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Real-time determination of kinetics of adsorption of lead(II) onto palm shell-based activated carbon using ion selective electrode

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Abstract

In this study, the kinetics of adsorption of Pb(II) from aqueous solution onto palm shell-based activated carbon (PSAC) were investigated by employing ion selective electrode (ISE) for real-time Pb(II) and pH monitoring. Usage of ISE was very appropriate for real-time adsorption kinetics data collection as it facilitated recording of adsorption data at very specific and short time intervals as well as provided consistent kinetics data. Parameters studied were initial Pb(II) concentration and agitation speed. It was found that increases in initial Pb(II) concentration and agitation speed resulted in higher initial rate of adsorption. Pseudo first-order, pseudo second-order, Elovich, intraparticle diffusion and liquid film diffusion models were used to fit the adsorption kinetics data. It was suggested that chemisorption was the rate-controlling step for adsorption of Pb(II) onto PSAC since the adsorption kinetics data fitted both the pseudo second-order and Elovich models well.
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Keywords: Adsorption kinetics; Palm shell-based activated carbon; Ion selective electrode; Pb(II)

1. Introduction

The presence of heavy metals in the environment has been a matter of major concern due to their toxicity to human. Lead is a highly toxic substance, exposure to which can bring about a wide spectrum of adverse health effects and has been known to cause severe poisoning in children. It is one of the most common contaminants found in wastewaters in a myriad of industries such as storage batteries, printing, painting, pigments, dying, and leaded glass. Unlike organic pollutants, the majority of which are susceptible to biological degradation, lead will not degrade into harmless end-products and will accumulate in living organisms (Günay et al., 2007). It is therefore essential that lead be reduced to an acceptable low concentration (based on local environmental regulation) from the wastewater

stream prior to final discharge to the environment. The permissible level of lead in effluent from industrial premises in Malaysia for final discharge to downstream of waterbodies, as stipulated by the Department of Environment, Malaysia (DOE, 2002) is 0.5 mg g^{-1}.

One of the most used methods of lead removal from aqueous solution is adsorption using low-cost adsorbents. An example of such adsorbent is activated carbon. Many reports have appeared on the development of low-cost activated carbon adsorbents developed from cheaper and readily available materials (Kurniawan et al., 2006). So far, there have been numerous studies on kinetics of metal adsorption onto activated carbon (Chen and Lin, 2001; Kadirvelu et al., 2002; Rao et al., 2006). However, it should be noted that these studies involved established manual techniques and there is no identified method of direct real-time monitoring of metal concentrations and pH in bulk solution for determining kinetics of activated carbon adsorption. Usage of real-time concentration and pH mon-

itoring technique for this purpose clearly offers additional benefits of rapidity and higher accuracy. One example of such application is utilization of ion selective electrode (ISE), an ion-specific sensor which detects concentration of a particular ion in a bulk solution and turns it into electrical potential that can be measured by a voltmeter (Lu et al., 2002). With regards to usage of palm shell-based activated carbon (PSAC) for removal of Pb(II) from aqueous solution, Issabayeva et al. (2006) first reported that PSAC contained significant amount of acidic functional groups and had high adsorption capacity for Pb(II), especially at pH 5 with an ultimate uptake of 95.2 mg g^{-1}. The main objective of this study is to determine the kinetics of adsorption of Pb(II) from aqueous solution onto PSAC by employing ISE for real-time Pb(II) and pH monitoring. Among the parameters analyzed were initial Pb(II) concentration, amount of Pb(II) adsorbed on PSAC and agitation speed. The data were fitted to several established adsorption kinetics model.

2. Methods

2.1. Palm shell activated carbon

Commercial granular palm shell-based activated carbon (PSAC) was obtained from Bravo Green Sdn Bhd, a local manufacturer based in Sarawak, Malaysia. PSAC was sieved to the desired particle size (0.6–1.0 mm), washed with deionized water and dried at 105 °C overnight. The BET surface area and pore diameter of PSAC were determined from N$_2$ adsorption isotherm at 77 K using the N$_2$ adsorption isotherm using ThermoFinnigan Sorptomatic 1990 Series analyzer. Elemental analysis of PSAC was performed using Flash EA 1112 ThermoFinnigan elemental analyzer. A pH 'drift' method was used to determine pH of point of zero charge (PH$_{PZC}$) (Lopez-Ramon et al., 1999; Mullet et al., 1999). The BET surface area, maximum pore volume, ash content as well as pH$_{PZC}$ of the PSAC were determined to be 941 m^2/g, 0.54 cm^3/g, 3.45% and 1.9, respectively. The high BET surface area as well as low pH$_{PZC}$ indicate that Pb(II) can be easily adsorbed since higher uptake rate of metal ions on surface was promoted when solution pH was higher than pH$_{PZC}$ (Mullet et al., 1999). As the pH$_{PZC}$ is low in this study, Pb(II) adsorption is expected to be high.

2.2. Kinetics adsorption study

All chemicals and reagents used were of analytical grade. A stock solution of Pb(II) (1000 ppm) was prepared by dissolving lead(II)perchlorate hydrate (Sigma–Aldrich) in sodium perchlorate solution (0.15 M) (Merck) and subsequently acidified with 5 ml of HClO$_4$ to prevent hydrolysis. Perchlorate metal salt was chosen due to its very poor complexation tendencies at low pH. Pb(II) solutions of desired concentrations were prepared from the stock solution with appropriate dilution and the initial pH was

adjusted to 5.0 ± 0.1 via addition of dilute perchloric acid or sodium hydroxide. This initial pH was selected due to its prevalence in Malaysian industrial wastewaters (DOE, 2002). pH measurements were conducted using Cyberscan 510 pH meter along with a temperature probe. A variable speed motor was used to drive a 3-blade Rushton turbine impeller. An ISE meter (Metrohm, model 781) was used to detect the real-time Pb(II) concentration in solution with another electrode acting as a reference. The effect of different initial concentrations of Pb(II) on the amount of lead adsorbed on PSAC and bulk solution pH profile was studied by agitating 200 ml solution together with 500 mg PSAC at 200 rpm via the Rushton turbine impeller for four hours. The Pb(II) concentration was monitored at every interval of 5 min. The effect of agitation speed on Pb(II) removal was also studied by agitating 200 ml of Pb(II) solution (120 ppm) at either 200, 300 or 400 rpm for 4 h. A blank control sample was used to determine the adsorption of Pb(II) on the wall of glass flask which was found to be negligible. The amount of Pb(II) adsorbed (mg g^{-1}) at time t was computed by using the following equation:

$$q_t = \frac{(C_0 - C_t)V}{M} \tag{1}$$

where C_o and C_t are the Pb(II) concentrations (mg l^{-1}) initially and at a given time t, respectively, V (l) is the volume and M (g) is the weight of PSAC.

3. Results and discussion

3.1. Chemical speciation of lead

In order to determine the chemical speciation of lead in a bulk solution containing perchlorate ions, a lead speciation diagram as affected by changes in pH was generated using VMINTEQ 2.50 software (Gustafsson, 2006). VMINTEQ 2.50 is a chemical equilibrium model for determination of metal speciation and solubility equilibria for natural waters. In this study, the concentrations of elements involved in the batch adsorption, namely, Pb^{2+}, Na$^+$ and ClO$_4^-$ were inputed into the software to generate concentration data for all species in the solution at a particular pH. The concentration data were then converted to percentages to relative to the total metal species in separate aqueous solutions for pH 1–14.

Fig. 1 shows the speciation profile of lead at varying pH with 0.15 M sodium perchlorate as background solution. The lead speciation plotted are relative to the total lead species and although different concentrations of lead are investigated in this study, only the speciation profiles are shown for 700 ppm metal concentration for reason of brevity. The profiles for any lead concentration from 20 to 700 ppm (not shown) are observed to be almost similar to the profiles shown for 700 ppm metal concentration. The percentages of free lead(II) ions are either 100% or almost 100% from pH 1–6. This indicates poor complexation tendencies at low pH which are favorable in
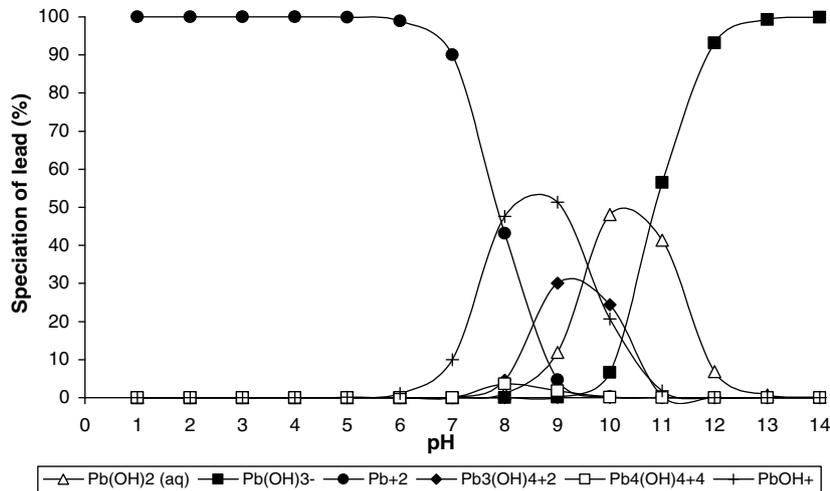
Fig. 1. Lead speciation relative to total lead species in aqueous solution.

minimizing interference due to metal complexation such as formation of metal hydroxide at pH > 6. This justifies the usage of sodium perchlorate as the background solutes.

3.2. Effect of initial Pb(II) concentrations on amount of Pb(II) adsorbed on PSAC

Fig. 2 shows the effect of initial Pb(II) concentrations on amount of Pb(II) adsorbed on PSAC. The usage of ISE clearly enables recording of adsorption data at very specific and short time intervals as well as in a more consistent manner as compared to conventional technique. The removal curves are single, smooth, and continuous, indicating the possibility of the formation of monolayer coverage of Pb(II) at the outer surface of PSAC (Ryu et al., 1999). The adsorption of Pb(II) ions is rapid initially and the uptake of Pb(II) ions increases with the initial Pb(II) concentration. The initial rapid uptake rate is due to the availability of the uncovered surface area of the adsorbent, since the adsorption kinetics depends on the surface area of the adsorbent. Initially, with a relatively bare surface, the available surface area is very large as compared to the density of Pb(II) ions and consequently, the initial rate of adsorption for the first 40 min is very high. With increasing coverage, the fraction of the bare surface rapidly diminishes and Pb(II) ions have to compete among themselves for the adsorption sites. Thus, the rate of adsorption becomes slower with the passage of time and reaches a constant value approaching equilibrium (Walker and Weatherley, 2001). It is also observed that the highest initial Pb(II) concentration at 300 ppm exhibited the fastest initial uptake rate.

3.3. Effect of initial Pb(II) concentrations on pH profile

Fig. 3 shows the effect of initial Pb(II) concentrations on pH profile. The bulk solution pH shows a sharp increase during the first 15 min of reaction period before reaching
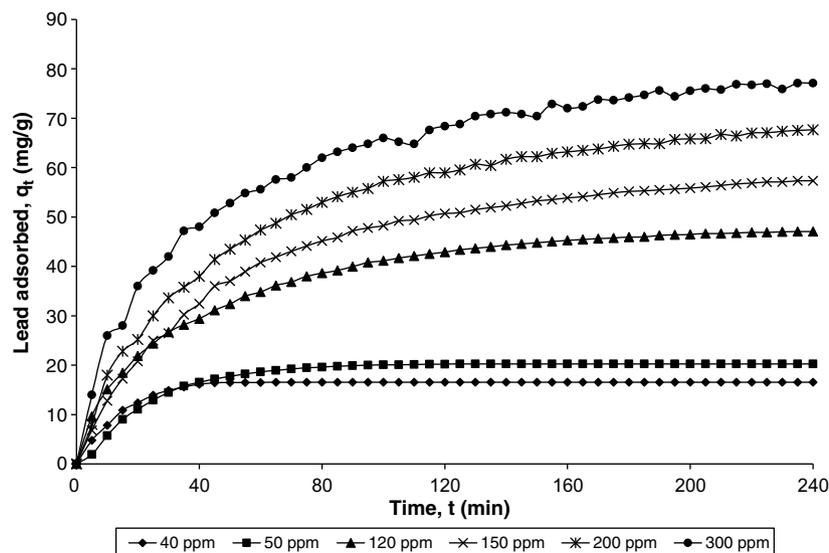

Fig. 2. Effect of initial Pb(II) concentrations on amount of Pb(II) adsorbed on PSAC.
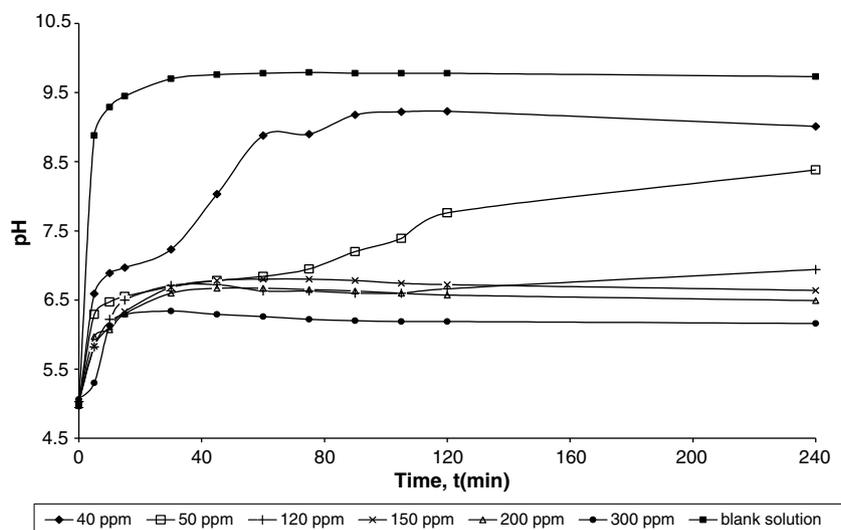
Fig. 3. Effect of initial Pb(II) concentrations on pH profile.

a plateau, indicating equilibrium. This is reflective of the low pH_{PZC} of PSAC at 1.9 which indicates high affinity of the surface of PSAC towards H^+ ions in bulk solution. This consequently causes rapid adsorption of H^+ ions and at the same time, swift reduction of H^+ in the bulk solution occurs and pH increases as a result. The increase of initial Pb(II) concentration from 40 to 120 ppm renders significant reduction of equilibrium pH from about 9 to 7 while further increases of the initial Pb(II) concentration to 300 rpm marginally reduce the equilibrium pH. This observation can be elucidated as such: in the bulk solution, as Pb(II) concentration increases, competition with H^+ (in bulk solution) for adsorption sites on PSAC increases at least twofold since each Pb(II) ion can occupy two adsorption sites provided by acidic functional groups. As a result, the amount of free H^+ ions that remains in the bulk solution increases, causing lower equilibrium pH. At initial Pb(II) concentration of 120 ppm, the amount of Pb(II) ions is sufficient to prevent mass H^+ adsorption and thus, the equilibrium pH is slightly acidic at about 6.9.

3.4. Effect of agitation speed on amount of lead adsorbed on PSAC

Agitation is an important parameter in adsorption phenomena, influencing the distribution of the solute in the bulk solution and the formation of the external boundary film (Grégorio et al., 2007). The initial rate of adsorption of Pb(II) ions by PSAC is more rapid at higher agitation speeds but Pb(II) concentration for all agitation speeds gradually approaches the same final adsorbed equilibrium concentrations on PSAC at about 47.6 mg g^{-1}. This can be explained by the fact that increasing agitation speed reduces the film boundary layer surrounding particles, thus increases the external film transfer coefficient (Onal, 2006) and the adsorption capacity (Weber and DiGiano, 1996). Under these conditions, the value of the external diffusion

coefficient becomes larger and subsequently the boundary layer becomes very thin and approaches to the laminar sublayer at high agitation speeds. This result is also in agreement with previous studies on dye adsorption onto activated clay (Ho et al., 2005) and shale oil ash (Al-Qodah, 2000).

3.5. Adsorption kinetics

Adsorption dynamics is useful to describe the solute uptake rate which controls the residence time of adsorbate uptake at the solid-solution interface. Five kinetics models were used to analyze adsorption kinetics at different initial Pb(II) concentrations and agitation speed, namely, pseudo-first-order, pseudo-second-order, Elovich equation, intra-particle diffusion and liquid film diffusion models.

The pseudo first-order model is presented by the following equation (Lagergren, 1898; Ho, 2004):

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \tag{2}$$

The plot of $\log(q_{e-}q_t)$ against t provides a linear relationship from which k_1, constant of pseudo first-order adsorption (min^{-1}) and q_e, adsorption capacity at equilibrium (mg g^{-1}) are determined from the slope and intercept of the plot, respectively, given that q_t is the adsorption capacity at time t, (mg g^{-1}).

The pseudo second-order model is presented by the following equation (Demirbas et al., 2004):

$$\left(\frac{t}{q_t}\right) = \frac{1}{k_2 q_e^2} + \frac{1(t)}{q_e} \tag{3}$$

The plot of t/q_t against t provides a linear relationship from which k_2, rate constant of pseudo second-order adsorption (g mg^{-1} min^{-1}) and q_e, adsorption capacity at equilibrium (mg g^{-1}) are determined from the slope and intercept of the

plot, respectively. The initial adsorption rate is presented by Eq. (4) (Ho, 2004):

$$h = kq_e^2 \qquad (4)$$

The Elovich model is presented by the following equation (Chien and Clayton, 1980; Sparks et al., 1980):

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \qquad (5)$$

where α is the initial adsorption rate (mg g^{-1} min^{-1}) and β is desorption constant (g mg^{-1}).

The intraparticle diffusion model is presented by the following equation (Weber and Morris, 1962):

$$q_t = k_{int}t^{0.5} \qquad (6)$$

where k_{int} is the intraparticle diffusion rate constant (mg g^{-1} min$^{-1/2}$). If intraparticle diffusion is involved in the adsorption process, then the plot of square root of time against the uptake (q_t) would result in a linear relationship and the intraparticle diffusion would be the controlling step if this line passes through the origin.

The liquid film diffusion model is presented by the following equation (Boyd et al., 1947; Gupta and Bhattacharyya, 2006):

$$\ln(1 - F) = -k_{fd}t \qquad (7)$$

where k_{fd} is the external mass transfer coefficient (min^{-1}). A linear plot of $\ln(1-F)$ vs t, whereby $F = q_t/q_e$, with zero intercept would suggest that the kinetics of the adsorption process is controlled by diffusion through the liquid film surrounding the solid adsorbent.

Table 1 shows the adsorption kinetics parameters of pseudo first-order and pseudo second-order models. It is observed that the adsorption kinetics data fit both models very well ($R^2 > 0.9$). Judging by the high R^2 values, it is surmised that the real-time data collection via ISE is a highly consistent and applicable technology for determination of adsorption kinetics. The first-order rate constants are determined to be between 0.0117 to 0.1276 min^{-1} and 0.0164 to 0.0191 min^{-1} for adsorption at different initial Pb(II) concentrations and agitation speeds, respectively. As observed in a good number of cases, the first-order mechanism suffered from inadequacies when applied to Pb(II) ions adsorption on activated carbon (Tan et al., 2007; Namasivayam and Prathapa, 2007). One of the major discrepancies was observed when q_e values obtained from Lagergren plots were compared with the experimental q_e values (Ho and McKay, 1998b). The experimental q_e values differ greatly from the corresponding values derived from the pseudo first-order equation. Thus, it is evident that good linearity of the Lagergren pseudo first-order plots is no assurance that the interactions will follow first-order kinetics. The adsorption data also fit the pseudo second-order model well judging by similar high R^2 values. Experimental and theoretical q_e values of the second-order model indicate better consistencies as compared to the first-order model as shown by significantly lower standard deviation (SD) values in general. These results imply that the adsorption system adheres to the pseudo second-order kinetics which further suggests that chemisorption is the rate-controlling step (Ho and McKay, 2000). Table 2 provides a comparison of the adsorption kinetics parameters

Table 1

Adsorption kinetics parameters of pseudo first-order and pseudo second-order models

Concentration (ppm)	Pseudo 1st order					Pseudo 2nd order				
	$q_{e,exp}$ (mg g^{-1})	k_1 (min^{-1})	$q_{e,cal\,1}$ (mg g^{-1})	R^2	SD (%)	k_2 (g mg^{-1} min^{-1})	H (mg g^{-1} min)	$q_{e,cal\,2}$ (mg g^{-1})	R^2	SD (%)
40	16.52	0.1276	39.26	0.9464	57.97	0.0886	29.17	18.15	0.9953	9.14
50	20.27	0.0442	22.30	0.9989	12.24	0.0622	41.53	25.84	0.9944	12.53
120	47.20	0.0180	36.16	0.9984	6.11	0.0255	69.91	52.36	0.9987	1.67
150	60.10	0.0159	52.37	0.9929	14.75	0.0165	89.46	73.53	0.9962	14.31
200	78.38	0.0117	64.55	0.9931	21.45	0.0171	111.27	80.65	0.9963	2.02
300	82.40	0.0136	60.42	0.9860	36.40	0.0205	142.04	83.33	0.9973	1.12
Agitation speed (rpm)										
200	47.60	0.0180	36.15	0.9984	9.25	0.0255	69.91	52.35	0.9987	2.85
300	49.42	0.0164	33.64	0.9906	33.84	0.0290	76.96	51.54	0.9995	5.23
400	48.75	0.0191	28.86	0.9874	68.35	0.0342	89.14	51.02	0.9996	5.23

Table 2

Comparison of adsorption kinetics parameters of Pb(II) on different adsorbents (based on maximum adsorption capacity)

Adsorbent	$q_{e,exp}$ (mg g^{-1})	k_1 (min^{-1})	k_2 (g mg^{-1} min^{-1})	pH	References
Viscum album L.	832.0	6.05	2.06	3	Erenturk and Malkoc (2007)
Euphorbia rigida activated carbon	257.36	9.612	0.000365	5	Gerçel and Gerçel (2007)
Clinoptilolite	38.69	0.025	0.00081	4.5	Günay et al. (2007)
Tree fern	38.1	–	0.00617	4.9	Ho (2005)
Palm shell activated carbon	82.40	0.0136	0.0205	5	This study

– denotes "data not available".

Table 3
Adsorption kinetics constants of Elovich, intraparticle diffusion and liquid film diffusion models

Concentration (ppm)	Elovich			Intraparticle diffusion		Liquid film diffusion	
	α (mg g^{-1} min^{-1})	β (g mg^{-1})	R^2	k_{int} (mg g^{-1} min$^{-1/2}$)	R^2	k_{fd} (min^{-1})	R^2
40	0.6154	0.3466	0.8121	0.8353	0.7085	0.1254	0.9464
50	2.0601	0.1645	0.9716	1.8309	0.9176	0.0441	0.9989
120	2.8285	0.0827	0.9982	3.7308	0.9899	0.0180	0.9984
150	2.9180	0.0575	0.9951	5.3624	0.9848	0.0159	0.9929
200	3.7424	0.0523	0.9942	5.9142	0.9919	0.0118	0.9931
300	5.8510	0.0516	0.9952	5.9423	0.9757	0.0105	0.9860
Agitation speed (rpm)							
200	2.8285	0.0827	0.9982	3.7308	0.9899	0.0180	0.9981
300	4.7897	0.0872	0.9986	3.5154	0.9775	0.0163	0.9906
400	8.0265	0.0970	0.9939	3.1481	0.9645	0.0191	0.9874

of Pb(II) on different adsorbents taken from numerous literatures.

Table 3 shows the adsorption kinetics constants of Elovich, intraparticle diffusion and liquid film diffusion models. The Elovich model does not predict any definite mechanism but has been found useful in describing predominantly chemical adsorption on highly heterogeneous adsorbents (Gupta and Bhattacharyya, 2006) and is useful for this study since it is postulated that Pb(II) ions are adsorbed to the activated carbon via chemisorptive bonds. The Elovich constants, α and β, at different initial concentrations have values in the ranges of 0.6154–5.8510 mg g^{-1} min^{-1} and 0.0516–0.3466 g mg^{-1}, respectively. With regards to three different agitation speeds, their α and β values are in the range of 2.8285–8.0265 mg g^{-1} min^{-1} and 0.0827–0.0970 g mg^{-1} correspondingly. Teng and Hsieh (1999) proposed that constant α is related to the rate of chemisorption while β is related to the surface coverage. The constants depend significantly on the amount of adsorbent with the adsorption constant, α, being the more sensitive parameter. Since α represents the initial rate of adsorption, the results indicate that the rate can be enhanced by increasing the initial Pb(II) concentration and agitation speed of the impeller. A higher value of α indicates that a better adsorption mechanism is observed. Similar results are also obtained by Ho and McKay for adsorption of Cu(II) on peat (Ho and McKay, 1998a).

In a batch system with rapid stirring, there is a possibility that the transport of adsorbate from solution into the pores (bulk) of the adsorbent is the rate-controlling step (McKay and McConvey, 1981). Diffusion from the solid–liquid interface to the interior of the solid particles plays a very important role (Walker and Weatherley, 2001). The single empirical resistance model used here assumes that diffusion occurs in the pore structure of the adsorbent and that this diffusion is described by Fick's second law. The intraparticle diffusion rate is obtained from the plots q_t versus $t^{1/2}$. In theory, the gradient of this line can be linearised into four regions representing different stages of mass transfer of adsorbates onto adsorbents (Tan et al., 2007). The initial stage represents external mass transfer,

with the following three stages representing intraparticle diffusion in the macro, meso and micropore structure of the adsorbent (Ho and McKay, 1998c). In this study, the intraparticle diffusion rate constant, k_{int}, has values from 0.8353 to 5.9423 mg g^{-1} min$^{-1/2}$ as for the case of different initial concentrations. With regards to different agitation speeds, the diffusion rate constant, k_{int}, ranges from 3.1481 to 3.7308 mg g^{-1} min$^{-1/2}$. It is likely that a large number of Pb(II) ions diffuse into the pores before being adsorbed (Gupta and Bhattacharyya, 2006). Nevertheless, although there is good linearity of plots created by the intraparticle diffusion model, they do not have a zero intercept. The plots' intercepts vary from 0.5603 to 14.84 indicating that intraparticle diffusion may not be the controlling factor in determining the kinetics of the process.

Diffusion from the bulk liquid phase to the surface of an adsorbent may play an important role in determining the rate processes. The rate constant for liquid film diffusion, k_{fd}, at different initial concentrations is within the range of 0.0105–0.1254 min^{-1}. At different agitation speeds, rate constants of liquid film diffusion, k_{fd}, vary from 0.0163 to 0.0191 min^{-1}. Again, the plots however, do not pass through the origin despite providing good linear plots. Thus, liquid film diffusion is surmised not to be the predominant mechanism for Pb(II) adsorption on PSAC.

4. Conclusions

In general, usage of ISE was very suitable for real-time adsorption kinetics data collection as it facilitated recording of adsorption data at very specific and short time intervals. The adsorption at higher initial Pb(II) concentrations occurred at a relatively faster rate whereas adsorption equilibrium was reached in a shorter period of time for lower initial Pb(II) concentrations. Adsorption of Pb(II) on PSAC was more rapid at higher agitation speeds than at lower speeds. Increases of initial Pb(II) concentration from 40 to 120 ppm renders significant reduction of equilibrium pH from about 9 to 7 while further increases of the former to 300 rpm marginally reduce the latter. The kinetics data

were marginally better fitted with pseudo second-order and Elovich models as compared to the other kinetics models. It is therefore suggested that chemisorption was the rate-controlling step for adsorption of Pb(II) onto PSAC.

Acknowledgements

References

Al-Qodah, Z., 2000. Adsorption of dyes using shale oil ash. Water Res. 34 (17), 4295–4303.

Boyd, G.E., Adamson, A.W., Myers, L.S., 1947. The exchange adsorption of ions from aqueous solutions by organic zeolites: II. Kinetics. J. Am. Chem. Soc. 69, 2836–2848.

Chen, J.P., Lin, M., 2001. Equilibrium and kinetics of metal ion adsorption onto a commercial H-type granular activated carbon: experimental and modeling studies. Water Res. 35 (10), 2385–2394.

Chien, S.H., Clayton, W.R., 1980. Application of Elovich equation to the kinetics of phosphate release and sorption in soil. Soil Sci. Soc. Am. J. 44, 265–268.

Demirbas, E., Kobya, M., Senturk, E., Ozkan, T., 2004. Adsorption kinetics for the removal of chromium(VI) from aqueous solutions on the activated carbons prepared from agricultural wastes. Water SA 30 (4), 533–540.

Department of Environment (DOE) 2002, Malaysian Environmental Quality Report, (2002) ISSN 0127-6433.

Erenturk, S., Malkoc, E., 2007. Removal of lead(II) by adsorption onto *Viscum album* L.: effect of temperature and equilibrium isotherm analyses. Appl. Surf. Sci. 253 (10), 4727–4733.

Gerçel, O., Gerçel, H.F., 2007. Adsorption of lead(II) ions from aqueous solutions by activated carbon prepared from biomass plant material of *Euphorbia rigida*. Chem. Eng. J. 132, 289–297.

Grégorio, C., Harmel, N.P., Frédéric, G., Capucine, R., 2007. Removal of C.I. basic Green 4 (Malachite Green) from aqueous solutions by adsorption using cyclodextrin-based adsorbent: kinetic and equilibrium studies. Sep. Purif. Technol. 53 (1), 97–110.

Günay, A., Arslankaya, E., Tosun, I., 2007. Lead removal from aqueous solution by natural and pretreated clinoptilolite: adsorption equilibrium and kinetics. J. Hazard. Mater. 146, 362–371.

Gupta, S.S., Bhattacharyya, K.G., 2006. Adsorption of Ni(II) on clays. J. Colloid Interf. Sci. 295 (1), 21–32.

Gustafsson, J.P., 2006. VMINTEQ 2.50 Software Manual (downloaded from http://www.lwr.kth.se/English/OurSoftware/vminteq/)," KTH, Department of Land and Water Resources Engineering, Stockholm, Sweden.

Ho, Y.S., 2004. Citation review of Lagergren kinetic rate equation on adsorption reactions. Scientometrics 59 (1), 171–177.

Ho, Y.S., 2005. Effect of pH on lead removal from water using tree fern as the sorbent. Biores. Technol. 96 (11), 1292–1296.

Ho, Y.S., McKay, G., 1998a. A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents. Trans. IChemE 76B, 332–340.

Ho, Y.S., McKay, G., 1998b. Sorption of dye from aqueous solution by peat. Chem. Eng. J. 70 (2), 115–124.

Ho, Y.S., McKay, G., 1998c. Kinetic models for the sorption of dye from aqueous solution by wood. Trans. IChemE 76B, 183–191.

Ho, Y.S., McKay, G., 2000. The kinetics of sorption of divalent metal ions onto sphagnum moss peat. Water Res. 34, 735–742.

Ho, Y.S., Chiang, C.C., Hsu, Y.C., 2005. Sorption kinetics for dye removal from aqueous solution using activated clay. Sep. Sci. Technol. 36, 2473–2488.

Issabayeva, G., Aroua, M.K., Sulaiman, N.M.N., 2006. Removal of lead from aqueous solutions on palm shell activated carbon. Biores. Technol. 97, 2350–2355.

Kadirvelu, K., Senthilkumar, P., Thamaraiselvi, K., Subburam, V., 2002. Activated carbon prepared from biomass as adsorbent: elimination of Ni(II) from aqueous solution. Biores. Technol. 81 (1), 87–90.

Kurniawan, T.A., Chan, G.Y.S., Lo, W.H., Babel, S., 2006. Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals. Sci. Total Environ. 366 (2–3), 409–426.

Lagergren, S., 1898. Zur theorie der sogenannten adsorption gelöster stoffe. Kungliga Svenska Vetenskapsakademiens, Handlingar 24 (4), 1–39.

Lopez-Ramon, M.V., Stoeckli, F., Moreno-Castilla, C., Carasco-Martin, F., 1999. On the characterisation of acidic and basic surface sites on carbons by various techniques. Carbon 37, 1215–1221.

Lu, J., Chen, R., He, X., 2002. A lead ion-selective electrode based on a calixarene carboxyphenyl azo derivative. J. Electroanal. Chem. 528, 33–38.

McKay, G., McConvey, I.F., 1981. The external mass transfer of basic and acidic dyes onto wood. J. Chem. Technol. Biotechnol. 31, 401–408.

Mullet, M., Fievet, P., Szymczyk, A., Foissy, A., Reggiani, J.C., Pagetti, J., 1999. A simple and accurate determination of the point of zero charge of ceramic membranes. Desalination 121, 41–48.

Namasivayam, C., Prathapa, K., 2007. Adsorptive removal of silica onto 'waste' Fe(III)/Cr(III) hydroxide: kinetics and isotherms. Coll. Surf. A 295 (1–3), 55–60.

Onal, Y., 2006. Kinetics of adsorption of dyes from aqueous solution using activated carbon prepared from waste apricot. J. Hazard. Mater. B 137, 1719–1728.

Rao, M.M., Ramesh, A., Rao, G.P.C., Seshaiah, K., 2006. Removal of copper and cadmium from the aqueous solutions by activated carbon derived from *Ceiba pentandra* hulls. J. Hazard. Mater. B129, 123–129.

Ryu, Z., Zheng, J., Wang, M., Zhang, B., 1999. Characterization of pore size distributions on carbonaceous adsorbents by DFT. Carbon 37 (8), 1257–1264.

Sparks, D.L., Zelazny, L.W., Martens, D.C., 1980. Kinetics of potassium desorption in soil using miscible displacement. Soil Sci. Soc. Am. J. 44, 1205–1208.

Tan, I.A.W., Hameed, B.H., Ahmad, A.L., 2007. Equilibrium and kinetic studies on basic dye adsorption by oil palm fibre activated carbon. Chem. Eng. J. 127 (1–3), 111–119.

Teng, H., Hsieh, C., 1999. Activation energy for oxygen chemisorption on carbon at low temperatures. Ind. Eng. Chem. Res. 38 (1), 292–297.

Walker, G.M., Weatherley, L.R., 2001. Adsorption of acid dyes from aqueous solution: the effect of adsorbent pore size distribution and dye aggregation. Chem. Eng. J. 77 (9), 201–206.

Weber, W.J., DiGiano, F.A., 1996. Process dynamics in environmental systems. John Wiley & Sons, Inc., New York.

Weber, W.J., Morris, J.C., 1962. Advances in water pollution research: removal of biologically resistant pollutants from waste waters by adsorption. In: Proceedings of the International Conference on Water Pollution Symposium, vol. 2, pp. 231–266.