

Single and binary adsorptions isotherms of Cd(II) and Zn(II) on palm kernel shell based activated carbon

Muhammad^{a,b}, T.G. Chuah^a, Yunus Robiah^a, A.R. Suraya^a, T.S.Y. Choong^{a*}

^aDepartment of Chemical and Environmental Engineering, Faculty of Engineering, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

Tel. +60 (3) 8946 6293; Fax +60 (3) 8656 7120; email: tsyc2@yahoo.co.uk

^bDepartment of Chemical Engineering, Faculty of Engineering, Malikussaleh University, Lhokseumawe-Aceh, Indonesia

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ABSTRACT

A batch adsorption study was conducted to investigate the suitability of palm kernel shell (PKS)-based activated carbon for the removal of cadmium and zinc ions from aqueous solutions. Single component equilibrium data were analyzed using the Langmuir, Freundlich and Redlich-Peterson isotherms. Overall, the Redlich-Peterson isotherm showed the best fit for all adsorption under investigation. As the binary adsorption is competitive, the extended Langmuir (EL) model could not predict well the binary component isotherm. Three correlative models, the modified extended Langmuir (MEL), modified extended Freundlich (MEF) and modified extended Redlich-Peterson (MERP) models were used to fit binary system equilibrium data. It was found that the binary isotherm data could be described well by the modified extended Langmuir model.

Keywords: Palm kernel shell; Cadmium; Zinc; Binary isotherm; Adsorption

1. Introduction

Heavy metal contamination exists in aqueous waste streams of many industries, such as metal plating, mining and agriculture. Heavy metals are not degradable and tend to accumulate in living organisms, causing various diseases and disorders [1–3]. Zinc and cadmium are among the harmful heavy metal waste produced. Table 1 shows the Environmental Quality Act 1974, Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979 in Malaysia with selected parameter limits of effluent of heavy metals [4].

Competitive adsorption is important in wastewater treatment because most compounds to be adsorbed exist in solution with other adsorbable compounds [5]. Con-

sequently, a mutual reduction of the adsorptive capacity of each of the competing species is usually encountered in these aqueous systems.

Vilar et al. [6] studied the equilibrium uptake of binary systems ($\text{Pb}(\text{II}) + \text{Cu}(\text{II})$, $\text{Pb}(\text{II}) + \text{Cd}(\text{II})$ and $\text{Pb}(\text{II}) + \text{Zn}(\text{II})$) by algae *Gelidium*. Srivastava et al. [7] studied the feasibility of using bagasse fly ash (BFA) as an adsorbent for the individual and simultaneous removal of $\text{Cd}(\text{II})$ and $\text{Ni}(\text{II})$ metal ions from aqueous solutions; Alimohamadi et al. [8] investigated the binary sorption of copper and lead ions onto microorganism (*Rhizopus arrhizus*) using several concentrations of $\text{Cu}(\text{II})$ and $\text{Pb}(\text{II})$. Lao et al. [9] evaluated the potential application of leonardite for the decontamination of $\text{Cd}(\text{II})$ and $\text{Pb}(\text{II})$ polluted water. Luna et al. [10] performed adsorption of $\text{Cd}(\text{II})$ and $\text{Zn}(\text{II})$ ions from binary systems by using sargassum filipendula. Baig et al. [11] used wheat straw to adsorb $\text{Ni}(\text{II})$ and $\text{Zn}(\text{II})$.

* Corresponding author.

Table 1

Environmental Quality Act 1974, Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979, Malaysia: Selected parameter limits of effluent of Standards A and B (Department of Environment, DOE, Malaysia)

Parameters	Standard	
	A*	B ⁺
Mercury (Hg), mg/L	0.005	0.05
Cadmium (Cd(II)), mg/L	0.01	0.02
Arsenic (As), mg/L	0.05	0.10
Lead (Pb(II)), mg/L	0.10	0.50
Chromium (Cr), trivalent, mg/L	0.20	1.0
Copper (Cu(II)), mg/L	0.20	1.0
Nickel (Ni), mg/L	0.20	1.0
Zinc (Zn(II)), mg/L	1.0	1.0
Iron (Fe), mg/L	1.0	5.0

* This standard applies to the industrial and development projects which are located within catchment areas (areas upstream of surface or above sub-surface water supply intakes, for the purpose of human consumption including drinking).

⁺ Not close to the water source

Mahamadi et al. [12] studied adsorption of Pb(II), Cd(II) and Zn(II) ions onto eichhornia crassipes in binary and ternary systems. Pérez-Marín et al. [13] investigated the adsorption of Cd(II), Zn(II) and Pb(II) by orange wastes in binary systems. Srivastava et al. [14] investigated the competitive adsorption of Cd(II) and Zn(II) ions from binary systems using rice husk ash as an adsorbent.

Adsorption of activated carbon represents a highly effective method to remove low concentration metal ions from water and wastewater [15]. Adsorption using low cost carbon sorbents such as palm kernel shell (PKS) may be an economical alternative technology for the treatment of metal contaminated waste streams. The possible use of palm shell as activated carbon precursor was highlighted by several investigators [16,17].

The objective of this work is to study the removal of cadmium and zinc ions using activated carbon produced from palm kernel shell. Single and binary adsorption equilibriums are modelled using different form of adsorption isotherms.

2. Material and methods

2.1. Materials

In this study, analytical grade Cd(NO₃)₂.4H₂O and Zn(NO₃)₂.6H₂O used in the experiments were supplied by Fisher Scientific, Malaysia. Stock solutions of metal ions were prepared using deionized water. All solutions were adjusted to pH 7.0 using dilute NaOH and HNO₃.

Table 2

Surface area and pore characteristics of PKS-based activated carbon [18]

Parameters	Value
Average particle size, mm	0.25–0.6
S_{BET} , m ² /g	1146
V_{micro} , cc/g	0.43
V_{meso} , cc/g	0.12
V_{total} , cc/g	0.582
D_{micro} , Å	5.3
D_{meso} , Å	26.1

The palm kernel shell (PKS) based activated carbon was donated by K.D. Technology Sdn. Bhd., in granular form with particle sizes of 0.25–0.60 mm. These PKS based activated carbon are produced by steam activation at temperature of approximately 1000°C in a horizontal rotary kiln with heat recovery system [18]. The product specification and characteristics of the PKS-based activated carbon are as listed in Table 2.

2.2. Procedure

The effect of pH was first studied. The initial pH of the solution was adjusted using either HNO₃ or NaOH (Fisher Scientific, Malaysia) to obtain the desired initial pH at the range from 2.0 to 8.0. Initial concentrations of the solution and the adsorbent mass were fixed at 10 mg/L and 0.5 g, respectively. Batch studies were carried out at 30±1°C to investigate the optimum initial pH that will give the highest percent removal after 1 h. The pH readings were measured with a pH meter (inoLab, Germany).

Batch sorption studies were performed at different concentrations (5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 mg/L) to obtain the equilibrium isotherms. The metals chosen for the investigation in single component studies were cadmium(II), and zinc(II). For isotherm studies, a series of 1000 ml conical flasks were employed. Each conical flask was filled with 500 ml of metal ion solution of varying concentrations and adjusted to pH 7.0. For binary isotherms studies, a 1:1 ratio of cadmium-zinc solution was prepared. The conical flask with heavy metal ions solution was then shaken using an orbital incubator shaker, which was operated at 150 rpm and 30±1°C (Sepilau Saintifik, Malaysia). When the desired temperature was reached, a known amount of PKS-based activated carbon was added into the conical flask. Overall, the equilibrium was reached after six hours (from contact time studies). To ensure equilibrium was attained, 96 h of shaking time were used for all equilibrium experiments for single and binary systems. After this, the activated carbon was separated and the clarified supernatant solution was carefully decanted. The concentration of the metal ions in the solution was analyzed using AAS (Hitachi, Ltd. Z-8100,

Japan.) at the maximum wavelength (λ_{\max}) of 228.8 nm for cadmium and 213.9 nm for zinc, respectively.

The adsorbed amount at equilibrium, q_e (mg/g), can be calculated from:

$$q_e = \frac{V(C_o - C_e)}{m} \quad (1)$$

where C_0 (mg/L) is the initial metal ions concentration in liquid phase, C_e (mg/L) is metal ion concentration in liquid phase at equilibrium, V (L) is total volume of metal ion solution and m (g) is mass of adsorbent.

3. Results and discussion

3.1. Effect of initial pH

One of the major parameters controlling the sorption of metals on sorbents is the value of pH. Variations in pH could change the characteristics and availability of metal ions in solution as well as the chemical status of the functional groups responsible for adsorption [19]. A change in pH affects the adsorptive process through dissociation of functional groups on the adsorbent surface active sites. Adsorption of various anionic and cationic species on such adsorbents can be explained on the basis of the competitive adsorption of H^+ and OH^- ions with the adsorbates. It is a common observation that the surface adsorbs anions favorably at lower pH due to presence of H^+ ions, whereas the surface is active for the adsorption of cations at higher pH due to the deposition of OH^- ions [20]. The effect of initial pH on the adsorption equilibrium was studied by varying the initial pH of the solution with initial concentrations of 10 mg/L.

Fig. 1 indicates the effect of initial pH on the removal of cadmium and zinc onto activated carbon from aqueous solutions. It can be seen that the percent removal was very low at strong acidic condition. The percent removal increased from 64.0% to 75.5% for cadmium, and from 34.3% to 48% for zinc at initial pH 5.0–7.0, respectively. The maximum percent removal was observed at initial pH 7.0. At $pH > 8.0$ chemical precipitation was observed i.e. the OH^- ions from the solution formed some complexes with Cd(II) and Zn(II). It was also observed that the final pHs were reduced by approximately one unit as compared to the initial pH. For further studies the optimum initial pH chosen for Cd(II) and Zn(II) was 7.0.

3.2. Single component isotherms

Nonlinear optimisation techniques have been applied to determine the isotherm parameters. The isotherm parameters were determined by minimising an error function using Microsoft Excel Solver. The error function used in this work is the sum of the square of the errors (SSE) defined as [21]:

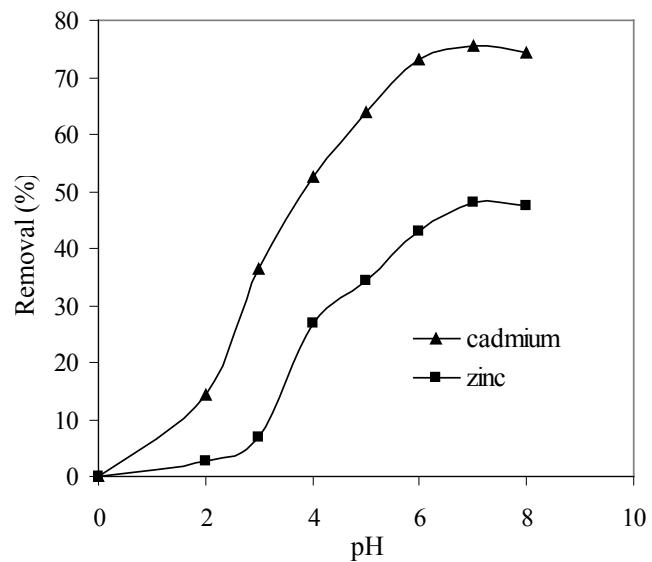


Fig. 1. Effect of the initial pH on adsorption of cadmium and zinc by PKS-based activated carbon at initial concentrations of 10 mg/L and a constant temperature of $30 \pm 1^\circ\text{C}$.

$$SSE = \sum_{i=1}^N \left(q_{e, \text{calc}} - q_{e, \text{exp}} \right)_i^2 \quad (2)$$

where the subscripts 'exp' and 'calc' indicated experimental and calculated values, and N the number of measurement.

The most widely used isotherm equation for modelling equilibrium is the Langmuir equation which is valid for monolayer sorption onto a surface with a finite number of identical sites which are homogeneously distributed over the sorbent surface and is given by Eq. (3) [22]:

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \quad (3)$$

where K_L indicates the solute adsorptivity (L/mg) and a_L is related to the energy of adsorption (L/mg). The Langmuir isotherm is characterized by a "plateau". The monolayer capacity of the Langmuir isotherm, q_m is given as [7]:

$$q_m = \frac{K_L}{a_L} \quad (4)$$

The Freundlich isotherm describes equilibrium on a heterogeneous surface where energy of the adsorption is not equivalent for all adsorption sites, thus allowing multi-layer adsorption. The Freundlich equation is given as [23]:

$$q_e = a_F C_e^{1/n} \quad (5)$$

where a_F is the Freundlich constant (L/mg) and n the Freundlich exponent. The larger the value of the adsorption capacity, a_F , the higher is the adsorption capacity. The more heterogeneous the surface, the closer $1/n$ is to zero.

Redlich-Peterson isotherm is an intermediate between Langmuir and Freundlich isotherms and can be described as [24]:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^\beta} \quad (6)$$

where K_R and a_R are parameters related to adsorption capacity (mg/g), and β is the heterogeneity factor (dimensionless).

The Redlich-Peterson isotherm incorporates the features of the Langmuir and Freundlich models. It has a more general form and includes a heterogeneity factor, β . The value of β lies between 0 and 1.

The Langmuir, Freundlich and Redlich-Peterson models for adsorption of cadmium and zinc onto PKS-based activated carbon were plotted in Fig. 2. The SSE and isotherm parameters for cadmium and zinc adsorption are presented in Table 3. The determination of the isotherm parameters for cadmium and zinc by nonlinear regression appears to give acceptable fits to the experimental data, especially the fitting of cadmium. As shown in Table 3, the values of β obtained for cadmium and zinc were very close to unity. Therefore the isotherm was approaching the Langmuir form. Indeed, the Langmuir and Redlich-Peterson isotherm overlapped each other as shown in Fig. 2.

Overall, the Redlich-Peterson isotherm model has the lowest SSEs for both cadmium and zinc, followed by the Langmuir model and the Freundlich model. However, the SSEs of Langmuir isotherms for both cadmium and zinc were only marginally higher than the Redlich-Peterson isotherm.

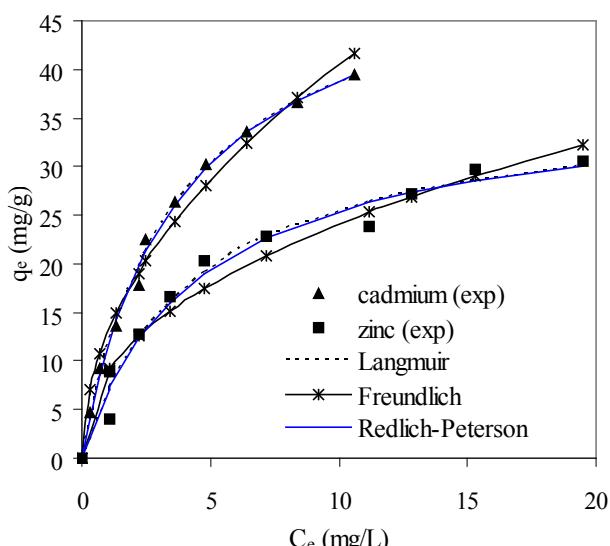


Fig. 2. Single component Langmuir, Freundlich and Redlich-Peterson isotherms and experimental data derived by nonlinear regression. The Langmuir and Redlich-Peterson isotherms overlapped each other.

Table 3

Langmuir, Freundlich and Redlich-Peterson isotherm parameters for single component adsorption of cadmium(II) and zinc(II) onto PKS-based activated carbon

Models	Cadmium(II)	Zinc(II)
Langmuir		
q_m , mg g ⁻¹	53.13	36.83
K_L , L mg ⁻¹	14.28	8.32
a_L , L mg ⁻¹	0.27	0.23
SSE	6.86	22.32
Freundlich		
a_F , mg g ⁻¹	12.86	8.83
$1/n$, L mg ⁻¹	0.49	0.44
SSE	31.33	45.86
Redlich-Peterson		
K_{RP} , mg g ⁻¹	14.79	8.48
a_{RP} , L mg ⁻¹	0.30	0.24
β	0.97	0.99
SSE	6.81	22.30

The maximum adsorption capacity (q_m), obtained from the Langmuir isotherm, of cadmium and zinc systems on PKS-based activated carbon are 53.13 mg/g and 36.83 mg/g, respectively. This showed that activated carbons used in this study had higher adsorption capacity on cadmium than zinc.

The adsorption capacities of cadmium and zinc onto PKS-based activated carbon were compared with other adsorbents reported in the literature, as summarized in Table 4. These were Eichhornia crassipes [12], rice husk [14], activated carbon (from bagasse) [25], Fontinalis antipyretica [26], bone char [27], synthetic zeolite A [28], crop milling waste (black gram husk) [29], vermiculite [30], tannic acid immobilised activated carbon [31], bentonite, zeolite 4A and zeolite 13X [32], bagasse fly ash [33], ceramium virgatum [34] and physic seed hull [35]. The adsorption capacity of PKS-based activated carbon is comparable to other adsorbents, except synthetic zeolite A which possessed nearly four times higher adsorption capacity of cadmium and zinc than that of PKS-based activated carbon. However the cost of synthetic zeolite is expected to be very much higher than the PKS-based activated carbon.

3.3. Binary component isotherms

Several isotherms have been proposed to describe equilibrium of binary mixture. These isotherms could be broadly divided into (a) predictive models where only individual isotherm parameters are used, and (b) correlative models where individual isotherm parameters and correction factors are used.

Table 4

Some values of q_m as reported in the literature on adsorption of cadmium and zinc ions using different adsorbents

Adsorbents	Metal ions	Monolayer adsorption, q_m (mg/g)	Reference
Activated carbon (from palm kernel shell)	Cd(II)	53.13	Present study
	Zn(II)	36.83	
Eichhornia crassipes	Cd(II)	9.92	[12]
	Zn(II)	7.18	
Rice husk ash	Cd(II)	3.04	[14]
	Zn(II)	5.88	
Activated carbon (from bagasse)	Cd(II)	38.03	[25]
	Zn(II)	31.11	
Fontinalis antipyretica	Cd(II)	29.2	[26]
	Zn(II)	15.1	
Bone char	Cd(II)	53.64	[27]
	Zn(II)	33.00	
Synthetic zeolite A	Cd(II)	194.45	[28]
	Zn(II)	179.77	
Crop milling waste (black gram husk)	Cd(II)	39.99	[29]
	Zn(II)	33.81	
Vermiculite	Cd(II)	63.34	[30]
	Zn(II)	71.89	
Tannic acid immobilised activated carbon	Cd(II)	1.51	[31]
	Zn(II)	1.23	
Zeolite 4A	Cd(II)	30.27	[32]
Zeolite 13X	Cd(II)	29.59	
Bentonite	Cd(II)	28.47	
Zeolite 4A	Zn(II)	42.82	
Zeolite 13X	Zn(II)	38.31	
Bentonite	Zn(II)	35.17	
Bagasse fly ash	Cd(II)	6.19	[33]
	Zn(II)	7.03	
Cerium virgatum	Cd(II)	39.70	[34]
Physic seed hull	Cd(II)	11.89	[35]
	Zn(II)	12.28	

The competitive effect of zinc ion (in equal concentration to cadmium) resulted in a decrease of cadmium sorption capacity in the binary system, as shown in Fig. 5. In the binary system sorption, the zinc ions bound stronger on the sites of PKS-based activated carbon. These results support the hypothesis that the preference of an adsorbent for metals was related to the existence of competitive binding with adsorbent surfaces [36]. In addition, there were possible interaction effects between different species in the solution and, in particular, potential interactions on the surface depending on the adsorption mechanism. The factors that affect the sorption preference of an adsorbent for different kinds of adsorbates may be related to the characteristics of the binding sites, the properties of the adsorbates and the solution chemistry. Nevertheless, it is

difficult to identify the exact mechanism from the physical and chemical properties of Cd(II) and Zn(II) ions which can explain the interactive mechanism and the increase in the selectivity for sorption of an adsorbate from the binary mixtures [12–14].

3.3.1. Predictive models

The single-component adsorption Langmuir isotherm can be extended to describe the adsorption for multisorbate solution as follows [37]:

$$q_{e,i} = \frac{K_{L,i}^0 C_{e,i}}{1 + \sum_{j=1}^N a_{L,i}^0 C_{e,j}} \quad (7)$$

where i is the number of components, $C_{e,i}$ is the equilibrium concentration of the component i in the multicomponent solution (mg/L), $q_{e,i}$ is the equilibrium uptake of the component i (mg/g), and $K_{L,i}^0$ and $a_{L,i}^0$ are the single component Langmuir parameters for component i . The extended Langmuir model assumes a homogeneous surface with respect to the energy of adsorption, no interaction between adsorbed species, and that all sites are equally available to all adsorbed species. The single-component parameter sets for the two heavy metals, obtained in section 3.2, were substituted into Eq. (7) to enable prediction of the binary component isotherms using the extended Langmuir (EL) isotherm. The EL model predictions and the experimentally measured values are presented in Fig. 3, respectively. The SSE values for the EL isotherm for both heavy metals are given in Table 5. From the SSE values, the quality of fit using the EL isotherm for zinc were rather good, however, the quality of fits for cadmium were very poor. From the ion interaction

analysis, the binary systems studied in this work were of competitive adsorption. As the extended Langmuir isotherms do not account for competitive adsorption, it is not surprised that it could not predict accurately the binary adsorption equilibrium [38].

3.3.2. Correlative models

Several isotherms have been proposed to describe equilibrium of competitive adsorption, namely the modified extended Langmuir (MEL), the modified extended Freundlich (MEF), and the modified extended Redlich-Peterson (MERP) models. These models are characterized by single metal system isotherm parameters and by additional correction factors estimated from the binary adsorption data.

For competitive adsorption, Schay [39] introduced the modified extended Langmuir model by incorporating interaction parameters, η :

$$q_{e,i} = \frac{K_{L,i}^0 (C_{e,i}/\eta_{L,i})}{1 + \sum_{j=1}^N a_{L,j}^0 (C_{e,j}/\eta_{L,j})} \quad (8)$$

where $\eta_{L,i}$ is the Langmuir correction coefficients of component i extracted from the competitive adsorption data.

The modified extended Freundlich isotherm is an empirical extension of the Freundlich isotherm whereby single component isotherm constants are combined with correlative constants derived from binary component equilibrium data [38].

The modified extended Freundlich model is restricted to binary component [40]:

$$q_{e,1} = \frac{a_{F,1}^0 C_{e,1}^{b_{F,1}^0 + b_{11}}}{C_{e,1}^{b_{11}} + a_{12} C_{e,2}^{b_{12}}} \quad (9)$$

and

$$q_{e,2} = \frac{a_{F,2}^0 C_{e,2}^{b_{F,2}^0 + b_{22}}}{C_{e,2}^{b_{22}} + a_{21} C_{e,1}^{b_{21}}} \quad (10)$$

where $a_{F,1}^0$ and $b_{F,1}^0$ are single-component Freundlich constants. To evaluate the correlative constants takes

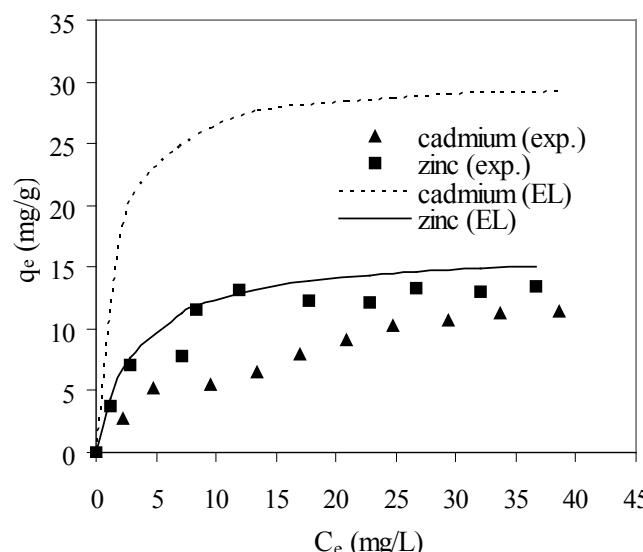


Fig. 3. Application of extended Langmuir (EL) isotherm model for simultaneous sorption of cadmium-zinc onto PKS-based activated carbon.

Table 5

Comparison of the binary system adsorption constants for each component evaluated from the modified extended Langmuir, modified extended Freundlich and modified extended Redlich-Peterson models for simultaneous sorption of cadmium and zinc onto PKS

Component	Modified extended Langmuir (MEL)			Modified extended Freundlich (MEF)						Modified extended Redlich-Peterson (MER)			
	$\eta_{L,1}$	$\eta_{L,2}$	SSE	b_{11}	a_{12}	b_{12}	b_{22}	a_{21}	b_{21}	SSE	η_1	η_2	SSE
Cadmium	15.94	6.05	11.12	0.50	10.54	0.34	—	—	—	10.94	21.87	12.74	13.45
Zinc	1.31	1.45	10.60	—	—	—	0.56	0.01	0.30	32.52	1.17	1.31	22.72

$b_{F,1}^0 + b_{11} = 1$ and $b_{F,2}^0 + b_{22} = 1$ in Eqs. (9) and (10), respectively [41].

Mathews [42] extended the three-parameter isotherm of Redlich and Peterson in a manner analogous to that used by Schay with the Langmuir isotherm:

$$q_{e,i} = \frac{K_{R,i}^0 (C_{e,i}/\eta_i)}{1 + \sum_{j=1}^N (a_{R,j}^0 C_{e,j}/\eta_j)^{\beta_j^0}} \quad (11)$$

where η_i is the correction coefficient of component i estimated from correlative multicomponent adsorption data. Parameters $K_{R,i}^0$, $a_{R,j}^0$ and β_j^0 are obtained from single component data.

The MEL, MEF and MERP models for adsorption of cadmium and zinc onto PKS-based activated carbon are plotted in Fig. 4. The model parameters of the MEL, MEF and MERP models estimated from binary adsorption data and their respective SSE are given in Table 6. Based on Fig. 4, the isotherm parameters for cadmium and zinc obtained using nonlinear regression method provided in Microsoft Excel Solver appeared to give acceptable fits to the experimental data.

Table 6 shows that the SSE values for all three correlative models for cadmium were relatively low, with the lowest being the MEF model. For equilibrium of zinc in

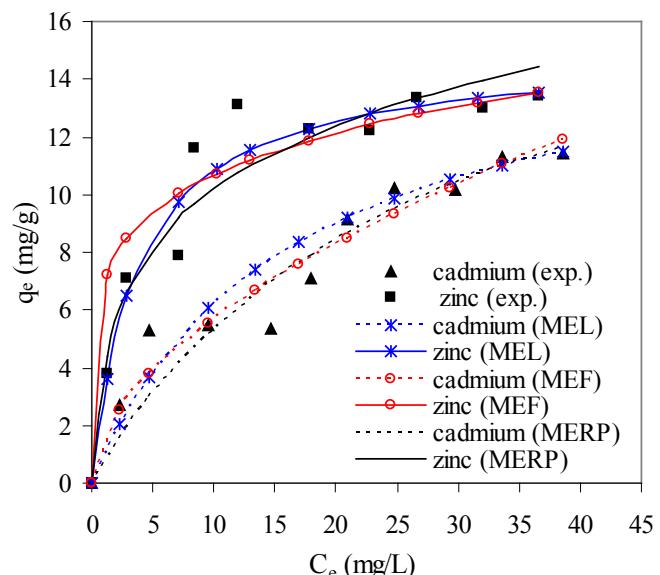


Fig. 4. Application of modified extended Langmuir (MEL), modified extended Freundlich (MEF) and modified extended Redlich–Peterson (MERP) for simultaneous sorption of cadmium–zinc onto PKS-based activated carbon.

Table 6
Comparison of the binary system adsorption constants for each component evaluated from the EL, MEL, MEF and MER models for simultaneous sorption of cadmium and zinc onto PKS

Isotherm models	Components	
	Cadmium	Zinc
Extended Langmuir (EL)		
SSE	3675.05	42.32
Modified extended Langmuir		
$\eta_{L,1}$	15.94	1.31
$\eta_{L,2}$	6.05	1.45
SSE	11.12	10.60
Modified extended Freundlich		
b_{11}	0.50	—
a_{12}	10.54	—
b_{12}	0.34	—
b_{22}	—	0.56
a_{21}	—	0.01
b_{21}	—	0.30
SSE	10.94	32.52
Modified extended Redlich–Peterson		
η_1	21.87	1.17
η_2	12.74	1.31
SSE	13.45	22.72

binary mixtures, the MEL model provided the lowest SSE, followed by the MERP and the MEF.

The data in Fig. 4 indicate that there is a strong competition in adsorptive capacity between zinc and cadmium. The uptakes of both zinc and cadmium were reduced in the binary mixtures. The adsorptive capacity of cadmium in the mixture is very much reduced by the presence of zinc, resulting in a much lower adsorptive capacity. Unlike single component system, the adsorptive capacity of cadmium in the binary mixtures is less than zinc.

Because of the competition between the two metal ion species for the surface sites, the individual adsorption constants cannot define exactly the binary adsorption behaviour. The phenomena of metal ions competition is complex and need further investigation. For that reason, better accuracy is achieved by using isotherms related to the individual isotherm parameters and to correction factors such as the competitive MEL model.

The values of the modified Langmuir coefficient (η) were much higher than 1.0 explaining why the extended Langmuir model used earlier could not predict well the binary-system adsorption. The use of the interaction term η improved the fit of the modified Langmuir model significantly.

The values of the modified Langmuir coefficient for zinc were close to unity, suggesting that the extended Langmuir model could also be used to predict the two-component data [43]. However, the modified Langmuir coefficient for cadmium were much greater than unity indicating that the extended Langmuir model could not be used to predict the binary-system adsorption [14].

4. Conclusion

Single component equilibrium data for both cadmium and zinc were found to be fitted best using the Redlich-Peterson model. The maximum adsorption capacity of cadmium and zinc on PKS-based activated carbon are 53.13 mg/g and 36.83 mg/g, respectively. However, the adsorption of cadmium in the binary system is lower than zinc.

The predictive models, namely the extended Langmuir described rather well the adsorption equilibrium of zinc in a binary mixture. However, they did not accurately predict the adsorption equilibrium of cadmium in a binary mixture. Correlative models were found to describe well the binary components adsorption equilibrium by using single component parameters and additional correction factors. Based on the sum of the square of the error, the adsorption isotherms of binary component metal ions are best fitted by the modified extended Langmuir model.

Symbols

a_F	— Freundlich constant , L/mg
a_L	— Langmuir constant for energy of the sorbent, L/mg
a_R	— Redlich-Peterson constants, L/mg
b_{ij}	— Correlation constants in empirical Freundlich
C_e	— Residue metal ions concentration remaining after adsorption, mg/L
C_o	— Initial dye concentration, mg/L
K_F	— Freundlich constant for adsorption capacities, L/mg
K_L	— Langmuir constant, L/mg
KR	— Redlich-Peterson constants, L/mg
$1/n$	— Freundlich exponent, surface heterogeneity
m	— Amount of activated carbon used for metal ions adsorption during equilibrium, g
N	— Number of points in data set
q_e	— Amount of metal ions adsorbed by activated carbon at equilibrium, mg/g
q_m	— Monolayer capacity of the Langmuir isotherm, mg/g
V	— Initial volume of metal ions used, L

Greek

β	— Redlich-Peterson exponent
$\eta_{L,i}$	— Langmuir correction coefficients of component i
η_i	— Redlich-Peterson correction coefficient of component i

References

- [1] Q. Yang, Y.L. Wang and Z Xing, Biosorption of cadmium by fungal biomass of *Aspergillus niger*, *Biomed. Environ. Sci.*, 18 (2005) 141–145.
- [2] G. León and M.A. Guzmán, Facilitated transport of copper through bulk liquid membranes containing different carriers: compared kinetic study, *Desalination*, 223 (2008) 330–336.
- [3] Z. Sun, Y. Wu, S. Yao, E. Liu and F. Li, Study on effective species of heavy metals in lacustrine sediment core from Xijiu Lake, Taihu Lake catchment, *China Environ. Earth Sci.*, 59 (2009) 371–377.
- [4] T.G. Chuah, A. Jumasiah, I. Azni, S. Katayon and T.S.Y. Choong, Rice husk as a potentially low-cost biosorbent for heavy metal and dye removal: an overview, *Desalination*, 175 (2005) 305–316.
- [5] P. Le Cloirec and C. Faur, Adsorption of organic compounds onto activated carbon—applications in water and air treatments, In: T.J. Bandosz, ed., *Activated Carbon Surfaces in Environmental Remediation*, Elsevier Ltd., 2006, pp. 375–419.
- [6] V.J.P. Vilar, C.M.S. Botelho and R.A.R. Boaventura, Effect of Cu(II), Cd(II) and Zn(II) on Pb(II) biosorption by algae *Gelidium*-derived materials, *J. Hazard. Mater.*, 154 (2008) 711–720.
- [7] V.C. Srivastava, I.D. Mall and I.M. Mishra, Equilibrium modeling of single and binary adsorption of cadmium and nickel onto bagasse fly ash, *Chem. Eng. J.*, 117 (2006) 79–91.
- [8] M. Alimohamadi, G. Abolhamad and A. Keshtkar, Pb(II) and Cu(II) biosorption on *Rhizopus arrhizus* modeling mono- and multi-component systems, *Minerals Eng.*, 18 (2005) 1325–1330.
- [9] C. Lao, Z. Zeledon, X. Gamisans and M. Sole, Sorption of Cd(II) and Pb(II) from aqueous solutions by a low-rank coal (leonardite), *Separ. Purif. Technol.*, 45 (2005) 79–85.
- [10] A.S. Luna, A.L.H. Costa, A.C.A. da Costa and C.A. Henriques, Competitive biosorption of cadmium(II) and zinc(II) ions from binary systems by *Sargassum filipendula*, *Bioresource Technol.*, 101 (2010) 5104–5111.
- [11] K.S. Baig, H.D. Doan and J. Wu, Multicomponent isotherms for biosorption of Ni²⁺ and Zn²⁺, *Desalination*, 249 (2009) 429–439.
- [12] C. Mahamadi and T. Nharingo, Competitive adsorption of Pb²⁺, Cd²⁺ and Zn²⁺ ions onto *Eichhornia crassipes* in binary and ternary systems, *Bioresource Technol.*, 101 (2010) 859–864.
- [13] A.B. Pérez-Marín, A. Ballester, F. González, M.L. Blázquez, J.A. Muñoz, J. Sáez and V.M. Zapata, Study of cadmium, zinc and lead biosorption by orange wastes using the subsequent addition method, *Bioresource Technol.*, 99 (2008) 8101–8106.
- [14] V.C. Srivastava, I.D. Mall and I.M. Mishra, Removal of cadmium(II) and zinc(II) metal ions from binary aqueous solution by rice husk ash, *Colloids Surfaces A: Physicochem. Eng. Aspects*, 312 (2008) 172–184.
- [15] S.A. Dastgheib and D.A. Rockstraw, A model for the adsorption of single metal ion solutes in aqueous solution onto activated carbon produced from pecan shells, *Carbon*, 40 (2002) 1843–1851.
- [16] M.Z. Hussien, R.S.H. Tarmizi, Z. Zainal, R. Ibrahim and M. Bardi, Preparation and characterization of active carbons from oil palm shells, *Carbon*, 34 (1996) 1447–1454.
- [17] W.M.A.W. Daud, W.A.W. Shabuddin and S.M. Zaki, The effects of carbonization temperature on pore development in palm-shell-based activated carbon, *Carbon*, 38 (2000) 1925–1932.
- [18] S.M. Mak, The characterization of steam-activated palm kernel shell activated carbons and the role of porosity in adsorption and catalytic applications, MSc thesis, Universiti Putra Malaysia, 2003.
- [19] A. Kapoor and T. Viraraghavan, Nitrate removal from drinking water, *J. Environ. Eng.*, 123 (1997) 371–380.
- [20] A. Jumasiah, Adsorption of basic and acid dyes using palm kernel shell-base activated carbon, MSc thesis, Universiti Putra Malaysia, 2005.
- [21] S.J. Allen, G. McKay and J.F. Porter, Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems, *J. Colloid Interf. Sci.*, 280 (2004) 322–333.
- [22] I. Langmuir, The adsorption of gases on plane surface of glass, mica and platinum, *J. Amer. Chem. Soc.*, 40 (1918) 1361–1403.
- [23] H.M.F. Freundlich, Over the adsorption in solution, *J. Phys. Chem.*, 57 (1906) 385–470.
- [24] O. Redlich and D.L Peterson, A useful adsorption isotherm, *J.*

- Phys. Chem., 63 (1959) 1024.
- [25] D. Mohan and K.P. Singh, Single and multicomponent adsorption of cadmium and zinc using activated carbon derived from bagasse — an agricultural waste, *Wat. Res.*, 36 (2002) 2304–2318.
- [26] R.J.E. Martins, R. Pardo and R.A.R. Boaventura, Cadmium(II) and zinc(II) adsorption by the aquatic moss *fontinalis* anti-pyretica: effect of temperature, pH and water hardness, *Wat. Res.*, 38 (2004) 693–699.
- [27] K.K.H. Choy and G. McKay, Sorption of metal ions from aqueous solution using bone char, *Environ. Intern.*, 31 (2005) 845–854.
- [28] A.M. El-Kamash, A.A. Zaki and M.A. El-Geleel, Modeling batch kinetics and thermodynamics of zinc and cadmium ions removal from waste solutions using synthetic zeolite A, *J. Hazard. Mater.*, B127 (2005) 211–220.
- [29] A. Saeed, M. Iqbal and M.W. Akhtar, Removal and recovery of lead(II) from single and multimetal (Cd, Cu, Ni, Zn) solutions by crop milling waste (black gram husk), *J. Hazard. Mater.*, 117 (2005) 65–73.
- [30] M.G. da Fonseca, M.M. de Oliveira and L.N.H. Arakaki, Removal of cadmium, zinc, manganese and chromium cations from aqueous solution by a clay mineral, *J. Hazard. Mater.*, B137 (2006) 288–292.
- [31] A. Ucer, A. Uyanik and S.F. Aygun, Adsorption of Cu(II), Cd(II), Zn(II), Mn(II) and Fe(III) ions by tannic acid immobilised activated carbon, *Separ. Purif. Technol.*, 47 (2006) 113–118.
- [32] G.P.C. Rao, S. Satyaveni, A. Ramesh, K. Seshaiah, K.S.N. Murthy and N.V. Choudary, Sorption of cadmium and zinc from aqueous solutions by zeolite 4A, zeolite 13X and bentonite, *J. Environ. Manage.*, 81 (2006) 265–272.
- [33] V.C. Srivastava, I.D. Mall and I.M. Mishra, Modelling individual and competitive adsorption of cadmium(II) and zinc(II) metal ions from aqueous solution onto bagasse fly ash, *Separ. Sci. Technol.*, 41 (2006) 2685–2710.
- [34] A. Sari and M. Tuzen, Biosorption of cadmium(II) from aqueous solution by red algae (*ceramium virgatum*): Equilibrium, kinetic and thermodynamic studies, *J. Hazard. Mater.*, 157 (2008) 448–454.
- [35] M. Mohammad, S. Maitra, N. Ahmad, A. Bustam, T.K. Sen and B.K. Dutta, Metal ion removal from aqueous solution using physic seed hull, *J. Hazard. Mater.*, 179 (2010) 363–372.
- [36] G. Yan and T. Viraraghavan, Heavy-metal removal from aqueous solution by fungus *Mucor rouxii*, *Wat. Res.*, 37 (2003) 4486–4496.
- [37] K.K.H. Choy, G. McKay and J.F. Porter, Sorption of acid dyes from effluents using activated carbon, *Resources, Conserv. Recycling*, 27 (1999) 57–71.
- [38] G. McKay and B. Al-Duri, Extended empirical freundlich isotherm for binary systems: A modified procedure to obtain the correlative constants, *Chem. Eng. Process.*, 29 (1991) 133–138.
- [39] G. Schay, On the thermodynamics of physical adsorption of gases (vapors) at the surface of solid adsorbents, *J. Colloid Interf. Sci.*, 35 (1971) 254–265.
- [40] F. Pagnanelli, M. Trifoni, F. Beolchini, A. Esposito and F. Veglio, Equilibrium biosorption studies in single and multi-metal systems, *Process Biochem.*, 37 (2001) 115–124.
- [41] C.J. Radke and J.M. Prausnitz, Thermodynamics of multisolute adsorption from dilute solutions, *AIChE J.*, 18 (1972) 761–768.
- [42] W. Fritz and E.U. Schlünder, Competitive adsorption of two dissolved organics onto activated carbon. I: Adsorption equilibria, *Chem. Eng. Sci.*, 36 (1981) 731–741.
- [43] Z. Aksu, U. Acikel, E. Kabasakal and S. Tezer, Equilibrium modelling of individual and simultaneous biosorption of chromium (VI) and nickel (II) onto dried activated sludge, *Wat. Res.*, 36 (2002) 3063–3073.