Adsorption of heavy metals from aqueous solutions by Mg–Al–Zn mingled oxides adsorbent
Mona El-Sayed, Gh. Eshaq and A. E. ElMetwally

ABSTRACT

In our study, Mg–Al–Zn mingled oxides were prepared by the co-precipitation method. The structure, composition, morphology and thermal stability of the synthesized Mg–Al–Zn mingled oxides were analyzed by powder X-ray diffraction, Fourier transform infrared spectrometry, N2 physisorption, scanning electron microscopy, differential scanning calorimetry and thermogravimetry. Batch experiments were performed to study the adsorption behavior of cobalt(II) and nickel(II) as a function of pH, contact time, initial metal ion concentration, and adsorbent dose. The maximum adsorption capacity of Mg–Al–Zn mingled oxides for cobalt and nickel metal ions was 116.7 mg g⁻¹, and 70.4 mg g⁻¹, respectively. The experimental data were analyzed using pseudo-first- and pseudo-second-order kinetic models in linear and nonlinear regression analysis. The kinetic studies showed that the adsorption process could be described by the pseudo-second-order kinetic model. Experimental equilibrium data were well represented by Langmuir and Freundlich isotherm models. Also, the maximum monolayer capacity, qmax, obtained was 113.8 mg g⁻¹, and 79.4 mg g⁻¹ for Co(II), and Ni(II), respectively. Our results showed that Mg–Al–Zn mingled oxides can be used as an efficient adsorbent material for removal of heavy metals from industrial wastewater samples.

Key words | adsorption, heavy metals, isotherm, kinetics, mingled oxides, water treatment

INTRODUCTION

Heavy metals produced and released during domestic, agricultural and industrial activities can create a serious hazard to the environment (Sathyavisal et al. 2008). The presence of heavy metals in the environment can be harmful to a variety of living species. Consequently, the removal of heavy metals from wastewater and water is important to protect public health (Donat et al. 2005). Industrial wastewater containing cobalt(II) and nickel(II) is common, because their compounds are widely used in many industrial applications such as electroplating, battery manufacturing, mining, metal finishing and forging, and metallurgical processes.

Heavy metals in solutions can be removed using several techniques such as precipitation, coagulation, chemical precipitation, adsorption, ozonation, membrane filtration and reverse osmosis (Karapinar & Donat 2009; Liu & Zhou 2010). Adsorption is recognized as an easy, economic, effective and promising method to remove heavy metals from water at low concentrations (Turk et al. 2009). Several investigations have focused on the use of low cost adsorbents, such as chitosan (Elwakeel 2010), waste materials (Gode et al. 2008), activated carbon (Monser & Adhoum 2002), coal (Gode & Moral 2008), and polymers (Jacques et al. 2007). However, most of these adsorbents have some flaws, for instance, excessive time requirements, high costs, and inefficiency. Layered double hydroxide (LDH), a class of anionic clay with high anion-exchange capacities, special structure and unique applications, also, known as hydrotalcite-like compounds, are bi-dimensional solids with positive charge excess in their brucite (Mg(OH)2)-like layers. LDHs have the structure formula of [M2-xM3+x(OH)2] [A_x/n].m H2O, where M²⁺ and M³⁺ are divalent and trivalent metal cations, respectively, and A is the anion. Since the interlayer anions are easily exchangeable, the anions in the interlayer can be exchanged by other anions; so high anion-exchange capability is the most remarkable characteristic of LDHs. Meanwhile, the ease of preparation and widely variable ways in which their components can be combined make LDHs useful for many applications (Hsu et al. 2007; Hamzah et al. 2011). Polymers, organic dyes, surfactants and organic acids could be used as a substitute for
the anions between the LDH layers. The LDH anion-exchange ability, large surface area and regeneration ability ensure that this adsorbent can be excellently utilized in wastewater purification (Roto et al. 2009). Given that the calcination products of LDHs are mixed oxides, which are solids with basic properties (Sanchez-Valente et al. 2000; Figueras et al. 2002), LDHs and their oxides have been successfully employed as adsorbents for a variety of anion species and/or pollutants (Inacio et al. 2001; You et al. 2002; Orthman et al. 2003; Cantu et al. 2005; Cardoso & Valim 2006). LDHs can take up anion species from solution by three different mechanisms: surface adsorption, interlayer anion exchange, and reconstruction of a calcined LDH by the ‘memory effect’ (Duan & Evans 2006). Studies conducted on their use for heavy metal removal are still few (Pérez et al. 2006; Pavlovic et al. 2009; Xuefeng et al. 2010; Donglin et al. 2011). We have considerable interest in the use of LDHs to remove heavy-metal ions from aqueous solution; their high anion-exchange ability, high uptake capacity, large surface area, flexible interlayer space, ease of preparation, low cost, stability and regeneration ability, ensure that this adsorbent can be excellently utilized in wastewater purification (Yasin et al. 2010; Hamzah et al. 2011). To the best of our knowledge, the adsorption of nickel and cobalt using Mg–Al–Zn mingled oxides has not yet been reported. Therefore, Mg–Al–Zn mingled oxides derived from hydrotalcite was selected to optimize the removal of cobalt and nickel metal ions from aqueous solution. The effects of different adsorption parameters, such as solution pH, contact time, initial metal concentration and adsorbent dose were studied. Equilibrium and kinetic studies were performed to describe the rate of the adsorption process. Different models were applied to determine the mechanisms of the adsorption process. Then, the possible application of Mg–Al–Zn mingled oxides in wastewater treatment was investigated.

**MATERIALS AND METHODS**

**Reagent and solutions**

All chemical agents were analytical reagent grade; Co(NO$_3$)$_2$·6H$_2$O, Ni(NO$_3$)$_2$·6H$_2$O, Al(NO$_3$)$_3$·9H$_2$O, K$_2$CO$_3$, and KOH salts were purchased from Sigma-Aldrich Co., Mg(NO$_3$)$_2$·4H$_2$O and Zn(NO$_3$)$_2$·6H$_2$O were purchased from LobaChemie Co. and the solutions were prepared with deionized water (18 MΩ-cm).

**Preparation and characterization of Mg–Al–Zn mingled oxides**

Mg–Al–Zn hydrotalcite with 15% wt of zinc was synthesized according to the procedures described (Bakr et al. 2016). The obtained sample was calcined at 450 °C for 5 h prior to adsorption. The crystal structure of Mg–Al–Zn mingled oxides sample was identified by X-ray diffraction (XRD) analysis, recorded in the range 2θ = 4–80° using a Philips powder diffractometer with Cu Kα radiation (k = 0.154 nm) operated at 40 kV and 40 mA. The spectra were recorded with a 20 step of 0.02° at a scanning rate of 2° · min$^{-1}$. The infrared spectra were obtained using a Fourier transform infrared spectrometer (FTIR) model Nicolet IS-10 FTIR, The samples were prepared as KBr discs and scanned over the range of 400–4,000 cm$^{-1}$ to identify the functional groups that are responsible for adsorption. Surface area, pore volume and average pore size calculations were analyzed by the Brunauer–Emmett–Teller (BET) equation with N$_2$ adsorption–desorption isotherms (Quantachrome Nova 3200 instrument, USA). The morphology of the samples was investigated by scanning electron microscopy (SEM); SEM images of the gold-coated catalysts were obtained (JEOL 5410 system operating at 40 kV). Thermal analysis of the samples including differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) was carried out using the differential thermal analyzer DTA-7 (Perkin-Elmer).

**Batch adsorption experiments**

In order to determine the adsorption capacities of Mg–Al–Zn mingled oxides for Co(II) and Ni(II) metal ions, as well as the effect of time, initial metal concentration, solution pH, and the adsorbent dose, adsorption experiments were performed by batch adsorption techniques. Standard stock solutions of Co(II) and Ni(II) metal ions containing 1,000 mg L$^{-1}$ were prepared from Co(NO$_3$)$_2$·6H$_2$O and Ni(NO$_3$)$_2$·6H$_2$O salts, of electrical conductivity 2.02 and 3.57 mS cm$^{-1}$, respectively, and diluted further with deionized water to obtain the lower concentration solutions. Metal solutions ranging from 300 mg L$^{-1}$ to 10 mg L$^{-1}$ were prepared, with electrical conductivities ranging from 650 μS cm$^{-1}$ to 29.3 μS cm$^{-1}$ and from 1,160 μS cm$^{-1}$ to 49.6 μS cm$^{-1}$ for Co(II) and Ni(II), respectively. A known volume of cobalt and nickel solutions of varying initial concentrations, taken in 50 mL stopper tubes at desired pH, was shaken with a fixed dose of adsorbent for a specified contact time in a thermostated shaking assembly. After equilibrium time, samples were filtered using 0.45 μm filter paper.
(Whatman), and metal concentrations were measured in filtrates of electrical conductivity ranging from 320 μS cm⁻¹ to 15.2 μS cm⁻¹ and from 980 μS cm⁻¹ to 25.8 μS cm⁻¹ for Co(II), and Ni(II), respectively. Metal concentration was analyzed by atomic absorption spectrophotometry (AAS), Hitachi model No. Z-7000. The amount of adsorbed metal ions by unit mass of adsorbent (qe in mg g⁻¹) was determined by the following mass balance equation:

\[ q_e = \frac{(C_0 - C_e)V}{m} \]

where \(C_0\) and \(C_e\) (mg L⁻¹) are the initial and equilibrium concentrations of metal ions, respectively, \(V\) is the volume of solution (L) and \(m\) is the mass of the adsorbent (g). The adsorption percentage was derived from the following equation:

\[ \text{Adsorption percentage} = \frac{(C_0 - C_e)}{C_0} \times 100 \]

Reproducibility of the measurements was determined in triplicate and the average values are reported. Relative standard deviations were found to be within ± 3.0%.

RESULTS AND DISCUSSION

Characterization

X-ray diffraction

The XRD patterns of Mg–Al–Zn mingled oxides before and after adsorption of cobalt and nickel are presented in Figure 1. Figure 1 diffraction pattern (a) reveals the absence of (003) and (006) reflection patterns, which is evidence for the destruction of hydrotalcite structure and disorderliness of the stacking layers upon calcination. The diffused peaks appearing at 35° and 40° are assigned to MgO. Figure 1 diffraction patterns (b) and (c) show that after adsorption of cobalt and nickel, the (003) and (006) reflection patterns emerge, which is ascribed to the memory effect of the hydrotalcite family. Bragg’s law is used to obtain the unit cell parameters \(c\) (22.8 Å) and \(a\) (3.04 Å); the obtained data assume a hexagonal stacking.

Infrared spectroscopy

The FTIR spectra of the Mg–Al–Zn mingled oxides before and after adsorption are shown in Figure 1. The intensity of the band assigning to \(\text{CO}_3^{2-}\) at 1,384 cm⁻¹ in the Mg–Al–Zn mingled oxides seems to be lower than the corresponding one in the Mg–Al–Zn hydrotalcite, signifying that most of the carbonate ions are eliminated. Moreover, the absence of a vibration band at 1,650 cm⁻¹ can be attributed to the removal of the interlayer \(\text{H}_2\text{O}\) during the calcination process. A strong band at 1,000 cm⁻¹ was ascribed to M–O vibration. The weak shoulder at 788 cm⁻¹ may be attributed to Al–O bond vibrations. The FTIR spectra of the Mg–Al–Zn mingled oxides after adsorption (b, c) reveal the emergence of a band at 1,650 cm⁻¹, which is assigned to O–H bending mode in the interlayer water molecule. The re-emergence of the interlayer \(\text{H}_2\text{O}\) is attributed to the memory effect of the hydrotalcite. Also, the band assigning to \(\text{CO}_3^{2-}\) at 1,384 cm⁻¹ becomes more intense. In addition, the broad band at 3,445–3,500 cm⁻¹ is assigned to the O–H stretching vibration of the water molecule in the brucite-like layers (Rives & Kannan 2000; Yang et al. 2002).

Scanning electron microscopy

The SEM images of the Mg–Al–Zn mingled oxides before and after metal ions adsorption are shown in Figure 1. The image of the Mg–Al–Zn mingled oxides before adsorption (a) reveals that the particles appear as homogeneous hexagonal platelets with porous structure that are well dispersed. The porous structure provides a good adsorption capacity for cobalt and nickel. The images of Mg–Al–Zn mingled oxides after adsorption (b, c) show that solids exhibit a reconstructed surface with a plate-like morphology that differs from that of the clean surface before adsorption.

Nitrogen adsorption–desorption

Nitrogen adsorption–desorption isotherm of the Mg–Al–Zn mingled oxides is shown in Figure 2(a). According to IUPAC classification, the isotherm is classified as a type II where no hysteresis is displayed. This type reveals the existence of plate-like particles in the form of aggregates, which give rise to slit-shaped pores with non-uniform size and shape. The surface area, pore volume and mean pore diameter of the LDH were evaluated by the BET equation and found to be 65.12 m² g⁻¹, 0.15 mL g⁻¹ and 48.8 Å, respectively. The high efficiency of the Mg–Al–Zn mingled oxides for cobalt and nickel adsorption can be attributed to the high surface area. Moreover, the existence of a comparatively huge number of narrow mesopores is known to furnish a high measurable adsorption capacity. Thus, it can be concluded that during
**Figure 1**  XRD patterns, FTIR spectra, and SEM images of Mg-Al-Zn mingled oxides, (a) before adsorption, (b) after adsorption of Co(II), and (c) after adsorption of Ni(II).

**Figure 2**  N$_2$ adsorption-desorption isotherm curves (a) and TGA and DSC curves (b) of Mg-Al-Zn mingled oxides.
the calcination of Mg–Al–Zn hydrotalcite, the interlayer spaces distortion increases, which results in an increase in the total pore volume, pore radius and surface area.

**Thermal analysis**

To investigate the phase transformations during the calcination process, TGA and DSC analyses were carried out for Mg–Al–Zn LDH before calcination as shown in Figure 2(b). The TGA and DSC curves show a weight loss accompanied by an endothermic peak at 210 °C. The weight loss and endothermic peak are attributed to the water elimination from internal surfaces and the external non-gallery surfaces. The second weight loss in the temperature range of 210–450 °C and the endothermic peak at 420 °C are assigned to the dehydroxylation of the brucite-like sheets as well as the decomposition of the carbonate anions (partial overlap) (Frost et al. 2005, 2005). Thus, it can be concluded that the temperature of calcination (450 °C) is enough to convert the prepared hydrotalcite into oxide. Moreover, the TGA and DSC analyses show that the structure of the obtained mixed oxide is preserved during the calcination process.

**Adsorption mechanism**

Compared to adsorption of anions by LDHs, the adsorption mechanisms of cations are relatively complicated and different cations may interact with LDHs in different ways. In general, the adsorption of cations onto LDHs may be via (a) isomorphic substitution, (b) surface precipitation of metal hydroxide onto the surface of LDHs, and/or (c) adsorption through bonding with surface hydroxyl groups of LDHs. In the light of the above XRD patterns and FTIR spectra after adsorption, the adsorption mechanism of Co(II) and Ni(II) metal ions onto Mg–Al–Zn mingled oxides adsorbent is thought to be a surface-stimulated precipitation reaction, which takes place as a result of the centralized elevated pH values (Park et al. 2007). In particular, the regenerated Mg–Al–Zn LDH via memory effect tends to attract the hydroxide ions around the positively charged layer of Mg–Al–Zn LDH and consequently induces the emergence of metal hydroxide on the LDH surface as displayed in Figure 3. The precipitated metal cations hinder the further precipitation of metal cations on the external surface of LDH. Finally, an equilibrium between the metal cations and metal hydroxide could be attained on the surface of LDH.

**Effect of pH solution**

The pH is an important factor affecting the removal of metal ions from aqueous solutions. Dependence of metal sorption on pH is related to both the metal chemistry in the solution and the ionization state of functional groups of the adsorbent which affects the availability of binding sites (Heidari et al. 2009; Ngomsik et al. 2009).

The leaching of Al(III), Zn(II), and Mg(II) metals from the adsorbent was studied as a function of pH over the range of 1–6. The pH was adjusted to the desired value by adding negligible amounts of 0.01 M HNO₃ or NaOH. After the equilibrium time, solutions were analyzed by AAS, and the results indicated that under acidic conditions (pH ≤ 2), 20%, 0.005%, and 0.18% ratios of Al(III), Zn(II), and Mg(III), respectively, released from the adsorbent. This means that the effect of pH on the dissolution of adsorbent was nil for Zn(II), neglected for Mg(II), and small for Al(III). The ratio of Al(III) decrease with increasing pH, and reaches nil at pH = 4.

![Figure 3](https://iwaponline.com/wst/article-pdf/74/7/1644/458619/wst074071644.pdf)

Figure 3 | Schematic diagram for adsorption process of Co(II) and Ni(II) onto Mg–Al–Zn mingled oxides.
In order to evaluate the influence of pH on adsorption of Co(II) and Ni(II) metal ions, the experiments were carried out in the pH range of 4–6. The pH ranges were chosen in order to avoid the leaching of adsorbent, and to avoid precipitation of metal ions in the form of metal hydroxides at pH > 6.

As shown in Figure 4(a), the removal efficiency of Co(II) and Ni(II) is obviously influenced by pH values and increased by increasing pH from 4 to 6 for Co(II) and Ni(II), and a maximum value was reached at an equilibrium pH of around 6.0 for Co(II) and pH < 6.0 for Ni(II).

At acidic conditions, most functional groups of the components are protonated and leave few available ionized groups. Competition between protons and metal species thus explains the weak adsorption efficiency in acidic media. To achieve high extraction efficiency without metal hydroxide precipitation, pH of 6.0 for Co(II) and pH of 5.5 for Ni(II) were selected for subsequent experiments. Several researchers (Ngomsik et al. 2006; Kandaha & Meunier 2007; Vázquez et al. 2009; White et al. 2009) have investigated the effect of pH on adsorption of metal ions and they have observed a maximum adsorption of metal ions between pH values 5 and 6.

**Effect of adsorbent dose**

The effect of Mg–Al–Zn mingled oxides adsorbent dose on the removal efficiency was studied at different dose (1–5 g L\(^{-1}\)) and is presented in Figure 4(b). The removal efficiency of Co(II) and Ni(II) metal ions increased from 55.5% to 100%, and from 34.4% to 96.6%, respectively, with increasing the amount of Mg–Al–Zn mingled oxides adsorbent dose from 1 g to 5 g, which could be attributed to increases in the adsorbent surface area and consequently increases in the number of adsorption sites available for the adsorption and the number of functional groups at Mg–Al–Zn mingled oxides surfaces; hence, more exchangeable surface sites are available to form complexes with metal ions.

**Effect of initial metal ion concentration**

The effect of initial concentration of Co(II), and Ni(II) metals on the amount adsorbed per unit mass of Mg–Al–Zn mingled oxides adsorbent, \(q_e\) (mg g\(^{-1}\)), as well as the removal efficiency, was studied over the range of \(C_0 = 10–300\) mg L\(^{-1}\) and is presented in Figure 5. It was found that the amount of Co(II) and Ni(II) ions adsorbed per unit mass of the adsorbent increased from 9.3 mg g\(^{-1}\) to 119.5 mg g\(^{-1}\), and from 7.3 mg g\(^{-1}\) to 69.8 mg g\(^{-1}\), respectively, whereas the removal efficiency decreased from 100% to 42.6%, and from 75.8% to 23.6%, respectively, by increasing the initial concentration from 10 mg L\(^{-1}\) to 300 mg L\(^{-1}\). At low concentration of the metal ions, plenty of readily accessible sites are available for adsorption, and consequently the adsorption is independent of the initial metal ion concentration. The extent of adsorption decreases for a fixed adsorbent content at a high metal ion concentration due to decreased number of available adsorption sites on adsorbent surface. Similar observations

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**Figure 4** | Effect of pH (a) and adsorbent dose (b) on the adsorption behavior of Co(II) and Ni(II), \(V = 0.02\) L, \(C_0 = 200\) mg L\(^{-1}\) and \(T = 298.15\) K.
have been reported for montmorillonite (Bhattacharyya & Gupta 2007) and sawdust (Yu et al. 2000).

**Effect of contact time and kinetic study**

In order to establish the equilibration time for maximum uptake, the adsorption behavior of Co(II), and Ni(II) was investigated as a function of contact time and the results are shown in Figure 5. The figure shows that the initial uptake rate of the two metals was very high and the adsorption increased sharply within the 2 hours of contact, then rises slowly and reaches the maximum uptake of 116.7 mg g⁻¹ and 70.4 mg g⁻¹ for Co(II) and Ni(II), respectively, after 4.0 h for initial metal concentrations of 200 mg L⁻¹. The fast removal rate in the beginning is attributed to the large number of adsorption sites available for adsorption and the rapid diffusion of metals from the solution to the external surfaces of Mg–Al–Zn mingled oxides at the initial stages. As time proceeds, the sites are gradually filled up, adsorption proceeds more slowly and the adsorbed metals accumulated on the surface sites, leading to the decrease in the adsorption rate at the later stages.

In order to identify the rate and kinetics of the adsorption process, two kinetic models, namely, the pseudo-first-order (PFO) and pseudo-second-order (PSO) in both their linear and non-linear forms, have been employed to fit the experimental data.

**Pseudo-first-order model**

The Lagergren rate equation (Ho et al. 2000; Ho 2004) is one of the most widely used rate equations describing the adsorption of a liquid/solid system based on solid capacity. The linear and non-linear forms of the PFO equation are given by Equations (3) and (4), respectively, as follows:

\[
\log \left( \frac{q_t}{q_e} \right) = \log \frac{q_e}{K_1 t} + \frac{1}{K_1 t}
\]

(3)

\[
q_t = q_e(1 - e^{-K_1 t})
\]

(4)

where \(q_e\) and \(q_t\) are the capacity of metal ions adsorbed (mg g⁻¹) at equilibrium and time \(t\) (h), respectively, and \(K_1\) is the PFO rate constant (h⁻¹).

**Pseudo-second-order model**

The PSO kinetic model (Ho 2006), expresses the rate of adsorption as a function of the adsorption capacity; however, it assumes that the rate-limiting step may be chemical adsorption, involving valence forces through the sharing or exchange of electrons between adsorbent and adsorbate. The linear and non-linear forms of the PSO kinetic model are given by Equations (5) and (6), respectively,
as follows (Khan et al. 2015):

\[ \frac{t}{q_t} = \frac{1}{K_2q_e} + \frac{1}{q_e}t \]  
(5)

\[ q_t = \frac{(K_2q_e^2t)}{(1 + K_2q_e)t)} \]  
(6)

where \( K_2 \) (g mg\(^{-1}\) h\(^{-1}\)) is the PSO rate constant for the adsorption process.

The calculated values of \( K_1, \) \( K_2, \) the theoretical \( q_{e,\text{calc}} \) and \( q_{e,\text{exp}} \) (mg g\(^{-1}\)), together with the correlation coefficients \( (R^2) \) obtained are tabulated in Table 1. The results indicate that \( q_{e,\text{calc}} \) values calculated from the linear PFO model did not give reasonable values with regard to the experimental uptake ones of Co(II) and Ni(II), while \( q_{e,\text{calc}} \) values obtained from non-linear PFO give a better match with the experimental ones. However, the \( R^2 \) values are low for both linear and non-linear PFO comparing with \( R^2 \) values obtained from PSO. Also, the results showed that for Co(II) metal ions, the linear PSO equation exhibited higher \( R^2 \) of 0.999, followed by the non-linear PFO model, then by the non-linear PSO, and finally by the linear PFO model. However, compared with the \( q_{e,\text{calc}} \) values of the models, the \( q_{e,\text{calc}} \) value of the nonlinear PFO model was considered to agree well with the experimental value \( q_{e,\text{exp}} \). For Ni(II) metal ions, the linear PSO equation has higher \( R^2 \) value, followed by the non-linear PSO model, then by the linear PFO model and finally by the non-linear PFO model. On the other hand, the \( q_{e,\text{calc}} \) values of the non-linear PFO model agree well with the experiment uptake ones \( q_{e,\text{exp}} \).

From the fit curves shown in Figure 6, it can be seen that linear PSO is predominant followed by non-linear PFO for Co(II), and both linear and non-linear curves of PSO are predominant for Ni(II). These results suggest that the second-order mechanism is predominant, in which the adsorption mechanism depends on the adsorbate and

<p>| Table 1 | The kinetic parameters obtained by using linear and non-linear forms for adsorption of Co(II), and Ni(II) on Mg–Al–Zn mingled oxides adsorbent |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|</p>
<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>( q_{e,\text{exp}} ) (mg g(^{-1}))</th>
<th>( q_{e,\text{calc}} )</th>
<th>( R^2 )</th>
<th>( K_1 ) (h(^{-1}))</th>
<th>Linear</th>
<th>Non-linear</th>
<th>Linear</th>
<th>Non-linear</th>
<th>Linear</th>
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<th>Non-linear</th>
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<tr>
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<td>116.7</td>
<td>1.4739</td>
<td>2.061</td>
<td>91.2</td>
<td>115.92</td>
<td>0.971</td>
<td>0.988</td>
<td>0.032</td>
<td>0.003</td>
<td>125.0</td>
<td>126.5</td>
<td>0.999</td>
<td>0.980</td>
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<tr>
<td>Ni(II)</td>
<td>70.4</td>
<td>1.4647</td>
<td>2.433</td>
<td>52.0</td>
<td>69.2</td>
<td>0.978</td>
<td>0.952</td>
<td>0.056</td>
<td>0.049</td>
<td>76.9</td>
<td>74.7</td>
<td>0.999</td>
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</table>

Figure 6 | Time dependence of Co(II) and Ni(II) adsorption onto Mg–Al–Zn mingled oxides, \( C_0 = 200 \text{ mg L}^{-1}, \) \( m = 0.02 \text{ g}, \) \( V = 0.02 \text{ L}, \) and \( T = 298.15 \text{ K}. \)
adsorbent, and the rate-limiting step may be a chemisorption process including valence forces through sharing or exchanging of electrons (Fang et al. 2014). This may be because the hydroxyl groups on the surface of adsorbent can create intensive interaction with Co(II) and Ni(II) metal ions through the electrostatic and chemical effects, where the mingled oxides tend to retrieve the hydroxyl groups via memory effect.

The low value of the rate constant ($K_2$) suggested that the adsorption rate decreased with the increase in time and the adsorption rate was proportional to the number of unoccupied sites (Gupta et al. 2010; Xu et al. 2012).

### Adsorption isotherms

The adsorption equilibrium data were further analyzed using Langmuir and Freundlich isotherm models to fit the adsorption isotherms. Linear and non-linear regression analysis was used to estimate various isotherm parameters and evaluate the best fitting model using the correlation coefficients.

The Langmuir model assumes that adsorption occurs in a monolayer with all adsorption sites identical, energetically equivalent and independent of each other. The Langmuir equations in linear and non-linear forms are expressed by Equations (7) and (8), respectively, as:

$$\frac{C_e}{q_e} = \frac{1}{bq_{\text{max}}} + \frac{C_e}{q_{\text{max}}}$$  

(7)

$$q_e = q_{\text{max}} \frac{bC_e}{(1 + bC_e)}$$  

(8)

where $C_e$ is the equilibrium metal ion concentration in the solution (mg L$^{-1}$); $q_e$ is the equilibrium metal ion concentration per unit mass of adsorbent (mg g$^{-1}$); $q_{\text{max}}$, the maximum adsorption capacity, is the amount of metal ions at complete monolayer coverage (mg g$^{-1}$); and $b$ (L mg$^{-1}$) is the Langmuir constant related to energy of adsorption. Langmuir parameters, $q_{\text{max}}$ and $b$, together with correlation coefficients are tabulated in Table 2.

The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant called the separation factor or equilibrium parameter, $R_L$ (Weber & Chakkravorti 1974). Values of $R_L$ indicate the shapes of isotherms to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable (0 < $R_L < 1$) or irreversible ($R_L = 0$).

$$R_L = \frac{1}{1 + bC_0}$$  

(9)

The Freundlich isotherm model is an empirical expression that encompasses the heterogeneity of the surface of the adsorbent, suggesting that binding sites are not equivalent and/or independent. The Freundlich isotherm parameters were calculated using the linear and non-linear forms, expressed by Equations (10) and (11), respectively, as follows:

$$\log q_e = \log K_f + \frac{1}{n_f} \log C_e$$  

(10)

$$q_e = K_f C_e^{1/n_f}$$  

(11)

where $K_f$ represents the adsorption capacity when metal ion equilibrium concentration equals 1, and $n_f$ represents the degree of dependence of adsorption with equilibrium concentration. Freundlich constants $K_f$ and $n_f$ are listed in Table 2.

The adsorption isotherm, and Langmuir and Freundlich models fitting the adsorption of Co(II), and Ni(II) are presented in Figure 7. On the basis of observation, it is reasonable to

<table>
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<tr>
<th>Metal Ion</th>
<th>$q_{\text{max}}$,calc</th>
<th>Linear</th>
<th>Non-linear</th>
<th>$K_L$</th>
<th>Linear</th>
<th>Non-linear</th>
<th>$R_L$</th>
<th>Linear</th>
<th>Non-linear</th>
<th>$R^2$</th>
<th>Linear</th>
<th>Non-linear</th>
<th>$R^2$</th>
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<td>Co(II)</td>
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<td>113.8</td>
<td>0.1739</td>
<td>0.191</td>
<td>0.0188-</td>
<td>0.3651</td>
<td>0.0172-</td>
<td>0.3436</td>
<td>0.994</td>
<td>0.967</td>
<td>28.445</td>
<td>32.82</td>
<td>3.378</td>
<td>3.906</td>
<td>0.957</td>
<td>0.971</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni(II)</td>
<td>83.33</td>
<td>79.44</td>
<td>0.0367</td>
<td>0.036</td>
<td>0.0833-</td>
<td>0.7315</td>
<td>0.0847-</td>
<td>0.7553</td>
<td>0.998</td>
<td>0.993</td>
<td>6.053</td>
<td>10.19</td>
<td>2.035</td>
<td>2.703</td>
<td>0.947</td>
<td>0.944</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
assume that the surface sites of Mg–Al–Zn mingled oxides adsorbent have higher affinity for cobalt than for nickel.

The results indicated that the values of Langmuir isotherm parameters obtained from linear and non-linear forms are comparable for Ni(II), and different for Co(II). On the other hand, the isotherm parameters obtained using the non-linear form of Freundlich were more accurate than that of the linear form for Co(II), and Ni(II).

Nonlinear regression is a more general method that can be used to estimate models’ parameters, and it can be applied even if the isotherm model cannot be linearized. For linearized regression, the major problem is the linearization step: modifying the original equation can violate the theories existing behind the model; so in fact the parameter estimation gives the best fitting parameters for the linear form of the model, not necessarily for the original nonlinear one. The mathematical reason for this is that the linear regression considers the standard deviations (so the differences between the measured and the calculated values) equally in each point. But, due to the linearization, the unity standard deviation in points of the linear form is not valid for the nonlinear form. Therefore, comparing the two methods, nonlinear regression is the most feasible method that can be used to estimate isotherm model parameters. Moreover, it deals with the original equations so that the problem of violating the model theories does not exist anymore. The obtained model parameters calculated using nonlinear regression are more relevant than those obtained with linear regression.

The adsorption isotherm studies indicate that the adsorptive behavior of Co(II) metal ions on Mg–Al–Zn mingled oxides adsorbent satisfies not only the Langmuir assumptions but also the Freundlich assumptions (non-linear form) with R² value of 0.971. On the other hand, the adsorption isotherm of Ni(II) was best described by the Langmuir isotherm model with R² value of 0.994.

The n_l values obtained from the Freundlich isotherm were >2, which supports the favorable adsorption of Co(II) and Ni(II) metal ions on this adsorbent. Furthermore, the fact that all the R_L values obtained from the Langmuir isotherm are in the range of 0.0172–0.3436 and 0.0847–0.7353 for all initial concentrations of Co(II) and Ni(II) metal ions, respectively, implies that the adsorption of Co(II) and Ni(II) metal ions onto Mg–Al–Zn mingled oxides adsorbent was favorable under the operating conditions being studied.

From the fit curves shown in Figure 7, it can be seen that the Langmuir isotherm model is predominant and fits the experimental data well, indicating that the binding energy on the whole surface of Mg–Al–Zn mingled oxides adsorbent is uniform and the whole surface of Mg–Al–Zn mingled oxides adsorbent has identical adsorption activity, forming an almost complete monolayer coverage of adsorbent, and the principal uptake mechanism of the adsorption process is chemosorption (Zhao et al. 2014).

On the basis of the Langmuir analysis, the values of maximum adsorption capacities (q_max) were determined to be 113.8 mg g⁻¹ and 79.4 mg g⁻¹ for Co(II) and Ni(II), respectively, comparable to the maximum adsorption capacity obtained from their adsorption isotherms.
(116.7 mg g⁻¹, 70.4 mg g⁻¹). Satisfactory fitting of the Langmuir model to the adsorption of cobalt and nickel on different adsorbents has also been reported by various researchers (Parab et al. 2006; Krishnan & Anirudhan 2008; Ahmadpour et al. 2009; Olgun & Atar 2011).

**Real waste water adsorption**

In order to survey the capability of the prepared adsorbent for removal of Co(II) and Ni(II) from a real wastewater sample, batch experiments were conducted on a produced wastewater sample associated with petroleum oil, collected from Petrobel Company. The measured physico-chemical characteristics are shown in Table 3. The results show that the produced wastewater contains a high concentrations of different ions, especially of total dissolved solids and electrical conductivity, which can interfere with adsorption of Co(II) and Ni(II) on the adsorbent. As shown in Figure 8, the adsorbent has a good tendency for adsorption of heavy metals, not only for Co(II) and Ni(II), but also for Pb(II), and the removal percentage increases as the adsorbent dose increases.

**Regeneration process**

The transformation of the mingled metal oxides into LDHs has been variously referred to as regeneration, reconstruction, restoration, rehydration or the calcination–rehydration process, structural memory effect or simply memory effect. The calcination of LDH containing carbonate as interlayer anion causes the formation of M²⁺M³⁺O solid solution capable of recovering the LDH layered structure upon treatment with water or aqueous solution containing various anions via the so-called memory effect. If the calcination temperature is too high, such as higher than 600 °C, stable M³⁺M²⁺2O₄ spinel and M²⁺O phases are formed and LDHs cannot be reconstructed (Cardoso & Valim 2004; Das et al. 2006). LDH Mg–Al–Zn mingled oxides were regenerated by calcination at 400 °C for 5 h before being reused as adsorbent. Adsorption results of Co(II) and Ni(II) using the regenerated LDH Mg–Al–Zn mingled oxides as the adsorbent after the thermal recycling is shown in Figure 9. It can be found that, after the first-cycle regeneration, LDH Mg–Al–Zn mingled oxides sorption capacity decreased from 116.7 mg g⁻¹ and 70.4 mg g⁻¹ to 100.3 mg g⁻¹ and 60.5 mg g⁻¹ for Co(II) and Ni(II), respectively, with adsorption efficiency of 86% compared with the original LDH Mg–Al–Zn mingled oxides. The progressive reduction after the second-cycle regeneration was decreased from 100.3 mg g⁻¹ to 90.1 mg g⁻¹ and from 60.5 mg g⁻¹ to 54.6 mg g⁻¹ for Co(II) and Ni(II), respectively, with adsorption efficiency of 90%, compared with the first-cycle.

It has been pointed out that the structural reconstruction of the heated material may be disturbed after the second and third thermal regeneration, and hence its crystallinity and adsorption ability decreased (Yanwei et al. 2015).

**Table 3 | Physico-chemical characteristics of real wastewater**

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.66</td>
</tr>
<tr>
<td>Density</td>
<td>1.060 g mL⁻¹</td>
</tr>
<tr>
<td>EC</td>
<td>106.5 mS cm⁻¹</td>
</tr>
<tr>
<td>TDS</td>
<td>79,400 mg L⁻¹</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>47,720 mg L⁻¹</td>
</tr>
<tr>
<td>Na⁺</td>
<td>26,200 mg L⁻¹</td>
</tr>
<tr>
<td>K⁺</td>
<td>570 mg L⁻¹</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>3,100 mg L⁻¹</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>940 mg L⁻¹</td>
</tr>
<tr>
<td>Co(II)</td>
<td>4.456 mg L⁻¹</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>3.234 mg L⁻¹</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>2.785 mg L⁻¹</td>
</tr>
<tr>
<td>Mn(II)</td>
<td>3.204 mg L⁻¹</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>4.336 mg L⁻¹</td>
</tr>
</tbody>
</table>

<sup>aEC: electrical conductivity.  
</sup><sup>bTDS: total dissolved solids.  
</sup>
CONCLUSION

The present study shows that Mg–Al–Zn mingled oxides can be used as a potential adsorbent for the removal of both Co(II) and Ni(II) from their aqueous solutions. The maximum adsorption capacity was 116.7 mg g⁻¹ and 70.4 mg g⁻¹ for Co(II) and Ni(II), respectively. The amount of metal ions adsorbed was found to vary with increasing initial solution pH up to a point at which metal ions are precipitated out in alkaline solution. The optimum pH was found to be 6 and 5.5 for the Co(II) and Ni(II), respectively. The experimental data obeyed the PSO rate equation. The equilibrium data of two metals fitted well to the Langmuir isotherm and Freundlich isotherm models, and the maximum adsorption capacity values were 113.8 mg g⁻¹ and 79.4 mg g⁻¹ for Co(II) and Ni(II), respectively. The results indicate that the adsorbent has good potential for cost-effective removal of heavy-metal ions from contaminated wastewater, comparable to the conventional adsorbents.

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