Aluminosilicate-based adsorbent in equimolar and non-equimolar binary-component heavy metal removal systems
Meng Xu, Pejman Hadi, Chao Ning, John Barford, Kyoung Jin An and Gordon McKay

ABSTRACT
Cadmium (Cd) and lead (Pb) are toxic heavy metals commonly used in various industries. The simultaneous presence of these metals in wastewater amplifies the toxicity of wastewater and the complexity of the treatment process. This study has investigated the selective behavior of an aluminosilicate-based mesoporous adsorbent. It has been demonstrated that when equimolar quantities of the metals are present in wastewater, the adsorbent uptakes the Pb$^{2+}$ ions selectively. This has been attributed to the higher electronegativity value of Pb$^{2+}$ compared to Cd$^{2+}$ which can be more readily adsorbed on the adsorbent surface, displacing the Cd$^{2+}$ ions. The selectivity can be advantageous when the objective is the separation and reuse of the metals besides wastewater treatment. In non-equimolar solutions, a complete selectivity can be observed up to a threshold Pb$^{2+}$ molar ratio of 30%. Below this threshold value, the Cd$^{2+}$ and Pb$^{2+}$ ions are uptaken simultaneously due to the abundance of Cd$^{2+}$ ions and the availability of adsorption sites at very low Pb$^{2+}$ molar ratios. Moreover, the total adsorption capacities of the adsorbent for the multi-component system have been shown to be in the same range as the single-component system for each metal ion which can be of high value for industrial applications.

Key words | binary-component adsorption, cadmium and lead removal, heavy metal separation, ion-exchange, mesoporous aluminosilicate-based adsorbent

INTRODUCTION
Heavy metals are found pervasively in soil and aqueous systems either naturally or as a result of anthropogenic human activities via agricultural, industrial and mining operations (Fu & Wang 2011). The presence of toxic heavy metals in excess quantities in the ecosystem has jeopardized the environmental sustainability and has posed particularly serious concerns regarding human health (Cheung et al. 2001; Sang et al. 2008). Hence, the removal of heavy metals from the environment, especially from the aquatic ecosystem, has received particular attention.

Among various wastewater treatment techniques, such as precipitation, coagulation–floculation, adsorption, membrane filtration and solvent extraction (Mavrov et al. 2003; Chuah et al. 2005; Larous et al. 2005; Wan Ngah & Hanafiah 2008; Pang et al. 2011), adsorption has been regarded as a simple, effective and environmentally friendly remediation process for the removal of heavy metals from effluent.

Various adsorbents have been developed and modified for pollutant remediation among which activated carbon is the most widely used class of adsorbents (Kadirvelu et al. 2001; Koby et al. 2005; Amuda et al. 2007). Although these materials are highly valued for their ability to remove dyes and organics from wastewater streams, they are comparatively inefficient for heavy metal sequestration in aqueous media. Ion exchange adsorbents/resins belong to another class of materials for the removal of heavy metal ions from wastewater (Dąbrowski et al. 2004). The ions, usually alkali metals or alkaline earth metals, bound to the charged groups on the surface of the ion-exchangers, can be exchanged with heavy metals possessing higher electronegativity values. Despite the high efficiency of ion exchange materials for heavy metal-laden...
wastewater treatment, their high cost is a major drawback. Accordingly, many researches have been devoted to the possibility of the utilization of natural mineral compounds, such as clays (Veli & Alyüz 2007), vermiculite (Malandrino et al. 2006) and soils (Bradl 2004) which exhibit ion exchange behavior. Nevertheless, their low metal uptake capacities hinder their widespread application in industry. In order to overcome the cost challenge while retaining high efficiency, it seems feasible to consider the employment of waste materials as precursors to produce adsorbents/ion exchangers. While numerous studies concerning the utilization of agricultural and industrial waste to produce activated carbon have been conducted, only limited reports have focused on aluminosilicate-based waste utilization as potential adsorbents/ion exchangers, most of which converted fly ash remaining after the combustion of coal to various types of zeolites as ion exchangers for wastewater treatment applications (Shih & Chang 1996; Apiratikul & Pavasant 2008; Wang et al. 2008; Qiu & Zheng 2009; Soço & Kalembliewicz 2013). Jo et al. used a mixture of bottom ashes from a power plant and dredged soil, as a mesoporous material, for heavy metal removal from wastewater (Jo et al. 2014). Also, chemically modified waste glass from cathode ray tubes was employed as an adsorbent to remove Pb2+ ions from wastewater (Pant & Singh 2013). Nevertheless, the metal adsorption capacities of these waste materials were found to be low in most of the cases, which restrains their practical applications in industrial wastewater treatment applications. The production of low-cost, efficient adsorbents from waste entails two-fold ecological advantages; transformation of burdensome waste materials into value-added products and their utilization for pollutant-laden wastewater treatment.

Hadi et al. (2015b) have produced a mesoporous-structured adsorbent material (Hadi et al. 2015a) from the nonmetallic fraction (NMF) of waste printed circuit boards and demonstrated its high efficiency in heavy metal adsorption in single-component systems (Hadi et al. 2015b, 2014). Although the simultaneous presence of two toxic heavy metals, such as Cd2+ and Pb2+, from various industrial wastewater is a common practice, only a few studies have dealt with the removal of Cd2+ and Pb2+ ions in binary systems. Also, to our best knowledge, the adsorption of non-equimolar heavy metals in multi-component systems has not been examined.

Hence, this research aims at studying the adsorption behavior of the activated waste PCB-derived adsorbent for the removal of Pb2+ and Cd2+ ions in single- and binary-component systems at various concentrations, pH values and adsorbent dosages. Also, since it is believed that the molar ratio of the metals present in wastewater affects the selectivity of the adsorbent, both equimolar and non-equimolar binary systems have been examined and the effect of metal ratio in selective behavior of the adsorbent material has been discussed.

**EXPERIMENTAL**

**Materials**

A local company in Hong Kong provided the micron-sized NMF (average particle size of 2 μm) as raw material. Potassium hydroxide (KOH, >85%), cadmium nitrate tetrahydrate (Cd(NO3)2.4H2O, >99%) and lead nitrate (Pb(NO3)2, >99%) were purchased from Sigma-Aldrich Company, UK.

**Adsorbent preparation and characterization**

The adsorbent material was prepared according to the procedure described in our previous work (Hadi et al.; Xu et al. 2014), using KOH as activating agent. The raw material, NMF, was impregnated with the activating agent at a weight ratio of 2:1 (KOH:NMF) with continuous stirring for 3 h at room temperature. After the mixing was completed, the slurry with deagglomerated NMF particles was transferred to a muffle furnace and heated to 250 °C at a rate of 5 °C min⁻¹ for 3 h under a nitrogen atmosphere (purity > 99.99%). Then, the furnace was cooled down to room temperature. The resultant material was washed with boiling water several times until the supernatant liquor was clear. Afterwards, the supernatant was drained and the activated material (A-NMF) was dried at 110 °C and stored in a desiccator for later experiments.

The textural properties and the surface chemistry of NMF and A-NMF were examined using a Coulter SA 3100 surface area analyzer by the nitrogen gas adsorption-desorption technique at 77 K after outgassing at 150 °C for 1 h, a PerkinElmer GX 2000 Fourier transform infrared spectroscopy (FTIR) and elemental analyzer. In addition, X-ray photoelectron spectroscopy (XPS, Physical Electronics PHI 5000) was used to investigate the surface atomic concentration of the materials.

**Adsorption studies**

Single- and binary-component adsorption of Pb2+ and Cd2+ ions was carried out to evaluate the adsorption behavior and capacity of the prepared activated material, A-NMF, under various conditions.
In a single-component system, 50 mL of metal solutions with initial concentrations in the range of 0.5 to 7 mmol.L\(^{-1}\) and a pH level 4 were placed in plastic bottles containing 50 mg adsorbent material and kept in a shaker at 150 rpm at a constant temperature of 25 °C. After the adsorption equilibrium was reached, the final pH values of the solutions were measured and the samples were withdrawn and filtered. Both initial and final metal concentrations of the solutions were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Optima 7300 DV, Perkin-Elmer, USA). The metal adsorption capacities of the adsorbent were calculated using the metal mass balance in aqueous and solid phases:

\[
(q_e - q_0) \times m = (C_o - C_e) \times V
\]

where \(q_0\) is the amount of metal on fresh adsorbent (mmol. g\(^{-1}\)); \(q_e\) is the equilibrium metal adsorption capacity (mmol.g\(^{-1}\)); \(V\) is the volume of the metal solution (L); \(m\) is the amount of adsorbent used (g); \(C_0\) and \(C_e\) are the initial and equilibrium concentrations of metal ions in the solution (mmol.L\(^{-1}\)), respectively.

For fresh adsorbent, no metal is present on the adsorbent surface, thus \(q_0 = 0\). Therefore, Equation (1) can be rearranged as (Rouquerol et al. 1999):

\[
q_e = \frac{(C_o - C_e) V}{m}
\]

The effect of pH on the adsorption behavior of the adsorbent-adsorbate system was studied by varying the initial pH value of the metal solution from 2 to 6 at a constant initial metal concentration of 5 mmol.L\(^{-1}\).

Similar adsorption experiments were employed for the binary-component system.

### Single- and binary-component equilibrium models

Various single- and binary-component adsorption models were applied to fit the adsorption isotherms. The models used in this study have been summarized in Table 1.

<table>
<thead>
<tr>
<th>Model</th>
<th>Assumptions</th>
<th>Equation</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>- Monolayer adsorption onto a homogeneous surface - Fixed and localized sites - No interaction between molecules</td>
<td>[q_e = \frac{K_L C_e}{1 + a_L C_e}]</td>
<td>(K_L, a_L)</td>
</tr>
<tr>
<td></td>
<td>Freundlich</td>
<td>[q_e = a_F C_e^n]</td>
<td>(a_F, \frac{1}{n})</td>
</tr>
<tr>
<td></td>
<td>Sips (Langmuir–Freundlich)</td>
<td>[q_e = \frac{K_{LF} C_e^{n_L}}{1 + a_{LF} C_e^{n_L}}]</td>
<td>(K_{LF}, a_{LF}, n_L)</td>
</tr>
<tr>
<td></td>
<td>Redlich–Peterson</td>
<td>[q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^{p_{RP}}}]</td>
<td>(K_{RP}, a_{RP}, p_{RP})</td>
</tr>
<tr>
<td></td>
<td>Extended Langmuir</td>
<td>[q_{el} = \frac{K_{L1}^0 C_{el}}{1 + \sum a_{L1}^0 C_{el}}]</td>
<td>(K_{L1}^0, a_{L1})</td>
</tr>
<tr>
<td></td>
<td>Extended Redlich–Peterson</td>
<td>[q_{el} = \frac{K_{RP1}^0 C_{el}}{1 + \sum a_{RP1}^0 C_{el}}]</td>
<td>(K_{RP1}^0, a_{RP1})</td>
</tr>
<tr>
<td></td>
<td>Modified extended Freundlich equation</td>
<td>[q_{el1} = \frac{K_{RF1}^0 C_{el}}{1 + \sum a_{RF1}^0 C_{el}}]</td>
<td>(K_{RF1}^0, a_{RF1})</td>
</tr>
<tr>
<td></td>
<td>Modified extended Freundlich equation</td>
<td>[q_{el2} = \frac{K_{RF2}^0 C_{el}}{1 + \sum a_{RF2}^0 C_{el}}]</td>
<td>(K_{RF2}^0, a_{RF2})</td>
</tr>
</tbody>
</table>

Table 1 | Summary of adsorption models applied in this study.
The calculated adsorption capacity, $q_{cal}$, was compared with the experimental adsorption capacity, $q_{exp}$, for each isotherm model. The sum of the squared errors (SSE) was used as the error function in this study and was calculated using Equation (3). The model parameters were determined to minimize the SSE values via the solver add-in function in Microsoft Excel which functions by applying an iterative method to find the optimum variables by minimizing the error function. The model with the least SSE value was selected as the best-fit model.

$$SSE = \sum (q_{exp} - q_{cal})^2$$ (3)

RESULTS AND DISCUSSION

Material characterization

The detailed characterization of the original and modified materials has been reported in our previous works (Hadi et al. 2013a, b). Table 2 shows the Brunauer–Emmett–Teller (BET) surface area and pore volume of NMF and A-NMF determined by nitrogen gas adsorption–desorption technique. As seen in this table, the raw material, NMF, is non-porous with a surface area below 1 m$^2$.g$^{-1}$, while the A-NMF has a surface area of 222 m$^2$.g$^{-1}$ which demonstrates that the activation process has resulted in successful development of a porous structure. The comparison of the developed surface area for A-NMF with the reported values for fly ash, which has a similar structure to NMF, shows that this surface area is either in the same range as the zeolites produced by fly ash using sophisticated processes (Pizarro et al. 2015; Zhou et al. 2015) or higher than the fly ash-based adsorbents produced (Kostova et al. 2015; Duta & Visa 2015; Itskos et al. 2015; Norris et al. 2015; Ogata et al. 2015). Also, the pore volumes show that the activated material mainly consists of mesopores. Based on CHNS elemental analysis, NMF contains more than 20% carbon in its structure while the carbon content of the A-NMF is found to be less than 2%. This shows that carbon has been burned off after the activation process. Carbon burn-off at such a low temperature has been related to the catalyzing effect of the presence of potassium and calcium (Yuan et al. 2011; Hadi et al. 2013c). Moreover, the XRF analysis demonstrates that the major composition of the A-NMF is silicon, aluminum and calcium originating from calcium aluminosilicate, a material commonly used as an adsorbent for wastewater treatment.

The chemistry of the adsorbent surface was examined by FTIR. Figure 1 shows the FTIR spectra of both NMF and A-NMF. The spectrum of A-NMF displays a strong, broad signal between 3,250 and 3,550 cm$^{-1}$, which is attributed to the presence of hydroxyl groups (–OH), whereas no hydroxyl group can be found before the activation process. This indicates that the dominant activation mechanism is the cleavage of the siloxane groups to form the silanol groups on the surface of the adsorbent. The peak located at 1,013 cm$^{-1}$ is assigned to the siloxane groups. This increase in the intensity of this peak after the activation has been related to the opening of the aluminosilicate tetrahedral cage which leads to the exposure of more siloxane groups to the surface of the material, consistent with pore development during the activation process. The XPS results also show the increase in the surface concentrations of silicon and oxygen groups confirming the FTIR results. Also, the existence of potassium ions on the surface of the adsorbent material, verified by XPS, confirms the successful doping of potassium ions which can potentially be exchanged with heavy metal ions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ m$^2$.g$^{-1}$</th>
<th>$V_{mic}$ cm$^3$.g$^{-1}$</th>
<th>$V_{meso}$ cm$^3$.g$^{-1}$</th>
<th>$V_{tot}$ cm$^3$.g$^{-1}$</th>
<th>$p/p_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMF</td>
<td>0.9</td>
<td>0.006</td>
<td>0</td>
<td>0.006</td>
<td>0.98</td>
</tr>
<tr>
<td>A-NMF</td>
<td>222</td>
<td>0.004</td>
<td>0.738</td>
<td>0.742</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Table 2 | Textural properties of the raw material, NMF, and activated material, A-NMF

Figure 1 | FTIR spectra of NMF and A-NMF.
Single-component adsorption

Single component equilibrium isotherms for the adsorption of Pb\(^{2+}\) and Cd\(^{2+}\) ions using A-NMF are shown in Figure 2. A-NMF is capable of both Cd\(^{2+}\) and Pb\(^{2+}\) ion uptake with high adsorption capacities.

The uptake is mainly coordinated by the functional groups present on the adsorbent surface and its porous structure. The preliminary adsorption results demonstrated that the untreated material (NMF) does not uptake any metal ion. This is because of the trivial surface area of the adsorbent and the existence of no active functional groups on its surface. However, the activated material A-NMF which has a well-defined mesoporous network with functionalized surface can uptake the single-component metal ions with high adsorption capacities of 3.2 mmol.g\(^{-1}\) for Pb\(^{2+}\) and 2.1 mmol.g\(^{-1}\) for Cd\(^{2+}\), showing higher affinity of this adsorbent material towards Pb\(^{2+}\) ion compared to Cd\(^{2+}\) ion. The comparison of these results with the adsorption capacities found in literature and the adsorption capacities of several commonly used commercial resins, summarized in Table 3, verifies the high efficiency of A-NMF as an adsorbent material to remove metal ions from effluents.

The single component adsorption isotherms are modeled using Langmuir, Freundlich, Sips (Langmuir–Freundlich) and Redlich–Peterson equations. The model parameters obtained to minimize the SSE together with the corresponding SSE values for all the isotherm equations are given in Table 4. Comparison of the SSE values for various model isotherms reveal that the Redlich–Peterson model shows the best fit to the experimental data for both Pb\(^{2+}\) and Cd\(^{2+}\) ions.

It is interesting to note that the Redlich–Peterson power constant, \(\beta_{RP}\), for both Pb- and Cd-containing systems approaches unity, which reduces the Redlich–Peterson equation to the Langmuir model. Accordingly, it can be concluded that these adsorbent–adsorbate systems exhibit Langmuirian behavior. The Langmuir adsorption model is based on the assumptions that the adsorption occurs at a fixed number of definite, localized and equivalent sites and each site can only hold one molecule. According to this hypothesis, there will be no interaction between the adsorbed molecules, even on adjacent sites. So the molecules are bound to the surface of the available neighboring sites and this explains the limitation of the maximum capacity even at higher solution concentrations. However, the experimental data do not completely fit the Langmuir isotherm and exhibit a slight deviation, implying that not all sites represented homogeneous ion exchange with identical ions. The heterogeneity originates from the fact that the adsorption is not only mediated by ion exchange with potassium ions, but also physisorption is involved in the adsorption process, which causes the surface to behave in a slightly heterogeneous manner. Although the mechanism cannot be completely described by the Langmuir assumption, the uptake seems to obey monolayer adsorption behavior since the metal ion is the only species involved in the adsorption process, which causes the surface to behave in a slightly heterogeneous manner. Although the mechanism cannot be completely described by the Langmuir assumption, the uptake seems to obey monolayer adsorption behavior since the metal ion is the only species that can bond with the functional groups on the adsorbent surface in the solution and multilayer adsorption may be inhibited by the repulsion force between the aqueous and adsorbed heavy metal ions. The fits of various models are shown in Figure 3 for comparison.

Equimolar binary-component adsorption

The binary adsorption isotherm of the Pb\(^{2+}\) and Cd\(^{2+}\) ions using A-NMF is shown in Figure 4. According to this figure, Pb\(^{2+}\) ions are preferentially adsorbed by A-NMF from the equimolar Pb\(^{2+}\)--Cd\(^{2+}\) system. At low initial metal concentrations, the adsorbent material adsorbs Pb\(^{2+}\) and Cd\(^{2+}\) ions simultaneously due to the profusion of available adsorption sites. With an increase in the metal concentration, Pb\(^{2+}\) displaces the Cd\(^{2+}\) ions and occupies all the available sites, leaving Cd\(^{2+}\) in solution. Considering that the dominant mechanism in this system is ion exchange on the surface of the adsorbent material, this selective behavior is believed to originate from the difference in the electronegativities of the two metal ions. Pb (2.33) has a
higher electronegativity compared to Cd (1.69) resulting in higher attraction of the Pb\(^{2+}\) ions to the negatively charged functional groups. This difference between the electronegativities of the two metals accounts for the higher affinity of the adsorbent material to the Pb\(^{2+}\) uptake which is more prone to compensate for its electron deficiency. The selective behavior of an adsorbent in a multi-component system can find significant applications, especially for the recovery and reuse of an individual metal from a multi-component medium.

As discussed in the previous section, the Langmuir-type isotherm properly described the rectangular-shape isotherm in the single-component systems. So the Langmuir-based multi-component models, extended-Langmuir and extended Redlich–Peterson models, were analyzed using two sets of Langmuir/Redlich–Peterson isotherm parameters obtained by the single-component modelling. However, both of these multi-component models fail to fit the experimental data in the binary-component system. This can be expected due to the selective behavior of the adsorbent in the Pb\(^{2+}\)–Cd\(^{2+}\) binary component. Indeed, extended Langmuir and extended Redlich–Peterson models are ideal isotherm models which assume that no interaction takes place between the components present in the adsorption medium. However, the competition between the two metal ions evidently verifies the occurrence of significant interaction between these two species, resulting in the non-ideality of the adsorption system. Moreover, the limitation of the model equation is

Table 3: Comparison of the adsorption capacities of A-NMF with reported adsorbents and commonly used commercial resins

<table>
<thead>
<tr>
<th>Adsorbent/Resin</th>
<th>Adsorption capacity mmol.g (^{-1})</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cadmium removal</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Present work</td>
<td>2.1</td>
<td>Corami et al. (2008)</td>
</tr>
<tr>
<td>Hydroxyapatite</td>
<td>1.618</td>
<td>Demirbas et al. (2005)</td>
</tr>
<tr>
<td>Amberlite IR 120</td>
<td>0.9</td>
<td>Mohan &amp; Singh (2002)</td>
</tr>
<tr>
<td>Activated carbon derived from bagasse</td>
<td>0.338</td>
<td>El-Kamash et al. (2005)</td>
</tr>
<tr>
<td>Synthetic zeolite A</td>
<td>1.85</td>
<td></td>
</tr>
<tr>
<td>Sodium bicarbonate modified sugarcane bagasse</td>
<td>1.68</td>
<td>Karnitz et al. (2007)</td>
</tr>
<tr>
<td>Pleurotus sapidus</td>
<td>1.15</td>
<td>Yalçınkaya et al. (2002)</td>
</tr>
<tr>
<td>Sawdust (cedrus deodor wood)</td>
<td>0.65</td>
<td>Memon et al. (2007)</td>
</tr>
<tr>
<td>Cassava tuber bark waste</td>
<td>0.23</td>
<td>Horsfall et al. (2006)</td>
</tr>
<tr>
<td>Sulfuric acid-treated wheat bran</td>
<td>0.90</td>
<td>Özer &amp; Pirinççi (2006)</td>
</tr>
<tr>
<td>Spent grain</td>
<td>0.15</td>
<td>Low et al. (2000)</td>
</tr>
<tr>
<td>Citric acid treated corn cob</td>
<td>0.49</td>
<td>Leyva-Ramos et al. (2005)</td>
</tr>
<tr>
<td>α-Ketoglutaric acid-modified magnetic chitosan</td>
<td>1.79</td>
<td>Yang et al. (2014)</td>
</tr>
<tr>
<td><strong>Lead removal</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Present work</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>Magnetic chitosan/graphene oxide composites</td>
<td>0.36</td>
<td>Fan et al. (2013)</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>0.13</td>
<td>Momčilović et al. (2011)</td>
</tr>
<tr>
<td>Carbon nanotubes</td>
<td>0.49</td>
<td>Kabbashi et al. (2009)</td>
</tr>
<tr>
<td>Amberlite IR 120</td>
<td>0.41</td>
<td>Demirbas et al. (2005)</td>
</tr>
<tr>
<td>Rice husk</td>
<td>0.58</td>
<td>Wong et al. (2005)</td>
</tr>
<tr>
<td>Peanut husk</td>
<td>0.14</td>
<td>Li et al. (2007)</td>
</tr>
<tr>
<td>Polymerized banana stem</td>
<td>0.44</td>
<td>Noeline et al. (2005)</td>
</tr>
<tr>
<td>Spent grain</td>
<td>0.17</td>
<td>Low et al. (2000)</td>
</tr>
<tr>
<td>Sodium bicarbonate modified sugarcane bagasse</td>
<td>0.96</td>
<td>Karnitz et al. (2007)</td>
</tr>
<tr>
<td>Medicago sativa (alfalfa) biomass</td>
<td>0.43</td>
<td>Tiemann et al. (2002)</td>
</tr>
<tr>
<td>Treated Azolla filiculoides with H(_2)O(_2)/MgCl(_2)</td>
<td>1.1</td>
<td>Taghi ganji et al. (2005)</td>
</tr>
</tbody>
</table>
Another reason for lack of appropriate fitting in the multicomponent system, when there is selectivity in the binary-component system, even the constant $K^0_{L,C}$ is larger than $K^0_{L,Pb}$, the equilibrium concentration of Pb$^{2+}$ is far less than that of Cd$^{2+}$. Since the numerators of these extended models are formed by multiplication of $C_{eq,i}$ and $K^0_{L,i}$, the extended Langmuir-based models can only provide reasonable estimates for multi-component systems as long as the $C_e$ values of the metal ion present in multi-component systems are close to each other, that is when the adsorption follows a simultaneous trend, not a selective trend.

Since predictive models assuming an ideal system are not effective in modeling this binary-component system, the modified extended Freundlich model as a non-ideal model with a heterogeneity factor has been used to fit the data. The extended Freundlich isotherm was originally proposed by Fritz and Schlunder (Fritz & Schlundert 1981). Later on, McKay and Al-Duri modified the evaluation of correlation factors so as to reduce the extensive calculation procedure (McKay & Al-Duri 1991). They obtained appropriate agreement between the experimental and calculated data for a dye/activated carbon system (Al-Duri et al. 1992). It is a method highly recommended for systems with significant non-ideal effects and heterogeneous surfaces. Figure 5 shows that the modified extended Freundlich model can predirectly predict the observed experimental data for this binary-component system.

Several literature have reported a decrease in the equilibrium adsorption capacity of the adsorbent in multicomponent systems. Kadirvelu et al. (2008) have observed that co-adsorption of Pb$^{2+}$ and Cd$^{2+}$ induces a drastic decrease in the adsorption capacity. Chiban et al. (2011) have also reported a reduction in the adsorption capacity of the adsorbent in a binary-component Pb$^{2+}$-Cd$^{2+}$ system. This trend has also been observed by several other researchers (Entezari & Soltani 2009). In this study, the added-up capacity of the adsorbent in the equimolar system is similar to that of the single-component system for Pb$^{2+}$ which suggests a strong interaction between the adsorbent active sites and both of the adsorbates. Hence, the efficiency of the adsorbent will not be sacrificed by the presence of other metal ions.

**Non-equimolar binary-component adsorption**

Since selectivity has been observed in the equimolar binary-component system, the effect of different metal ratios on the selectivity of the adsorption is of importance, since depending on the dominance of the metal ion in the solution, the selective behavior of an adsorbent may change to simultaneous behavior. Adsorption capacities, $q_e$, for each metal ion have been determined at various Cd$^{2+}$:Pb$^{2+}$ ratios and are plotted against the molar ratio of Pb$^{2+}$, the more dominant species in this case. The molar ratio of Pb$^{2+}$ is defined as the molar ratio of the Pb$^{2+}$ concentration over the total metal concentration. As illustrated in Figure 6, it is observed that when the Pb$^{2+}$ ion is at low Pb$^{2+}$ molar ratio (below 30%), the other metal will have the chance to be adsorbed simultaneously due to its higher concentration and thus higher probability of contact between Cd$^{2+}$ ions and the active adsorption sites. Once the concentration ratio of Pb$^{2+}$ ions is above the threshold concentration of 30%, the adsorbent material, A-NMF, exhibits complete selective

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**Table 4 | Model parameters of single component metal adsorption using A-NMF**

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameter</th>
<th>Unit</th>
<th>Pb$^{2+}$</th>
<th>Cd$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$K_L$</td>
<td>L·g$^{-1}$</td>
<td>205</td>
<td>88.8</td>
</tr>
<tr>
<td></td>
<td>$a_L$</td>
<td>L·mmol$^{-1}$</td>
<td>64.6</td>
<td>42.6</td>
</tr>
<tr>
<td></td>
<td>$SSE$</td>
<td></td>
<td>0.358</td>
<td>0.0125</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$a_F$</td>
<td>mmol·g$^{-1}$·(L·mmol$^{-1}$)$^b$</td>
<td>2.76</td>
<td>1.99</td>
</tr>
<tr>
<td></td>
<td>$n$</td>
<td></td>
<td>0.150</td>
<td>0.057</td>
</tr>
<tr>
<td></td>
<td>$SSE$</td>
<td></td>
<td>2.94</td>
<td>0.0034</td>
</tr>
<tr>
<td>Sips (Langmuir–Freundlich)</td>
<td>$K_{LF}$</td>
<td>mmol·g$^{-1}$·(L·mmol$^{-1}$)$^{n_{LF}}$</td>
<td>84.4</td>
<td>8.15</td>
</tr>
<tr>
<td></td>
<td>$a_{LF}$</td>
<td>(L·mmol$^{-1}$)$^{n_{LF}}$</td>
<td>57.7</td>
<td>3.06</td>
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<tr>
<td></td>
<td>$n_{LF}$</td>
<td></td>
<td>0.804</td>
<td>0.214</td>
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<tr>
<td></td>
<td>$SSE$</td>
<td></td>
<td>0.248</td>
<td>0.0028</td>
</tr>
<tr>
<td>Redlich–Peterson</td>
<td>$K_{RP}$</td>
<td>L·g$^{-1}$</td>
<td>256</td>
<td>343</td>
</tr>
<tr>
<td></td>
<td>$a_{RP}$</td>
<td>(L·mmol$^{-1}$)$^{\beta_{RP}}$</td>
<td>82.5</td>
<td>170</td>
</tr>
<tr>
<td></td>
<td>$\beta_{RP}$</td>
<td></td>
<td>0.966</td>
<td>0.955</td>
</tr>
<tr>
<td></td>
<td>$SSE$</td>
<td></td>
<td>0.224</td>
<td>0.0026</td>
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adsorption behavior towards the Pb$^{2+}$ ions implying the drastic effect of the electronegativity compensating for the lower Pb$^{2+}$ concentration in a range of 30–50%. This selectivity is evidently retained with the increase of the Pb$^{2+}$ molar ratio above 50%, where by the electronegativity and higher Pb$^{2+}$ content have additive effects.

In order to investigate the behavior of the binary system at different total metal concentrations when the dominant Pb$^{2+}$ species is at low Pb$^{2+}$ molar ratio, the capacities against equilibrium concentrations with different metal ratios are shown in Figure 7(a)–(c). At metal ratios of Cd$^{2+}$:Pb$^{2+}$ = 6:4 and 7:3, when the total metal concentrations are low, there are unoccupied adsorption sites readily available to adsorb the competing Cd$^{2+}$ ions, together with the dominant Pb$^{2+}$ ions. By increasing the total concentration of the metal ions, displacement takes place as Pb$^{2+}$ ions, the dominant species, displaces the Cd$^{2+}$ ions on the surface of the adsorbent, resulting in the inhibition of the Cd$^{2+}$ uptake.

However, according to Figure 7(c), where the Pb$^{2+}$ ions only account for 20% of the total metal concentration, the Cd$^{2+}$ ions are not fully displaced by the Pb$^{2+}$ ions during the adsorption process even at high total metal concentrations. This is because of the low Pb$^{2+}$ concentrations leaving abundant available adsorption sites for the

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Figure 3: Model fitting with various adsorption models to single-component adsorption of (a) Pb$^{2+}$ and (b) Cd$^{2+}$ by A-NMF.

Figure 4: Equimolar binary adsorption of Pb$^{2+}$ and Cd$^{2+}$ by A-NMF. Experimental conditions: 50 mL metal solution initial pH = 4, initial concentration for each metal = 0.5–6 mmol L$^{-1}$, Pb$^{2+}$:Cd$^{2+}$ = 1, 0.05 g adsorbent, equilibrium time = 5 days.

Figure 5: Fit of the modified extended Freundlich adsorption model to Pb$^{2+}$–Cd$^{2+}$ binary-component system.
competitive Cd\textsuperscript{2+} ion. The highest Pb\textsuperscript{2+} concentration in this system (Cd\textsuperscript{2+}:Pb\textsuperscript{2+} = 8:2) is 2.2 mmol.L\textsuperscript{-1} and the corresponding adsorption capacity for Pb\textsuperscript{2+} at this concentration is 2.0 mmol.g\textsuperscript{-1}, which is below the saturation capacity. Initially, the adsorbent preferentially adsorbs the Pb\textsuperscript{2+} ions on the surface, and subsequently, the Cd\textsuperscript{2+} ions are adsorbed on the remaining available sites until saturation. It is notable that the added-up total capacity in this system is 3.1 mmol.g\textsuperscript{-1} which is in the same range as previously studied Pb\textsuperscript{2+}-dominated systems. The trend in this figure also indicates the reduction, but not inhibition, of Cd\textsuperscript{2+} adsorption by increasing the total metal concentration. When the molar ratio of the Pb\textsuperscript{2+} ions is further reduced to 10% of the total metal present in the solution, the added-up capacity is decreased to around 2 mmol.g\textsuperscript{-1}. It is due to the fact that at such a low Pb\textsuperscript{2+} concentration, the Cd\textsuperscript{2+} ions play the major role in determining the adsorption capacity. Because the maximum adsorption capacity of the adsorbent for Cd\textsuperscript{2+} is only 2.1 mmol.g\textsuperscript{-1}, the added-up capacity in such a low level of Pb\textsuperscript{2+} ions is similar to the single-component Cd\textsuperscript{2+} adsorption (see Figure 6).

**pH effect**

One of the most important parameters which affects the metal uptake capacity of adsorbent materials is the pH value of the metal solutions. The adsorption capacities of the material for Pb\textsuperscript{2+} and Cd\textsuperscript{2+} ions at various pH values in single- and binary-component systems are shown in Figure 8.
In single-component systems, A-NMF uptakes trivial quantities of the metal ions at a very low pH value of 2. With an increase in the pH values of the solutions from 2 to 3.5, the metal adsorption capacities increase drastically. As the pH values are further increased above 3.5, the metal uptakes gradually reach a plateau. This trend has also been observed by other researchers (Pérez-Marín et al. 2011). This behavior is attributed to the competition between metal ions and hydrogen ions. At low pH values, the concentration of hydrogen ions present in the solution is sufficiently high to compete with the metal ions to occupy the available surface sites which leads to lower adsorption capacities. As the pH values of the solutions increase, the metal ions can easily capture the adsorption sites due to the lesser protonation of the surface sites, resulting in higher metal uptakes.

In the binary system, a complete selective behavior has been observed irrespective of the pH. The trend of change in the adsorption capacity of Pb\(^{2+}\) ions from the binary effluent is also similar to the single-component system. However, the Cd\(^{2+}\) ions are not adsorbed from the binary solution at any pH values. It is also interesting to note that, while some literature report the reduction in the adsorption capacity of the adsorbent in multi-component systems compared to the single-component solutions (Srivastava et al. 2006; Lam et al. 2007), the adsorption capacity of the adsorbent for Pb\(^{2+}\) ions does not change in the presence of Cd\(^{2+}\) ions, which can be highly advantageous.

The equilibrium pH values have been measured and all the results show that no precipitation occurs during the experiments.

**CONCLUSION**

In this work, single- and binary-component adsorptions for Pb\(^{2+}\) and Cd\(^{2+}\) ions using waste printed circuit board-based adsorbent (A-NMF) have been performed. Although the untreated material is incapable of adsorbing any metal ion, the activated material (A-NMF) has high adsorption capacities of 3.2 mmol.g\(^{-1}\) and 2.1 mmol.g\(^{-1}\) for Pb\(^{2+}\) and Cd\(^{2+}\), respectively, in single component systems. The best fit model for both of the single-component adsorption systems has been found to be the Redlich-Peterson model. Since the power parameter in this model approaches unity, the adsorption mechanism of the metal ions has been proposed to be Langmuirian, indicative of monolayer adsorption on a homogeneous surface. Furthermore, A-NMF shows distinctive adsorption selectivity towards Pb\(^{2+}\) in a Pb\(^{2+}\)-Cd\(^{2+}\) equimolar binary-component system irrespective of the pH value of the metal solution. When the molar ratio of Pb\(^{2+}\) decreases to a threshold value of 30%, no significant change in selectiveness is observed. Further decrease in the Pb\(^{2+}\) molar ratio results in the simultaneous uptake of the two metals. This is attributed to the higher collision of the Cd\(^{2+}\) ions with the active adsorption sites due to higher accessibility of these ions. At Pb\(^{2+}\) molar ratio as low as 10%, the behavior of the system closely approaches that of the Cd\(^{2+}\) single-component system. Also, it has been demonstrated that the adsorption capacity of the adsorbent material for Pb\(^{2+}\) ions does not decrease in the binary-component system compared to
the single-component system, which can be of high significance in industrial applications.

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