Adsorption of Heavy Metal Ions on Surface of Functionalized Oil Palm Empty Fruit Bunch Fibers: Single and Binary Systems
(Penjerapan Ion Logam Berat pada Permukaan Terfungsi Gentian Tandan Kosong Kelapa Sawit: Sistem Tunggal dan Penduaan)

MOHD SHAIFUL SAJAB*, CHIN HUA CHIA, SARANI ZAKARIA & MIKA SILLANPÄÄ

ABSTRACT

The functionalization of surface charges on oil palm empty fruit bunch (EFB) fibers was modified by grafted carboxylic acid and polymer amine groups. Single and binary adsorption of Cu(II), Ni(II), Mo(VI) and As(V) were investigated by competitiveness in the adsorbents. The mechanism of each metal ion was deliberately studied on kinetics-diffusion (intraparticle diffusion) and isotherm adsorption models (Langmuir and Freundlich). Competitiveness of metal ions was found in the selectivity of Cu(II) > Ni(II) and Mo(VI) > As(V) in the binary solution. The regeneration of adsorbents was performed up to five cycles of an adsorption/desorption process and the reduction of adsorption performance was less than 14.5%. Therefore, this promises low-cost adsorbents for metal ion uptake, showing potential for removal and recovery in industrial wastewater treatment.

Keywords: Binary adsorption; desorption; isotherm; kinetics; low-cost adsorbent

ABSTRAK

Pemfungsian cas permukaan pada gentian kosong tandan kelapa sawit (EFB) telah terubah suai dengan cantuman kumpulan asid karboksil dan polimer amina. Penjerapan tunggal dan penduaan bagi Cu(II), Ni(II), Mo(VI) dan As(V) telah dikaji dengan persaingan penjerapan dalam bahan penjerap. Mekanisme bagi setiap logam berat telah dipertimbangkan ke atas kinetik-resapan (resapan intrazarah) dan model penjerapan isoterma (Langmuir dan Frendulich). Persaingan ion logam berat telah dijumpai pada pemilihan bagi Cu(II) > Ni(II) dan Mo(VI) > As(V) dalam larutan penduaan. Penjanaan semula bahan penjerap telah dijalankan sehingga lima kali kitaran proses penjerapan/nyahjerapan dan pengurangan prestasi penjerapan adalah kurang dari 14.5%. Oleh itu, ia menjanjikan bahan penjerap kos-rendah bagi pengambilan ion logam, menunjukan potensi bagi penyingkiran dan pemulihan dalam rawatan air buangan industri.

Kata kunci: Bahan penjerap kos-rendah; isoterma; kinetik; nyahjerapan; penjerapan penduaan

INTRODUCTION

Hazardous heavy metals can have serious effects on human physiology and biological systems (Ayhan 2008). Severe environmental problems over the years have led to strict regulation of wastewater discharge from industry. However, the attention has focused on less developed countries, as a result of their recent rapid growth of industry and the high cost of wastewater treatment. Loose regulation authority in some countries is also a main cause of untreated effluents disposed into the ecosystem (Hardoy et al. 1992).

Various techniques of wastewater treatment have been well investigated for their performance and ability to remove hazardous pollution from effluent (O'Connell et al. 2008). However, to achieve cost-effective industrial waste treatment, the adsorption technique may be the cheapest method widely available and it encompasses regeneration of the adsorbent (Ayhan 2008). Activated carbon is recommended for the treatment of wastewater due to its great adsorption capability. However, low-cost adsorbents from minerals, waste products and agriculture are more promising for wide application (Babel & Kurniawan 2003;

Bailey et al. 1999). Several studies have reported decent adsorption capacity from a modified low-cost adsorbent that is comparable to the commercially used adsorbent (Wan Ngah & Hanafiah 2008).

Agro-based materials as low-cost adsorbents have been considered in agricultural countries with large amounts of agriculture waste produced every year. Malaysia is one of the largest palm oil producers in the world. The oil palm industry can generate extensive amounts of by-products (e.g. empty fruit bunch (EFB) fibers) (Zakaria et al. 2013). Oil palm EFB fibers have been proposed as adsorbent material due to high amounts of hydroxyl groups, which can be modified to enhance adsorption capability. In previous research, we focused on modified EFB fibers via carboxylic and amine groups grafted and demonstrated good adsorption capabilities for dye removal (Sajab et al. 2013).

The multi-component adsorbates in simultaneous adsorption have compelled many researchers to investigate the mechanism behavior of multiple adsorbates on adsorbents. The competitiveness of adsorbates from ionic

interaction and selectivity of the adsorbent (adsorbate charges and radius ions) are the main factors contributing the effect of multi-component adsorption. Since multiple metal ions are more likely to exist in wastewater effluent, various studies have been performed on promising adsorbents for various applications (Akbari et al. 2015; Merrikhpour & Jalali 2013; Mohan & Chander 2000; Wang & Li 2009; Xiao & Thomas 2004).

The aim of the present study was to investigate the adsorption behavior of heavy metal ions, i.e. Cu(II), Ni(II), Mo(VI) and As(V)), in single and binary systems on the surface functionalization of oil palm EFB fibers. The intraparticle diffusion model was used to explain the adsorption kinetics and accessibility of the heavy metal ions, while Langmuir and Freundlich isotherm models were used to study the adsorption mechanism and predict maximum adsorption capacity of the adsorbent. The possibilities of regeneration and recycling of the adsorbent were investigated in up to five cycles.

EXPERIMENTAL DETAILS

PREPARATION OF ADSORBENT

Oil palm EFB fibers were prepared according to the previous study (Sajab et al. 2013). Surface functionalization on the EFB fibers was carried out with a ratio of 100 g/L of the fibers individually in solutions of 0.6 M citric acid and 5% polyethylenimine (w/v) (MW ~750,000, 50 wt. % in H_2O). Carboxylic acid-grafted EFB fibers (CA-EFB) underwent an esterification process from being heated to 120°C, while polymer amines grafted EFB fibers (PA-EFB) were cross-linked with glutaraldehyde (1% v/v). Modified EFB fibers were washed several times to completely remove excess chemicals. Adsorbents were dried and kept in desiccators for further use.

PREPARATION OF METAL ION SOLUTIONS

Stock solutions of Cu(II), Ni(II), Mo(VI) and As(V) from Sigma-Aldrich were prepared. The concentrations of metal ions were analyzed by several wavelengths, Cu(II) at 324.7 nm, Ni(II) at 221.6 nm, Mo(VI) at 202.0 nm and As(V) at 189.0 nm, using inductively coupled plasma optical atomic emission spectrometry (ICP-OES) model iCAP 6300 (Thermo Electron Corporation, USA). The pH's metal ion solution was adjusted from diluting NaOH and HNO_3 solutions. Aliquot of the diluted HNO_3 solution was controlled to elude precipitation of metal ions.

ADSORPTION EXPERIMENTS

Kinetic adsorption experiments were conducted in a flask containing a modified EFB fiber dosage of 1 g/L and metal ion solution. The initial pH and concentration of the metal ion solution varied (pH3-9 and 25-150 mg/L). The mixture was stirred at a constant speed of 250 rpm with a magnetic stirrer for 4 h until equilibrium was achieved. During the adsorption, aliquots of solution (~0.1 mL) were withdrawn at the preferred time intervals, filtered and analysed. The adsorbed concentration of metal ion solution at time t, q_t (mmol/g), was calculated using the following:

$$q_t = \frac{(C_0 - C_t)V}{m},$$ (1)

where C_0 and C_e are the initial and equilibrium concentrations of the metal ion solution (mmol/L), respectively; V is the volume of the solution (mL); and m is the mass of the adsorbent (g).

Adsorption isotherm was performed in a series of concentrations of metal ion solutions (10, 25, 50, 100, 150 mg/L) at different temperatures (20, 40 and 60°C). The mixture of 20 mL of metal ion solution and 0.05 g of modified EFB fibers was placed in a rotary shaker with a controlled temperature at a constant speed of 200 rpm for 24 h. The final concentration of the metal ion solution (C_e) at equilibrium was measured to calculate the adsorbed amount of metal ions at final equilibrium (q_e) using the following:

$$q_e = \frac{(C_0 - C_e)V}{m}.$$ (2)

Binary components adsorption experiments were conducted using the same charges of metal ion solution. The mixtures of metal ion solution (Cu(II)/Ni(II) and Mo(VI)/As(V)) were stirred with selectivity of adsorbents (CA-EFB and PA-EFB fibers).

DESORPTION AND REGENERATION STUDIES

The adsorption was done with sufficient amounts of metal ions (150 mg/L) adsorbed in modified EFB fibers. The adsorbent was washed with deionized water to remove excess metal ion solution and dried overnight at 60°C. A desorption experiment was carried out using different eluent solutions (0.1 M) of HCl, CH_3COOH and NaOH. The mixture of 20 mL of eluent and 0.05 g of fiber adsorbent was stirred for 6 h. The amount of metal ions desorbed from fibers was calculated using the following:

$$\text{Amount of dyes desorbed} (\%) = \frac{\text{Concentration desorbed (mg/L)}}{\text{Concentration adsorbed (mg/L)}} \times 100\%.$$

(3)

Desorbed EFB fibers were washed to remove excess eluent and dried until a constant weight. Regeneration of EFB fibers was performed up to five cycles using a similar concentration of metal ion solution at 20°C.

RESULTS AND DISCUSSION

EFFECT OF PH

The adsorption edge (Figure 1) responds on the pH-dependence of the adsorption metal ion onto EFB fibers by ion exchange (Plazinski & Rudzinski 2010). The

adsorption efficiency of Cu(II) and Ni(II) increases at pH>5. In contrast, Mo(VI) and As(V) escalated otherwise at pH<7. Attributions of carboxyl and amine groups on the CA-EFB and PA-EFB fibers have increased the surface charge of the adsorbents and served as electrostatic attraction for metal ion adsorption (Sajab et al. 2013). Thus, the competition of different charges of the aqueous solution and metal ions contributed to the low adsorption uptake (Hu et al. 2015; Maiti et al. 2012). Moreover, reduction of Cu(II) and Ni(II) uptakes at the higher pH>7 may be the result of the precipitation that occurs by hydroxide formation of OH– ions from solution (Mohan & Singh 2002). The optimum pH in metal ion solution (Cu(II), Ni(II) = pH7 and Mo(VI), As(V) = pH3) was chosen for subsequent adsorption studies.
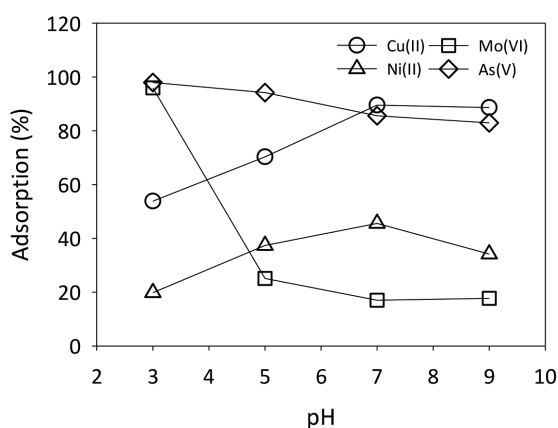

FIGURE 1. Effect of pH on adsorption of metal ions solution Cu(II) and Ni(II) onto CA-EFB, Mo(VI) and As(V) onto PA-EFB (adsorbate dosage: 25 mg/L; pH3-9; temperature: 20°C)

ADSORPTION KINETICS

The pseudo adsorption kinetics model is well known for its acceptability of experimental data. The obtained kinetics constant can be used to compare the different adsorbent limitations (Maiti et al. 2012). To further understand the adsorption behavior, the intraparticle diffusion model is more suitable to gain insight into the adsorption mechanism (Qiu et al. 2009). This model was used to predict the mechanism of the adsorbate molecules to diffuse towards the adsorbent site (Weber & Morris 1963):

$$q_t = k_i t^{1/2} + C, \qquad (4)$$

where k_i is the intraparticle diffusion constant; and C is the constant for any experiment (mmol/g) as in the slope of plot of q_t against $t^{1/2}$. Two assumptions can be made from the plot; first, if the straight line passes through the origin, the intraparticle diffusion is the rate controlling step and second, the adsorption process may involve other mechanisms along with intraparticle diffusion. The linearity of the intraparticle diffusion (Figure 2) and
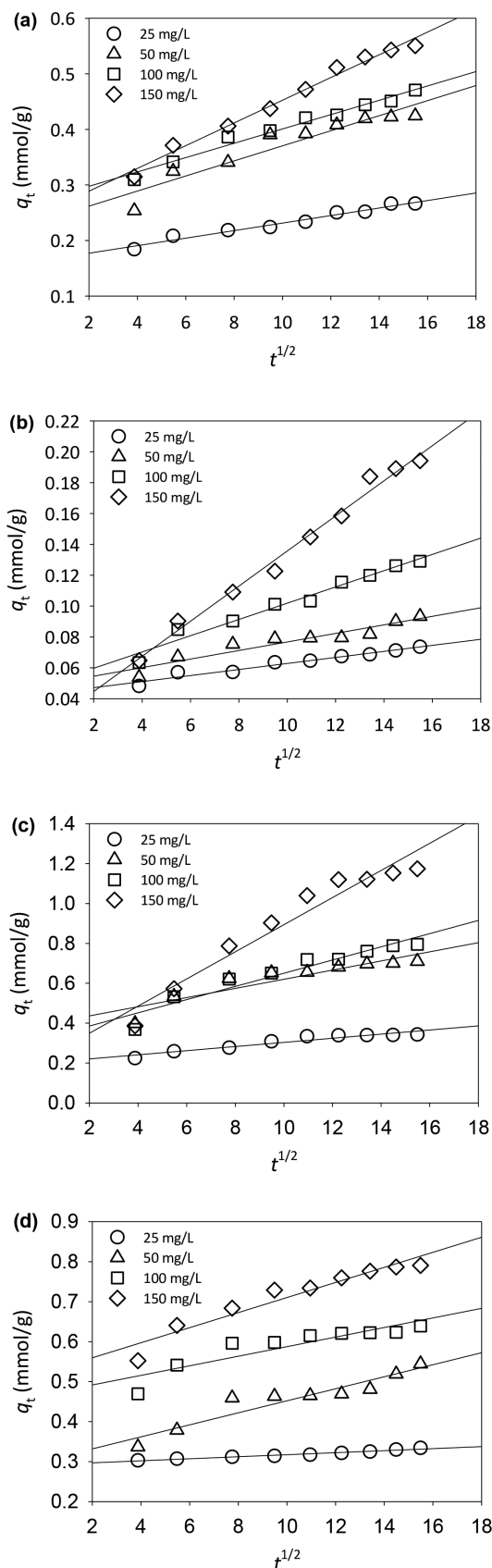

FIGURE 2. Plot linearized intraparticle diffusion from experimental data of: (a) Cu(II) onto CA-EFB, (b) Ni(II) onto CA-EFB, (c) Mo(VI) onto PA-EFB and (d) As(V) onto PA-EFB (adsorbate dose: 25-150 mg/L; temperature: 20°C; pH: 3 & 7)

calculation of the constant are summarized in Table 1. Observation of the single-line intraparticle diffusion model may suggest that adsorption occurs within a short time. To determine the initial adsorption, R_i is modified from (5) to the following (Wu et al. 2009):

$$q_{ref} = k_i t_{ref}^{1/2} + C, \qquad (5)$$

where t_{ref} is the longest time in the adsorption process and q_{ref} is the adsorption capacity at tref. Subtracting (5) from (4), the derived equation is as follows:

$$q_{ref} - q_t = k_i \left(t_{ref}^{1/2} - t^{1/2} \right). \qquad (6)$$

Rearrangement of (6) yields:

$$\left(\frac{q_t}{q_{ref}} \right) = 1 - R_i \left[1 - \left(\frac{t}{t_{ref}} \right)^{1/2} \right], \qquad (7)$$

where, which is defined as the initial adsorption factor and expressed as:

$$R_i = \frac{q_{ref} - C}{q_{ref}} = 1 - \left(\frac{C}{q_{ref}} \right), \qquad (8)$$

where R_i is the value of the ratio of the initial adsorption amount; and C is the final adsorption amount, q_{ref}. The initial adsorption behavior can be assumed as no existence initial adsorption ($R_i = 1$), weak initial adsorption ($1 > R_i > 0.9$), intermediate initial adsorption ($0.9 > R_i > 0.5$), strong initial adsorption ($0.5 > R_i > 0.1$) or approaching complete initial adsorption ($R_i < 0.1$) (Wu et al. 2009). The values of the initial adsorption calculated (R_i), presented in Table 1, were observed as the intermediate initial adsorption behavior existing in low-concentration metal ions and eventually weak initial adsorption when increasing the initial concentration (Ofomaja 2010).

ADSORPTION ISOTHERM

Briefly, the derivation of Langmuir assumed monolayer adsorption between the adsorbate molecules and adsorbent medium, while the Freundlich model explains the heterogeneous adsorption behavior of the adsorption mechanism.

The Langmuir isotherm model can be expressed as (Langmuir 1916):

$$q_e = \frac{Q_0 b C_e}{1 + b C_e}, \qquad (9)$$

where Q_0 is the maximum adsorption capacity per unit mass of adsorbent (mmol/g); and b is a constant related to the adsorption energy (L/mmol). To determine whether adsorption is 'favorable' or 'unfavorable', a dimensionless constant separation factor or equilibrium parameter, R_L, was calculated using the following:

$$R_L = \frac{1}{1 + b C_m}, \qquad (10)$$

where b is the Langmuir constant (L/mmol); and C_m is the highest initial metal ion concentration (mmol/L). The value of R_L indicates the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$).

The modified Langmuir model for multi-component adsorption is expressed as (Zhi-rong et al. 2008):

$$q_{e.i} = \frac{Q_{0.i} b_i C_{e.i}}{1 + \sum_{j=1}^{N} b_j C_{e.j}}, \qquad (11)$$

where $q_{e.i}$ is equilibrium adsorption for i metal ions (mmol/g) at equilibrium concentration (mg/L); b_i and $Q_{0.i}$ is the Langmuir constant (L/mmol) and maximum adsorption capacity per unit mass of adsorbent for i metal ions; and j is the number of metal ions in the system solution.

TABLE 1. Calculated kinetics constant intraparticle diffusion on metal ions adsorption

Metal ions	Initial concentration (mg/L)	Intraparticle diffusion		
		k_i (mmol/g min)	R_i	r^2
Cu(II)	25	0.0068	0.360	0.971
	50	0.0129	0.385	0.977
	100	0.0136	0.501	0.897
	150	0.0205	0.550	0.987
Ni(II)	25	0.0020	0.411	0.958
	50	0.0028	0.474	0.898
	100	0.0053	0.619	0.971
	150	0.0114	0.887	0.987
Mo(VI)	25	0.0103	0.416	0.911
	50	0.0230	0.449	0.829
	100	0.0331	0.599	0.920
	150	0.0680	0.798	0.945
As(V)	25	0.0025	0.126	0.970
	50	0.0022	0.291	0.894
	100	0.0021	0.339	0.807
	150	0.0019	0.399	0.924

The Freundlich isotherm model is expressed as (Freundlich 1906)

$$q_e = K_F C_e^{1/n_F},\qquad(12)$$

where K_F and $1/n_F$ are the Freundlich constants; with K_F representing the relative adsorption capacity of the adsorbent; and n_F representing the degree of dependence of adsorption on the equilibrium concentration of metal ions. The experimental data were plots for the non-linearized Langmuir and Freundlich models (Figure 3) and the calculated isotherm constants are summarized in Table 2. The correlation coefficient, r^2, of both models mostly fit (~0.9) given the nearly high correlation of the Langmuir model in the adsorption of Cu(II) and Ni(II), while the Freundlich model fit better in Mo(VI) and As(V). Due to the probabilities of both models fitting, the adsorption mechanism of monolayer and heterogeneous adsorbate/adsorbent may appear in the process.

The maximum adsorptions acquired from Langmuir, stated as Cu(II) and Ni(II) on CA-EFB fibers, were 1.996 and 0.134 mmol/g and adsorptions of Mo(VI) and As(V) on PA-EFB fibers were 1.957 and 0.980 mmol/g, respectively. The adsorption capacity of the metal ions increased at the lower temperature of 20°C rather than at the higher temperature of 60°C, which shows that the adsorption behavior was exothermic (Demirbas et al. 2006).

DESORPTION AND REGENERATION

The desorption efficiencies differ depending on eluent selection (Figure 4). Strong acids, such as HCl, have higher desorption of Cu(II) and Ni(II), up to 68.4 and 17.53 %, respectively, however, Mo(VI) and As(V) were easily desorbed using NaOH, at 98.6 and 73.1%, respectively. Strong acids and bases are assisted to desorb metal ions formed by electrostatic attraction, suggesting ion exchanges on the surface of the EFB fibers (Mall et al. 2006). The adsorption performance of Cu(II), Ni(II), Mo(VI) and As(V) after five cycles of adsorption/desorption shows a slight reduction of 6.7, 17.6, 12.2 and 17.9%, respectively (Table 4). The smaller ionic radius of metal ions may easily penetrate the small pores of the adsorbent and diffuse much faster on the adsorbent (Wang & Li 2009). However, the desorption capability of these metal ions became much more difficult, which resulted in less sustainability for adsorbent regeneration.

BINARY ADSORPTION

The binary adsorption of the cationic metal ions Cu(II) and Ni(II) shows the high affinity of Cu(II) versus Ni(II) toward CA-EFB fibers (Figure 5(a)), while Mo(VI) exhibited slightly good adsorption capacity in the mixtures of Mo(VI)/As(V) (Figure 5(b)). The values of the initial adsorption factor, R_i, of Cu(II), Ni(II),
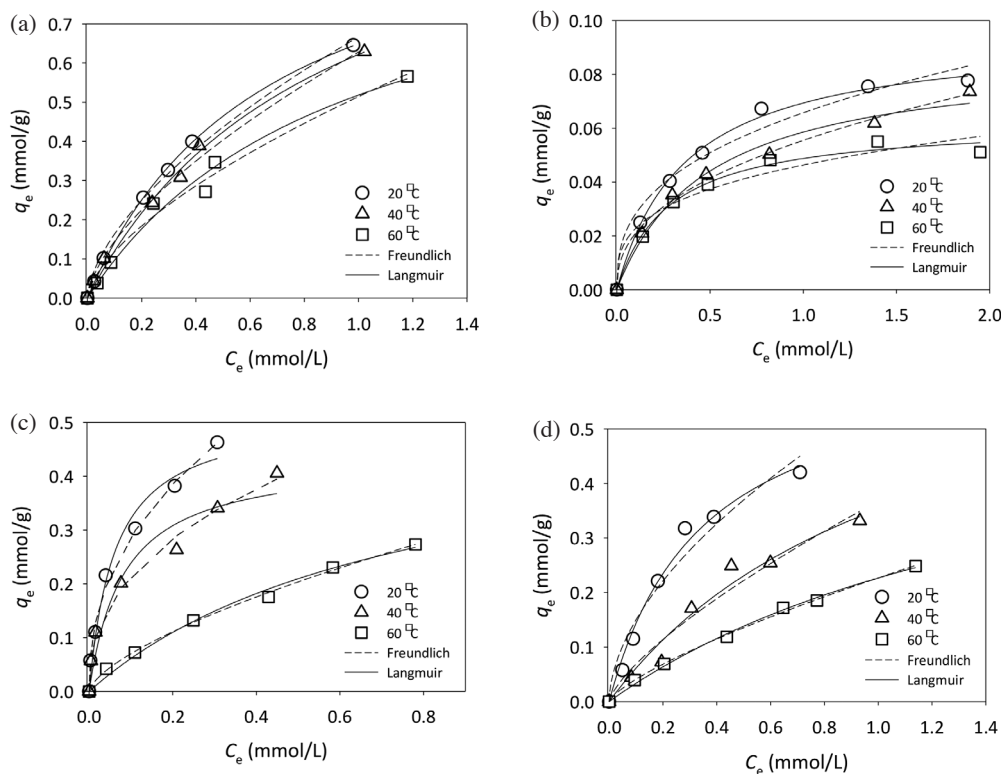

FIGURE 3. Non linearized isotherm adsorption of Langmuir and Freundlich of: (a) Cu(II) onto CA-EFB, (b) Ni(II) onto CA-EFB, (c), Mo(VI) onto PA-EFB and (d) As(V) onto PA-EFB (adsorbate dose: 25-150 mg/L; temperature: 20ºC; pH: 3 & 7)

TABLE 2. Calculated isotherm constants of Langmuir and Freundlich on metal ions
adsorption of Cu(II), Ni(II), Mo(VI) and As(V)

Metal ions	Temperatures (°C)	Langmuir model				Freundlich model		
		Q_0	b	R_L	r^2	K_F	n	r^2
Cu(II)	20	1.164	1.14	0.385	0.993	0.52	1.64	0.991
	40	1.077	1.51	0.323	0.999	0.48	1.57	0.993
	60	1.004	1.06	0.401	0.981	0.35	1.56	0.979
Ni(II)	20	0.095	2.71	0.151	0.993	0.06	2.70	0.952
	40	0.087	2.04	0.119	0.975	0.05	2.36	0.989
	60	0.062	3.55	0.191	0.977	0.01	3.22	0.906
Mo(VI)	20	1.275	16.2	0.041	0.974	0.53	2.35	0.993
	40	1.237	12.1	0.053	0.930	0.23	2.46	0.989
	60	0.508	1.30	0.344	0.987	0.18	1.51	0.997
As(V)	20	0.750	2.88	0.165	0.983	1.78	0.34	0.940
	40	0.643	0.89	0.390	0.958	1.37	0.25	0.939
	60	0.629	0.56	0.502	0.995	1.35	0.14	0.997

Note, Q_0 (mmol/g) = maximum adsorption capacity; b (L/mg) = constant related to adsorption the adsorption energy; R_L = equilibrium parameter; K_F (mmol/g) $(L/mg)^{1/n}$ = relative adsorption capacity; n = degree of dependence of adsorption; r^2 = coefficient correlation
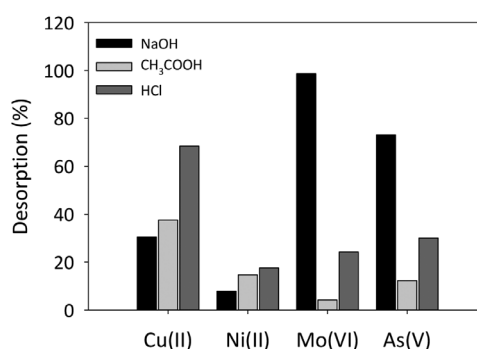

FIGURE 4. Desorption of metal ions on different eluents of NaOH, CH₃COOH
and HCL (adsorbate dose: 150 mg/L; temperature: 20°C; pH: 3 & 7)

TABLE 3. Regeneration of EFB fibers up to five cycles adsorption performances of
Cu(II), Ni(II), Mo(VI) and As(V)

Cycle	Adsorption (%)			
	Cu(II)	Ni(II)	Mo(VI)	As(V)
1	88.9	56.8	79.2	80.9
2	88.0	56.6	73.8	76.5
3	87.7	55.4	71.4	72.5
4	85.7	53.1	71.0	67.1
5	82.9	46.8	70.6	66.4

Mo(VI) and As(V) are 0.687, 0.512, 0.983 and 0.515, respectively. In the binary adsorption system of Cu(II)/ Ni(II), although both the metal ions show intermediate initial adsorption, the Cu(II) ions may have slightly higher initial adsorption than Ni(II). In the Mo(VI)/ As(V) system, Mo(VI) shows weak initial adsorption, which differs from the initial adsorption behaviors of As(V). Theoretically, the advantage of a smaller ionic radius of these metal ions provides higher accessibility of Ni(II) > Cu(II) and As(V) > Mo(VI) (Lide 1998; Şengil & Özacarb 2013). Thus, the smaller ionic radius of Ni(II) shows a shorter time for the metal ions to
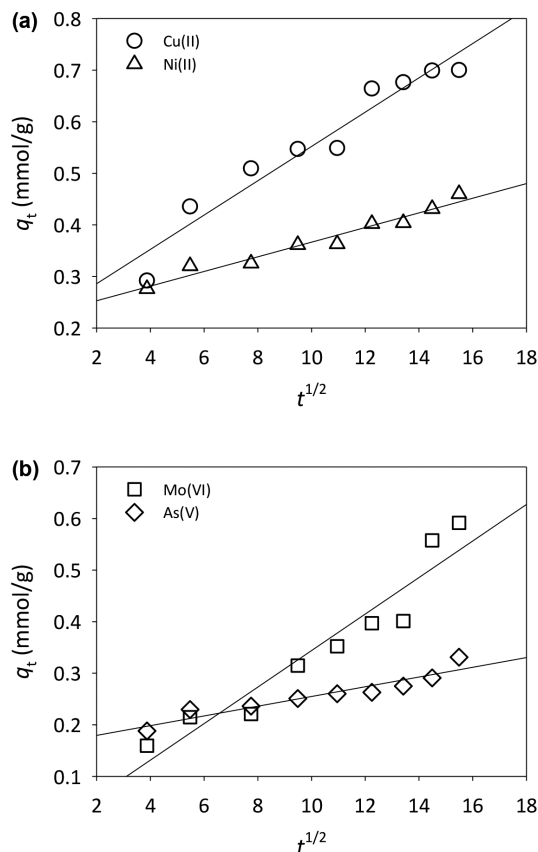
FIGURE 5. Adsorption competitiveness of metal ions, binary adsorption of (a) Cu(II) and Ni (II) onto CA-EFB and (b) Mo(VI) and As (V) onto PA-EFB (adsorbate dose: 100 mg/L; temperature: 20°C; pH: 3-7)

achieve an equilibrium state than Cu(II). The same behavior goes for the accessibility of As(V) to the PA-EFB fibers than Mo(VI). These different amounts of adsorbate uptake on the adsorbent can be assumed in the speciation in solution, surface heterogeneity and accessibility of adsorbate to the porous structure and adsorbate/adsorbent interactions (Xiao & Thomas 2004). The affinity of the divalent metal ions approaching the adsorbent may be due to the low ratio of the primary hydration number, N, and the hydrated radius, R_H, of metal divalent metal ions. This suggests that the small ratio of N/R_H has higher Columbic energy of attraction to the amorphous oxides of the adsorbent (Hokkanen et al. 2013; Trivedi & Axe 2001).

To extend the variation of competitive adsorption performance in each metal ion, the values of maximum adsorption in mixtures of the metal ions solution, Q_{0mix}, were calculated from the experimental data fitted by modified Langmuir and presented in Table 4. The competitiveness affecting metal ion uptake may be assumed from the ionic interaction on the metal ions. The ratio of the maximum adsorption from the Langmuir, from single-component adsorption Q_0 and binary adsorption Q_{0mix}, can represent the ionic interaction of metal ions (Mohan & Chander 2000). The interaction affecting adsorption can be assumed to be promoted by the presence of other metal ions (Q_{0mix} / Q_0 > 1); no interaction exists between the metal ions (Q_{0mix}

TABLE 4. Maximum adsorption capacity of binary adsorption of Cu(II)/Ni(II) and Mo(VI)/As(V)

Metal ions	Langmuir	Langmuir-modified		Q_{0mix}/Q_0
	Q_0	Q_{0mix}	r^2	
	Single	Binary		Binary
Cu(II)	1.164	0.533	0.993	0.458
Ni(II)	0.095	0.337	0.998	3.547
Mo(VI)	1.275	0.315	0.981	0.169
As(V)	0.750	0.282	0.996	0.376

/ Q_0 = 1) and adsorption is suppressed by the presence of other metal ions (Q_{0mix} / Q_0 < 1).

The speciation of metal ions on the fibers has many preferences related to solution chemistry, physicochemical properties of metal ions and characteristics of the binding sites, but these preferences are not conclusive with regard to the selectivity of metal ions on the adsorbent (Mahamadi & Nharingo 2010). Additionally, the different selectivity of the metal ion uptake may be due to specific ion exchange on the EFB fibers, type of metals or different experimental techniques (Merrikhpour & Jalali 2013).

CONCLUSION

In this study, both chemically modified CA-EFB and PA-EFB fibers performed well on adsorption capability based on cationic and anionic charge of metal ions. The competitive adsorption of the metal ions of Cu(II)/Ni(II) and Mo(VI)/As(V) demonstrated that the selectivity of metal ion uptake depended on the speciation of metal ions on the surface charges of the EFB fibers. The reduced adsorption rate efficiency from single to binary metal ions was significant, showing that the suppression resulting from the presence of metal ions reduced the adsorption performance in EFB fibers.

REFERENCES

Akbari, M., Hallajisani, A., Keshtkar, A.R., Shahbeig, H., Ghorbanian, S.A. 2015. Equilibrium and kinetic study and modeling of Cu(II) and Co(II) synergistic biosorption from Cu(II)-Co(II) single and binary mixtures on brown algae *C. indica*. *J. Env. Chem. Eng.* 3: 140-149.

Ayhan D. 2008. Heavy metal adsorption onto agro-based waste materials: A review. *J. Hazard. Mater.* 157: 220-229.

Babel, S. & Kurniawan, T.A. 2003. Low-cost adsorbents for heavy metals uptake from contaminated water: A review. *J. Hazard. Mater.* 97: 219-243.

Bailey, S.E., Olin, T.J., Bricka, R.M. & Adrian, D.D. 1999. A review of potentially low-cost sorbents for heavy metals. *Water. Res.* 33: 2469-2479.

Demirbas, A., Sari, A. & Isildak, O. 2006. Adsorption thermodynamics of stearic acid onto bentonite. *J. Hazard. Mater.* 135: 226-231.

Freundlich, H.M.F. 1906. Over the adsorption in solution. *J. Phys. Chem.* 57A: 385-470.

Hardoy, J.E., Mitlin, D. & Satterthwaite, D. 1992. *Environmental Problems in Third World Cities*. London: Earthscan.

Hokkanen, S., Repo, E. & Sillanpää, M. 2009. Competitive biosorption of Pb2+, Cu2+ and Zn2+ ions from aqueous solutions onto valonia tannin resin. *J. Hazard. Mater.* 166: 1488-1494.

Hu, H., Zhang, J., Lu, K. & Tian, Y. 2015. Characterization of *Acidosasa edulis* shoot shell and its biosorption of copper ions from aqueous solution. *J. Env. Chem. Eng.* 3: 357-364.

Langmuir, I. 1916. The constitution and fundamental properties of solids and liquids. Part. I: Solids. *J. Am. Chem. Soc.* 39: 2221-2295.

Lide, D.R. 1998. *Handbook of Chemistry and Physics*. Boca Raton: CRC Press.

Mahamadi, C. & Nharingo, T. 2010. Competetitive adsorption of Pb2+, Cd2+ and Zn 2+ ions onto *Eichhornia crassipes* in binary and ternary systems. *Bioresour. Technol.* 101: 859-864.

Mall, I.D., Srivastava, V.C., Kumar, G.V.A. & Mishra, I.M. 2006. Characterization and utilization of mesoporous fertilizer plant waste carbon for adsorptive removal of dyes from aqueous solution. *Colloid. Surf. A* 278: 175-187.

Maiti, A., Basu, J.K. & De, S. 2012. Experimental and kinetic modeling of As(V) and As(III) adsorption on treated laterite using synthetic and contaminated groundwater: Effects of phosphate, silicate and carbonate ions. *Chem. Eng. J.* 191: 1-12.

Merrikhpour, H. & Jalali, M. 2013. Comparative and competitive adsorption of cadmium, copper, nickel, and lead ions by Iranian natural zeolite. *Clean. Technol. Environ. Policy.* 15: 303-316.

Mohan, D. & Chander, S. 2000. Single component and multi-component adsorption of metal ions by activated carbons. *Colloid. Surf.* A 177: 183-196.

Mohan, D. & Singh, K.P. 2002. Single- and multi-component adsorption of cadmium and zinc using activted carbon derived from bagasse: An agricultural waste. *Water. Res.* 36: 2304-2318.

O'Connell, D.W., Birkinshaw, C. & O'Dywer, T.F. 2008. Heavy metal adsorbents prepared from the modification of cellulose: A review. *Bioresour. Technol.* 99(15): 6709-6724.

Ofomaja, A.E. 2010. Intraparticle diffusion process for lead(II) biosorption onto mansonia wood sawdust. *Bioresour. Technol.* 101: 5868-5876.

Plazinski, W. & Rudzinski, W. 2010. Heavy metals binding to biosorbents. Insights into non-competetitive models from a simple pH-dependent model. *Colloid. Surf. B* 80: 133-137.

Qiu, H., Lv, L., Pan, B.C., Zhang, Q.J., Zhang, W.M. & Zhang, Q.X. 2009. Critical review in adsorption kinetic models. *J. Zhejiang. Univ. Sci. A* 10: 716-724.

Sajab, M.S., Chia, C.H., Zakaria, S. & Khiew, P.S. 2013. Cationic and anionic modifications of oil palm empty fruit bunch fibers for the removal of dyes from aqueous solutions. *Bioresour. Technol.* 128: 571-577.

Şengil, I.A. & Özacarb, M. 2013. Removal of heavy metals from aqueous solutions by succinic anhydride modified mercerized nanocellulose. *Chem. Eng. J.* 223: 40-47.

Trivedi, P. & Axe, L. 2001. Predicting divalent metal sorption to hydrous Al, Fe, and Mn oxides. *Environ. Sci. Technol.* 35: 1779-1784.

Xiao, B. & Thomas, K.M. 2004. Competitive adsorption of aqueous metal ions on an oxidized nanoporous activated carbon. *Langmuir* 20: 4566-4578.

Wan Ngah, W.S. & Hanafiah, M.A.K.M. 2008. Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review. *Bioresour. Technol.* 99: 3935-3948.

Wang, X.S. & Li, Z.Z. 2009. Competitive adsorption of nickel and copper ions from aqueous solution using nonliving biomass of the marine brown alga *Laminaria japonica*. *Clean. Soil. Air. Water.* 37: 663-668.

Weber, W.J. & Morris, J.C. 1963. Kinetics of adsorption on carbon from solution. *J. Sanit. Eng. Div. Am. Soc. Civ. Engrs.* 89: 31-59.

Wu, F.C., Tseng, R.L. & Juang, R.S. 2009. Initial behavior of intraparticle diffusion model used in the description of adsorption kinetics. *Chem. Eng. J.* 153: 1-8.

Zakaria, S., Ahmadzadeh, A. & Roslan, R. 2013. Flow properties of novolak-type resin made from liquefaction of oil palm empty fruit bunch (EFB) fibres using sulfuric acid as a catalyst. *BioResources* 8(4): 5884-5894.

Zhi-Rong, L., Li-Min, Z., Peng, W., Kai, Z., Chuang-Xi, W. & Hui-Hua, L. 2008. Competitive adsorption of heavy metal ions on peat. *J. China. Univ. Mining. Technol.* 18: 225-260.

Chin Hua Chia & Sarani Zakaria
School of Applied Physics, Faculty of Science and Technology
Universiti Kebangsaan Malaysia
43600 Bangi, Selangor Darul Ehsan
Malaysia

Mohd Shaiful Sajab*
Research Center for Sustainable Process Technology (CESPRO)
Faculty of Engineering and Built Environment
Universiti Kebangsaan Malaysia
43600 Bangi, Selangor Darul Ehsan
Malaysia

Mika Sillanpää
Faculty of Technology
Lappeenranta University of Technology
Patteristonkatu 1, FI-50100 Mikkeli
Finland

*Corresponding author; email: mohdshaiful@ukm.edu.my