stalks	49.89	–	Martinez et al. [11]

4. Conclusions

The kinetics of adsorption and the equilibrium adsorption of Pb^{2+} onto CAMC were examined. Based on the FTIR and zeta potential analyses of CAMC, this study suggests that the addition of carboxyl functional groups to CAMC produced the negatively charged surface and increased the amount of bonding with the positively charged Pb^{2+}. The mass of Pb^{2+} adsorbed per unit mass of CAMC declined as the CAMC dose increased. The pseudo-second-order model and Freundlich model were good for fitting the adsorption kinetics and equilibrium data, respectively. This study found that the adsorption of Pb^{2+} onto CAMC was spontaneous and endothermic, and driven by a physisorption process.

Acknowledgment

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Symbols

k_2 — pseudo-second-order rate constant
k_i — intraparticle diffusion rate constant
C — constant in intraparticle diffusion model
C_e — equilibrium concentration of Pb^{2+}
q — amount of Pb^{2+} adsorbed onto CAMC at time t
q_e — amount of Pb^{2+} adsorbed onto CAMC at equilibrium
q_m — maximum amount of Pb^{2+} adsorption at equilibrium
t — time
C_0 — initial Pb^{2+} concentration
K_L — Langmuir constant
K_F — Freundlich constant
n — exponent in Freundlich isotherm
R — universal gas constant
T — absolute temperature

References

[1] K.S. Low, C.K. Lee, S.M. Mak, Sorption of copper and lead by citric acid modified wood, Wood Sci. Technol. 38 (2004) 629–640.

[2] S.E. Abdel-Aal, Y. Gad, A.M. Dessouki, The use of wood pulp and radiation-modified starch in wastewater treatment, J. Appl. Polym. Sci. 99 (2006) 2460–2469.

[3] T. Vaughan, C.W. Seo, W.E. Marshall, Removal of selected metal ions from aqueous solution using modified corncobs, Bioresour. Technol. 78 (2001) 133–139.

[4] Q. Feng, Q. Lin, F. Gong, S. Sugita, M. Shoya, Adsorption of lead and mercury by rice husk ash, J. Colloid Interf. Sci. 278 (2004) 1–8.

[5] K.S. Low, C.K. Lee, S.Y. Wong, P.L. Tang, Metal soprtion enhancement of rice hull through chemical modification, Environ. Technol. 21 (2000) 1239–1244.

[6] C.R.T. Tarley, S.L.C. Ferreira, M.A.Z. Arruda, Use of modified rice husks as a natural solid adsorbent of trace metals: characterisation and development of an on-line preconcentration system for cadmium and lead determination by FAAS, Microchem. J. 77 (2004) 163–175.

[7] A. Shukla, Y.H. Zhang, P. Dubey, J.L. Margrave, S.S. Shukla, The role of sawdust in the removal of unwanted materials from water, J. Hazard. Mater 95 (2002) 137–152.

[8] G. Güçlü, G. Gürdağ, S. Özgümüş, Competitive removal of heavy metal ions by cellulose graft copolymers, J. Appl. Polym. Sci. 90 (2003) 2034–2039.

[9] P. Brown, I.A. Jefcoat, D. Parrish, S. Gill, E. Graham, Evaluation of the adsorptive capacity of peanut hull

pellets for heavy metals in solution, Adv. Environ. Res. 4 (2000) 19–29.

[10] S.S. Ahluwalia, D. Goyal, Removal of heavy metals by waste tea leaves from aqueous solution, Eng. Life Sci. 5 (2005) 158–162.

[11] M. Martinez, N. Miralles, S. Hidalgo, N. Fiol, I. Villaescusa, J. Poch, Removal of lead(II) and cadmium(II) from aqueous solutions using grape stalk waste, J. Hazard. Mater. 133 (2006) 203–211.

[12] S. Wang, L. Wang, W. Kong, J. Ren, C. Liu, K. Wang, R. Sun, D. She, Preparation, characterization of carboxylated bamboo fibers and their adsorption for lead(II) ions in aqueous solution, Cellulose 20 (2013) 2091–2100.

[13] M. Fan, D. Dai, B. Huang, Fourier transform infrared spectroscopy for natural fibres, in: S. Salih (Ed.), Fourier Transform – Materials Analysis, InTech, 2012, doi: 10.5772/35482, ISBN: 978-953-51-0594-7. Available from: http://www.intechopen.com/books/fourier-transform-materials-analysis/fourier-transform-infrared-spectroscopy-for-natural-fibres.

[14] A. Reffas, V. Bernardet, B. David, L. Reinert, M.B. Lehocine, M. Dubois, N. Batisse, L. Duclaux, Carbons prepared from coffee grounds by H_3PO_4 activation: Characterization and adsorption of methylene blue and Nylosan Red N-2RBL, J. Hazard. Mater. 175 (2010) 779–788.

[15] X. Ma, F. Ouyang, Adsorption properties of biomass-based activated carbon prepared with spent coffee grounds and pomelo skin by phosphoric acid activation, Appl. Surf. Sci. 268 (2013) 566–570.

[16] X. Li, Y. Tang, X. Cao, D. Lu, F. Luo, W. Shao, Preparation and evaluation of orange peel cellulose adsorbents for effective removal of cadmium, zinc, cobalt and nickel, Colloids Surf. A. 317 (2008) 512–521.

[17] L.S. Silva, L.C.B. Lima, F.C. Silva, J.M.E. Matos, M.R. Santos, L.S. Santos Junior, K.S. Sousa, Edson C. da Silva Filho, Dye anionic sorption in aqueous solution onto a cellulose surface chemically modified with aminoethanethiol, Chem. Eng. J. 218 (2013) 89–98.

[18] N.D. Thanh, H.L. Nhung, Cellulose modified with citric acid and its absorption of Pb^{2+} and Cd^{2+} ions, 13rd International Electronic Conference on Synthetic Organic Chemistry, 2009.

[19] G. Blanchard, M. Maunaye, G. Martin, Removal of heavy metals from waters by means of natural zeolites, Water Res. 18 (1984) 1501–1507.

[20] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, Chem. Eng. J. 70 (1998) 115–124.

[21] W.J. Weber Jr., J.C. Morris, Kinetics of adsorption on carbon from solution, J. Sanit. Eng. Div. ASCE 89 (1963) 31–59.

[22] Y.P. Ting, F. Lawson, I.G. Prince, Uptake of cadmium and zinc by the alga Chlorella vulgaris: Part 1. Individual ion species, Biotechnol. Bioeng. 34 (1989) 990–999.

[23] A.S. Franca, L.S. Oliveira, A.A. Nunes, C.C.O. Alves, Microwave assisted thermal treatment of defective coffee beans press cake for the production of adsorbents, Bioresour. Technol. 101 (2010) 1068–1074.

[24] A. Özcan, E.M. Öncü, A.S. Özcan, Kinetics, isotherm and thermodynamic studies of adsorption of Acid Blue 193 from aqueous solutions onto natural sepiolite, Colloids Surf. A 277 (2006) 90–97.

[25] A. Özcan, A.S. Özcan, Adsorption of Acid Red 57 from aqueous solutions onto surfactant-modified sepiolite, J. Hazard. Mater. 125 (2005) 252–259.

[26] B. Royer, N.F. Cardoso, E.C. Lima, V.S.O. Ruiz, T.R. Macedo, C. Airoldi, Organofunctionalized kenyaite for dye removal from aqueous solution, J. Colloid Interface Sci. 336 (2009) 398–405.

[27] B. Royer, N.F. Cardoso, E.C. Lima, T.R. Macedo, C. Airoldi, A useful organofunctionalized layered silicate for textile dye removal, J. Hazard. Mater. 181 (2010) 366–374.

[28] G. Akkaya, İlhan Uzun, F. Güzel, Kinetics of the adsorption of reactive dyes by chitin, Dyes Pigm. 73 (2007) 168–177.

[29] I. Langmuir, The constitution and fundamental properties of solids and liquids. II: Liquids, J. Am. Chem. Soc. 39 (1917) 1848–1906.

[30] H.M.F. Freundlich, Over the adsorption in solution, J. Phys. Chem. 57 (1906) 385–470.

[31] M. Stephen, N. Catherine, M. Brenda, K. Andrew, P. Leslie, G. Corrine, Oxolane-2,5-dione modified electrospun cellulose nanofibers for heavy metals adsorption, J. Hazard. Mater. 192 (2011) 922–927.

[32] C.L. Sun, C.S. Wang, Estimation on the intramolecular hydrogen-bonding energies in proteins and peptides by the analytic potential energy function, J. Mol. Struct. 956 (2010) 38–43.

[33] S. Qu, F. Huang, S. Yu, G. Chen, J. Kong, Magnetic removal of dyes from aqueous solution using multi-walled carbon nanotubes filled with Fe_2O_3 particles, J. Hazard. Mater. 160 (2008) 643–647.