



## Removal of heavy metal ions by iron oxide coated sewage sludge

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### ABSTRACT

The municipal sewage sludge was modified with iron oxide employed in metal ions removal. The surface modification method was proposed and the effect of parameters in the preparation was studied. The iron oxide coated sludge had higher surface area, pore volume and iron content, compared to uncoated sludge. The suitable conditions for removal of Cu(II), Cd(II), Ni(II) and Pb(II) ions from solutions were investigated using batch method. The suitable pH value in the extraction was 7 for adsorption of Cd(II) and Ni(II), 6 for Cu(II) and 5 for Pb(II) ions. The presence of NaNO<sub>3</sub>, Ca(NO<sub>3</sub>)<sub>2</sub> and Na<sub>2</sub>SO<sub>4</sub> in metal solution in the concentration of 0.01 M and 0.50 M could reduce the removal efficiency. The adsorption isotherms for the adsorption of the metal ions were defined by Langmuir relation. The maximum adsorption capacity of the iron oxide coated sludge for Cu(II), Cd(II), Ni(II) and Pb(II) was 17.3, 14.7, 7.8 and 42.4 mg g<sup>-1</sup>, respectively. The adsorption kinetics for every metal ions followed pseudo-second order model. The metal removal from wastewater by iron oxide coated sludge was also demonstrated.

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### 1. Introduction

An increase in amount of sewage sludge generated by wastewater treatment plant is the main factor of surplus sludge problem. There are few methods that have been used to dispose or utilize the sludge, e.g. incineration, landfill, application to farmland and forestry [1]. The reuse of sewage sludge is an attractive alternative that is being widely studied. The potential applications of sludge are governed by its properties. Many researchers have focused on making the use of sludge as adsorbents due to high carbon content in biochemical sludge [2]. It is considered as low cost material for producing adsorbents and has been used as starting material in the preparation of high surface area adsorbents (e.g. activated carbon) [2]. The application of sewage sludge and the adsorbents derived from sewage sludge in water treatment has been widely investigated. They have been used in the removal of organic pollutants [3,4] and toxic metal ions [5–7]. To improve the adsorption efficiency of adsorbents derived from sewage sludge, the surface modification is an alternative. This work focuses on the modification of sewage sludge surface with iron oxide for the application in metal removal.

Iron oxides precipitates are promising adsorbents for metal ions and organic compounds [8–10]. However, most iron oxide are only available as fine powder and the used of iron oxide powder is limited by difficulty in separation of the solid from solution. The coating

of iron oxide on solid supporting media was proposed and different media have been used. Both inorganic support (e.g. sand, silica, cement) and organic support (e.g. granular activated carbon, biomass) were employed [11–17]. The use of low cost materials such as natural zeolite, municipal solid waste melted slag and silica gel waste was also proposed [18–20]. It was demonstrated in these researches that these iron oxide coated media could remove toxic metal ions from water. The adsorption capacity seems to depend on the surface properties of the coated materials which could be related to the nature of the supporting materials. In this work, the municipal sewage sludge is chosen as low cost supporting material for iron oxide coating. The modification method is proposed. The obtained adsorbents were characterized and used in removal of Cu(II), Cd(II), Ni(II) and Pb(II) ions. The effect of pH and interfering ions on the removal efficiency were studied. The adsorption isotherms and kinetics were also investigated.

### 2. Materials and methods

The municipal sewage sludge used in this study was collected from the sludge thickener in wastewater treatment plants in Bangkok, Thailand (Jatujak, Huaykwang and Chong nonsi plant). The sludge sample was first dried in the open air, crushed and sieved into a uniform size of less than 0.2 mm. Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Carlo Erba Reagenti, Rodano) was used in the coating. The metal ion solutions used for adsorption experiments were prepared by stepwise dilution of 1000 mg L<sup>-1</sup> standard solutions (BDH Laboratory supplies). The ionic strength and pH of metal solutions were controlled by 0.05 M sodium acetate buffer (Carlo Erba). The pH was adjusted to

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the desired value using either NaOH or HCl (Merck) solutions. All reagents and solvents were analytical grade and used as received.

The concentration of metal ions was determined by flame atomic absorption spectrometer (FAAS) (Perkin-Elmer, Analyst 100). The iron oxide-coated sewage sludge was characterized for specific surface area and pore size using a surface area analyzer (Quantachrome, Autosorb-1) on nitrogen adsorption principle. The specific surface area was calculated by Brunauer–Emmet–Teller method (BET). The carbon content of the adsorbents was determined using CHNS/O Analyzer (LECO: CHN 2000). The iron oxide content in the adsorbents was determined using USEPA METHOD 3050B [21].

### 2.1. Preparation of iron oxide-coated sewage sludge

A modified precipitation method was adopted [13,22]. The municipal sewage sludge was collected and treated at a specified pretreatment temperature for 3 h before coating. The amount of 5 g sewage sludge was added to 10 mL of solution containing 2.0 g  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (2.77%, w/v, Fe). The pH of the mixture was adjusted to the desired value with NaOH. The mixture was stirred for 1 h, dried at 105 °C for 20 h and then washed with de-ionized water to remove unattached oxide until the pH of the runoff water was constant (pH 7–8). The solid was dried at 105 °C for 24 h and finally stored in a capped bottle for further use. The effects of pretreatment temperature, pH of ferric solution and amount of ferric nitrate were studied. The effect of coating parameters was evaluated by comparing the adsorption capacity for Cu(II) ions of the adsorbents obtained from different preparation conditions.

### 2.2. Adsorption experiments

The adsorption experiments were carried out using a batch method. The experiment was performed by adding 0.01 g adsorbent to 10 mL of solution containing metal ions (Cu(II), Cd(II), Ni(II) or Pb(II)). The initial concentration was 20 mg L<sup>-1</sup> (pH 5) for Cu(II), Cd(II) and Ni(II) and 30 mg L<sup>-1</sup> (pH 4) for Pb(II) ions. The mixture was stirred for 1 h at room temperature to assure the adsorption equilibrium. The solid was separated by centrifugation and the solution was analyzed by a flame atomic absorption spectrometer to determine the residual metal concentration. The adsorption kinetics was studied using different adsorbent doses (1, 5 and 10 g L<sup>-1</sup>) with an initial concentration of 50, 30, 20 and 200 mg L<sup>-1</sup> for Cu(II), Cd(II), Ni(II) and Pb(II), respectively. The adsorption isotherm experiments were carried out by varying the initial concentration of metal solutions and the temperature was controlled at 25.0 ± 1.0 °C. All experiments were performed in triplicate.

## 3. Results and discussion

### 3.1. Preparation and characterization of iron oxide coated sludge

The effect of pH of ferric solution, amount of Fe and sludge pretreatment temperature was investigated and evaluated by comparing the adsorption capacity for Cu(II) ions of the coated sludge obtained. The results are summarized in Table 1. When increased the pH of ferric solution from 2 to 12, the adsorption capacity of the coated sludge also increased. The modification at pH higher than 3 was attributed to the adsorption of ferric hydroxide precipitate ( $\text{Fe}(\text{OH})_3$ ) on the surface [23]. When sludge was coated by iron oxide at pH 12, the adsorption capacity increased from 15.3 mg g<sup>-1</sup> of non-coated sludge to 17.3 mg g<sup>-1</sup>. The pH of 12 was chosen for iron oxide coating.

Then, the amount of ferric nitrate used in the coating was varied within a range of 0.25 to 5.0 g in 10 mL solution (0.35–6.93%, w/v, Fe) for coating of 5 g sludge. The adsorption capacity for Cu(II) ions

**Table 1**

Effect of pH, amount of Fe and pretreatment temperature on the adsorption capacity of the obtained adsorbents.

| Parameters                                 | Adsorption capacity for Cu (mg g <sup>-1</sup> ) |               |
|--|--|---------------|
|  | Non coated sludge                                | Coated sludge |
| Sludge <sup>a</sup>                        | 15.3 ± 0.1                                       |               |
| pH of ferric solution <sup>b</sup>         |  |               |
| 2  |  | 9.4 ± 0.3     |
| 7  |  | 15.3 ± 0.1    |
| 12   |  | 17.3 ± 0.1    |
| Amount of Fe (% w/v) <sup>c</sup>          |  |               |
| 0.35                                       |  | 17.5          |
| 0.69                                       |  | 16.1 ± 0.4    |
| 1.39                                       |  | 17.0 ± 0.4    |
| 2.77                                       |  | 19.7 ± 0.1    |
| 4.16                                       |  | 19.6 ± 0.2    |
| 6.93                                       |  | 19.8 ± 0.1    |
| Pretreatment temperature (°C) <sup>d</sup> |  |               |
| No treatment                               | 13.3 ± 0.4                                       | 15.4 ± 0.1    |
| 100  | 13.1 ± 0.4                                       | 17.9 ± 0.3    |
| 300  | 10.6 ± 0.3                                       | 19.1 ± 0.1    |
| 500  | 6.2 ± 0.2  | 16.7 ± 0.4    |

<sup>a</sup> Non pretreated sludge.

<sup>b</sup> Coating of non pretreated sludge with ferric solution 0.69% (w/v) Fe.

<sup>c</sup> Coating of non pretreated sludge with ferric solution at pH 12.

<sup>d</sup> Coating with ferric solution 2.77% (w/v) Fe at pH 12.

of the coated sludge increased in increasing the ferric concentration from 0.35 to 2.77% (w/v) and attained a constant value when using higher concentrations. These results can be explained by the limited surface of sludge. When an excessive amount of ferric nitrate was used, the uncoated iron oxide would be removed by washing at the end of preparation process. Therefore, the concentration of 2.77% (w/v) Fe was proposed for the coating. Nevertheless, the suitable concentration can be changed depending on the nature of the sludge (i.e. surface area, particle size).

Furthermore, the effect of sludge pretreatment was investigated. The sludge used in this experiment was collected from water treatment of different batches from that of the previous experiments. Hence, the adsorption capacity of the non coated sludge was slightly different from the value observed previously (Table 1). The sludge was treated at 100, 300 or 500 °C before use. The pretreated sludge was then coated with iron oxide using the condition recommended previously. The non coated sludge which undergone thermal treatment had lower adsorption capacity for Cu(II) ions than untreated sludge. The higher adsorption efficiency of the untreated sludge could be attributed to the presence of organic matter on the sludge. When the sludge was treated at 300 °C and 500 °C, the volatile organic matters were removed, resulting in a decrease in adsorptive sites on surface. In contrast, when the treated sludge was coated with iron oxide, the adsorption capacity of the products increased significantly in increasing treatment temperature from 100 °C to 300 °C. The treated sludge might have surface characteristics that are more suitable for iron oxide coating, compared to untreated sludge and sludge treated at 100 °C. However, when the sludge was treated at 500 °C before coating, the adsorption capacity of the coated solid was lower than the other adsorbents prepared from treated sludge. It is probably due to the reduction in carbon content in the sludge after the pretreatment at 500 °C under air atmosphere and open system (Table 2). Therefore, the sludge treated in open atmosphere at very high temperature like 500 °C is not a suitable support for iron oxide coating.

To investigate the repeatability of the proposed method, the coating was repeated using sludge of the same batch. The sludge was pretreated at 300 °C and coated with ferric solution (2.77%, w/v) having pH 12. The obtained coated sludge had adsorption capacity for Cu(II) within the range of 15.3–17.9 mg g<sup>-1</sup>, with the average of 16.4 mg g<sup>-1</sup> (n = 15). These adsorption capacities are

**Table 2**  
Characterization of non coated and coated sludge.

| Parameters                                     | Non treated and non coated sludge | Pretreated and non coated sludge | Pretreated and coated sludge |
|--|-----------------------------------|----------------------------------|------------------------------|
| Surface area (m <sup>2</sup> g <sup>-1</sup> ) | 6.31                              | 35.59                            | 59.26                        |
| Pore volume (cm <sup>3</sup> g <sup>-1</sup> ) | 0.04                              | 0.10                             | 0.14                         |
| Pore size (Å)                                  | 240.0                             | 109.7                            | 92.5                         |
| Fe amount (mg g <sup>-1</sup> ) <sup>a</sup>   | 24.6 ± 0.1                        | 31.2 ± 0.2                       | 72.8 ± 1.1                   |
| Carbon content (%)                             | 17.78                             | 7.90                             | 6.79                         |

<sup>a</sup> Mean ± SD (n = 3).

higher than that of non coated sludge (13 mg g<sup>-1</sup>). The results show that when use the proposed method, there would be a slight difference in adsorption capacity of the products obtained. Since the coating of iron oxide on the surface occurred via physisorption, the coating may not occur in the same extent each time.

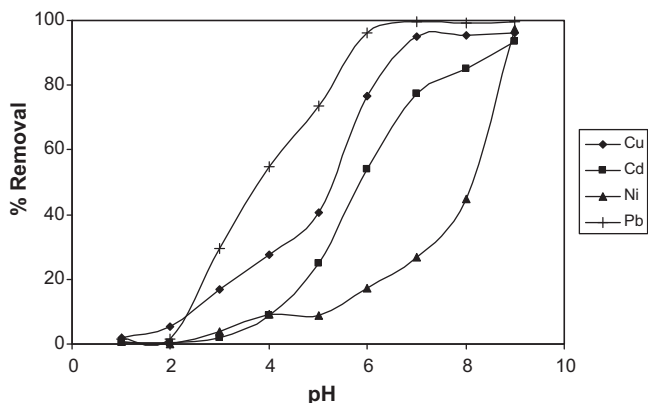
### 3.2. Characterization of iron oxide coated sludge

The physical characteristics and chemical composition of the coated sludge were investigated and compared to non coated sludge (Table 2). The pore size of the coated sludge was smaller than that of non coated sludge, resulting in higher surface area and larger pore volume. The increase in surface area could be attributed to the presence of porous iron oxide on the surface. The same results were observed by Xu and Axe [13] when silica was coated with iron oxide. In their study, the surface area of the iron oxide coated on silica support was calculated from experimental results and the surface area of 78 m<sup>2</sup> g<sup>-1</sup> was reported.

When treated the sludge before coating, the carbon content of the treated sludge decreased significantly due to the loss of the volatile organic substances. The Fe amount also increased from 24.6 to 31.2 mg g<sup>-1</sup>. The reduction of carbon content after pretreatment led to a higher proportion of Fe in the sludge. When coated the treated sludge with iron oxide, the Fe amount increased to 72.8 mg g<sup>-1</sup>.

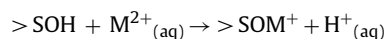
### 3.3. Effect of pH on metal removal and iron leaching

The effect of pH on the removal of Cu(II), Cd(II), Ni(II) or Pb(II) ions from solution was investigated by varying the pH of metal solution within the range of 1–9 (Fig. 1). In strong acid solution (pH between 1 and 2), only a slight amount of metal ions could be removed. When the pH of the solution increased from 2 to 8, the removal efficiency increased. In solution having low pH value, there would be a competition between protons and metal ions in



**Fig. 1.** Effect of pH of metal solutions on removal efficiency (concentration 30 mg L<sup>-1</sup> Pb(II), 30 mg L<sup>-1</sup> Ni(II), 20 mg L<sup>-1</sup> Cu(II) and 20 mg L<sup>-1</sup> Cd(II); adsorbent dose 1 g L<sup>-1</sup>).

the adsorption on surface hydroxyl groups, resulting in low metal adsorption. Moreover, when the active sites are protonated, the surface becomes positively charged and consecutive adsorption of metal ions in solution on the surface is less likely to occur. Regarding the pH<sub>PZC</sub> of iron oxide (pH<sub>PZC</sub> goethite = 8.78 [13]), in solution having pH value lower than pH<sub>PZC</sub> of iron oxide, the surface hydroxyl sites could be protonated and positively charged. On the other hand, the active sites are deprotonated when the solution pH is higher than pH<sub>PZC</sub>, resulting in negatively charged sites and the adsorption of metal cations on iron oxide could possibly take place via electrostatic interaction with the negatively charged sites on iron oxide surface [24]. However, in this study, the removal of metal ions was observed in solutions having pH values less than pH<sub>PZC</sub> of iron oxide, therefore, the adsorption of metal ions on iron oxide surface would occur via non-electrostatic interaction. The possible mechanism of metal ions (M<sup>2+</sup>) adsorption on iron oxide surface (>SOH) is shown below [25].



When the pH of solution increased, the degree of protonation on surface hydroxyl groups also decreased and the metal adsorption is more favorable, resulting in an increase in removal efficiency.

At pH 6 and higher, the precipitation of Pb(II) and Cu(II) as metal hydroxide was likely to occur. The removal of metal ions at these pH values could be attributed to both metal hydroxide precipitation and metal ions adsorption. The suitable pH for adsorption of Cd(II) and Ni(II) is 7 and for Cu(II) and Pb(II) is 6 and 5, respectively. Nevertheless, the suitable pH may change depending on the concentration of the metal ions in solution. The results observed in our study is in agreement with those of Peng et al. [26] and Chen et al. [27], who investigated the adsorption of metal ions by iron oxide modified carbon nanotubes and sand, respectively.

The leaching amount of iron from the adsorbents to the metal solutions was determined. The dissolution of iron oxide coating was observed in the solution having pH below 3. The leaching of iron from the adsorbents into metal solutions was in the range of 57–60 mg g<sup>-1</sup> adsorbent at pH 1 and 3–6 mg g<sup>-1</sup> adsorbent at pH 2. The disappearance of iron oxide from the surface would lower the adsorption efficiency of the adsorbent and therefore explain the low removal efficiencies observed at pH 1 and 2.

### 3.4. Adsorption isotherms

In order to study the adsorption behavior of the metal ions on the adsorbents, the experiments for adsorption isotherms were carried out at 25 °C. The pH of metal solutions was controlled at 5 for Cu(II), Cd(II) and Ni(II) and 4 for Pb(II). The experimental data were fitted to Langmuir and Freundlich isotherm equation [28,29]. Langmuir isotherm (Eq. (1)) assumes the adsorption onto the homogeneous surface with specific number of equivalent sites. On the other hand, Freundlich isotherm (Eq. (2)) represents the sorption onto the heterogeneous surface.

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (1)$$

$$\log q_e = \log K_f + \frac{1}{n}(\log C_e) \quad (2)$$

The parameter  $q_e$  and  $C_e$  represent the amount of metal ions adsorbed at equilibrium (mg g<sup>-1</sup>) and the concentration at equilibrium (mg L<sup>-1</sup>), respectively. The Langmuir constant ( $b$ ) related to the binding energy and the maximum adsorption capacity ( $q_m$ ) can be determined from the intercept and the slope of the linear plot between  $C_e/q_e$  and  $C_e$ . The Freundlich constants,  $K_f$  and  $n$  represent capacity (mg g<sup>-1</sup>) and intensity of the adsorption and can be calculated from the intercept and slope of the linear plot of  $\log q_e$

**Table 3**

Langmuir and Freundlich constants for adsorption of metal ions onto iron oxide coated sludge.

| Metal | Langmuir constants          |                           |       | Freundlich constants        |      |       |
|-------|-----------------------------|---------------------------|-------|-----------------------------|------|-------|
|       | $q_m$ (mg g <sup>-1</sup> ) | $b$ (L mg <sup>-1</sup> ) | $R^2$ | $K_f$ (mg g <sup>-1</sup> ) | $n$  | $R^2$ |
| Cu    | 17.3                        | 0.74                      | 0.956 | 3.98                        | 3.68 | 0.918 |
| Cd    | 14.7                        | 8.65                      | 0.998 | 2.24                        | 2.78 | 0.924 |
| Ni    | 7.8                         | 2.20                      | 0.983 | 0.99                        | 2.54 | 0.969 |
| Pb    | 42.4                        | 62.3                      | 0.990 | 6.98                        | 3.03 | 0.986 |

versus  $\log C_e$ , respectively. The Langmuir and Freundlich constants are summarized in Table 3.

Regarding the correlation coefficients, the experimental data fit Langmuir isotherm better than Freundlich isotherm for the adsorption of all metal ions. Therefore, the adsorption of these metal ions onto the iron oxide coated sludge occurred in monolayer regime, with the maximum adsorption capacity of 0.27 mmol g<sup>-1</sup> for Cu(II), 0.20 mmol g<sup>-1</sup> for Pb(II) and 0.13 mmol g<sup>-1</sup> for Cd(II) and Ni(II). The adsorption capacity of iron oxide coated sludge for metal ions is compared to the capacity of the other adsorbents in Table 4. The adsorbents obtained in this study show relatively good adsorption capacities compared to the sewage sludge, adsorbents derived from sewage sludge and other iron oxide modified adsorbents.

### 3.5. Effect of adsorbent dose and adsorption kinetics

The adsorption kinetics was investigated when used different adsorbent doses. When the adsorbent dose was increased, the adsorption equilibrium was attained in a shorter time and higher removal efficiency was achieved due to the increase in number of adsorptive sites (Fig. 2). On the other hand, the adsorption capacity,

**Table 4**

Comparison of adsorption capacity of iron oxide coated sludge with other adsorbents.

| Adsorbents   | Adsorption capacity (mmol g <sup>-1</sup> )    | References |
|--|--|------------|
| Sewage sludge (chemical pyrolysis)                       | Ni (0.155), Cd (0.149)                         | [5]        |
| Sewage sludge ash  | Cu (0.052), 0.065)                             | [30]       |
| Carbon nanotubes-iron oxide magnetic composites          | Cu (0.71), Pb (0.51)                           | [26]       |
| Multiwall carbon nanotube/iron oxide magnetic composites | Ni (0.16)                                      | [27]       |
| Zeolite-iron oxide magnetic composites                   | Pb (0.59)                                      | [31]       |
| Magnetite modified alginic acid                          | Pb (1.75)                                      | [32]       |
| Alumina-supported iron oxide                             | Pb (0.14)                                      | [33]       |
| Iron oxide coated waste silica gel                       | Ni (0.072), Cu (0.053), Pb (0.039), Cd (0.038) | [20]       |
| Iron oxide modified sewage sludge                        | Cu (0.27), Pb (0.21), Ni (0.13), Cd (0.13)     | This work  |

considered as amount of metal ions adsorbed per gram of adsorbents, decreased in increasing the adsorbent dose. An increase in adsorbent dose resulted in a reduced proportion of metal ions amount in solution with respect to the number of active sites on adsorbent, which may lead to a change in adsorption equilibrium. Furthermore, when the adsorbent dose increased, the unsaturation of active sites on surface occurred and therefore, the adsorption capacity decreased [34].

In order to investigate the adsorption kinetics, Lagergren pseudo-first order and pseudo-second order kinetics model [35,36]

**Table 5**

Pseudo-second order kinetics parameter and constants for adsorption of metal ions onto iron oxide coated sludge.

| Metal            | Adsorbent dose (g L <sup>-1</sup> ) | $q_{e,exp}^a$ (mg g <sup>-1</sup> ) | Pseudo-second order                           |                                     |          |
|------------------|-------------------------------------|-------------------------------------|---|-------------------------------------|----------|
|                  |                                     |                                     | $k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> ) | $q_{e,cal}^b$ (mg g <sup>-1</sup> ) | $R^{2c}$ |
| Cu <sup>2+</sup> | 1                                   | 12.8                                | 0.050   | 13.1                                | 0.9999   |
|                  | 5                                   | 8.2                                 | 0.084   | 8.3                                 | 0.9997   |
|                  | 10                                  | 4.7                                 | 0.401   | 4.7                                 | 0.9999   |
| Cd <sup>2+</sup> | 1                                   | 7.9                                 | 0.189   | 7.9                                 | 0.9999   |
|                  | 5                                   | 4.4                                 | 0.351   | 4.4                                 | 0.9998   |
|                  | 10                                  | 2.7                                 | 1.033   | 2.7                                 | 0.9999   |
| Ni <sup>2+</sup> | 1                                   | 3.9                                 | 0.052   | 4.2                                 | 0.9927   |
|                  | 5                                   | 2.2                                 | 0.294   | 2.2                                 | 0.9977   |
|                  | 10                                  | 1.5                                 | 4.879   | 1.5                                 | 1        |
| Pb <sup>2+</sup> | 1                                   | 33.7                                | 0.019   | 34.1                                | 0.9993   |
|                  | 5                                   | 17.7                                | 0.107   | 17.8                                | 0.9999   |
|                  | 10                                  | 9.7                                 | 0.637   | 9.7                                 | 1        |

<sup>a</sup> The sorption capacity obtained by the experiments.

<sup>b</sup> The sorption capacity obtained by the calculation using linear equation.

<sup>c</sup> The correlation coefficients of pseudo-second order model.

**Table 6**

Removal efficiencies of iron oxide coated sewage sludge in the presence of salts.

| Salts                             | Concentration (mol L <sup>-1</sup> ) | %Removal <sup>a</sup> |            |            |            |
|-----------------------------------|--------------------------------------|-----------------------|------------|------------|------------|
|                                   |                                      | Pb(II)                | Cu(II)     | Cd(II)     | Ni(II)     |
| No salt                           | –                                    | 59.7 ± 0.2            | 41.8 ± 0.1 | 25.4 ± 0.2 | 14.2 ± 0.3 |
| NaNO <sub>3</sub>                 | 0.01                                 | 56.7                  | 43.9 ± 0.1 | 25.4       | 12.2 ± 0.3 |
|                                   | 0.50                                 | 42.7 ± 0.2            | 38.7 ± 0.2 | 20.9       | 5.5 ± 0.3  |
| Ca(NO <sub>3</sub> ) <sub>2</sub> | 0.01                                 | 48.6 ± 0.3            | 35.2 ± 0.4 | 15.9 ± 0.1 | 1.0 ± 0.3  |
|                                   | 0.50                                 | 38.3 ± 0.8            | 24.6 ± 0.1 | 8.0 ± 0.2  | 0.8 ± 0.3  |
| Na <sub>2</sub> SO <sub>4</sub>   | 0.01                                 | – <sup>b</sup>        | 39.5 ± 0.2 | 17.4       | 7.5 ± 0.3  |
|                                   | 0.50                                 | – <sup>b</sup>        | 27.2 ± 0.2 | 9.2 ± 0.2  | 6.2 ± 0.6  |

Initial concentration: 30 mg L<sup>-1</sup> (Pb(II)), 20 mg L<sup>-1</sup> (Cd(II), Cu(II) and Ni(II)).

<sup>a</sup> Mean ± SD (n = 3).

<sup>b</sup> Pb precipitated as PbSO<sub>4</sub>.

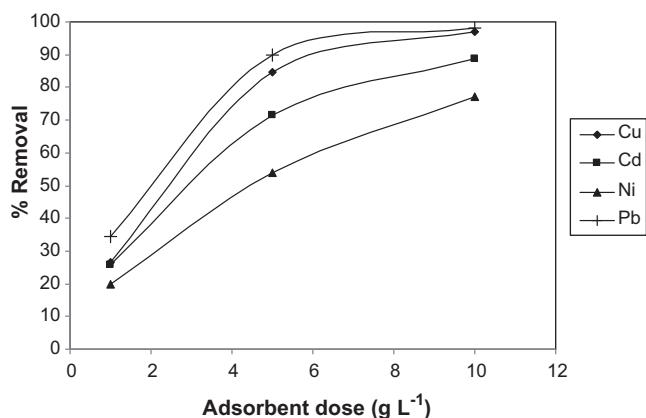


Fig. 2. Effect of adsorbent dose on removal efficiency (concentration: 48 mg L<sup>-1</sup> Cu(II), 30 mg L<sup>-1</sup> Cd(II), 20 mg L<sup>-1</sup> Ni(II) and 99 mg L<sup>-1</sup> Pb(II); pH 5 for Cu(II), Cd(II), Ni(II) and pH 4 for Pb(II)).

were adopted and the equations of these two models are expressed in Eqs. (3) and (4), respectively,

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e} \quad (4)$$

where  $q_e$  and  $q_t$  are the adsorption capacity (mg g<sup>-1</sup>) at equilibrium and at contact time  $t$  (min). The parameter  $k_1$  and  $k_2$  represent the rate constant of the pseudo-first order model (min<sup>-1</sup>) and pseudo-second order model (g mg<sup>-1</sup> min<sup>-1</sup>) and can be calculated from the slope and the intercept the linear plot between  $\log(q_e - q_t)$  against  $t$  and  $t/q_t$  against  $t$ , respectively.

The plots of pseudo-first order kinetics were not linear for the adsorption of every metal ions, therefore, only the results from pseudo-second order kinetics plots are summarized in Table 5. The correlation coefficients for the linear fitting of the data with the pseudo-second order model were close to 1.000 and the calculated  $q_e$  values ( $q_{e,cal}$ ) also agreed very well with the experimental  $q_e$  values ( $q_{e,exp}$ ), indicating a good fit of the kinetics model to the experimental data. The results show that the adsorption kinetics of metal ions onto iron oxide coated sludge could be described by pseudo second order kinetics model. By this model, it is assumed that (i) the adsorption occurred via chemisorptions, (ii) the adsorption followed a monolayer regime on the adsorbent surface and (iii) the rate of adsorption occurred rapidly at the initial step of adsorption [37]. The rate constant of the pseudo-second order ( $k_2$ ) increased in increasing adsorbent dose; therefore the adsorption equilibrium was attained in a shorter time.

### 3.6. Effect of salts on metal removal efficiency

In general, there are ions other than toxic metal ions coexisting in water and these ions may affect the adsorption of the metal ions by the adsorbents. The effect of the presence of other ions should be taken into account. In this work, NaNO<sub>3</sub>, Ca(NO<sub>3</sub>)<sub>2</sub> or Na<sub>2</sub>SO<sub>4</sub> was added to the metal solutions separately with a concentration of 0.01 mol L<sup>-1</sup> and 0.50 mol L<sup>-1</sup>. The results are summarized in Table 6. The presence of NaNO<sub>3</sub>, Ca(NO<sub>3</sub>)<sub>2</sub> and Na<sub>2</sub>SO<sub>4</sub> in solutions resulted in a significant reduction of removal efficiencies. When increased the concentration of salt, the removal efficiency decreased. These results could be explained by the competition between metal ions of interest and other cations for adsorption onto iron oxide surface.

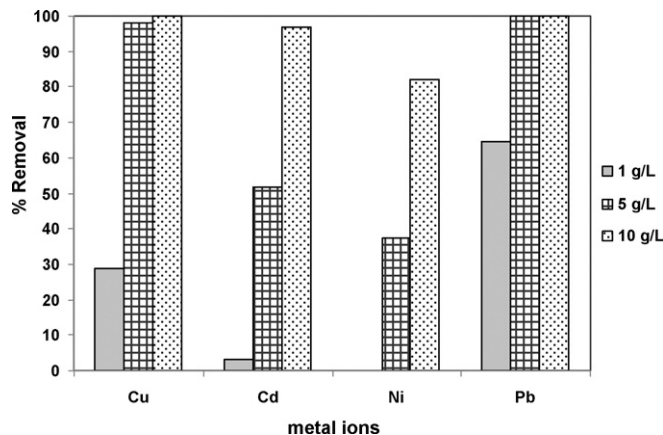


Fig. 3. Removal of metal ions from wastewater containing mix metals ions using iron oxide coated sludge of different doses.

### 3.7. Removal of metal ions from mixed metals solutions and from wastewater

In wastewater, several metals could be present and competitive adsorption onto adsorbent could occur, resulting in a change in removal efficiency for each metal. In this study, the metal removal efficiencies were determined when used in mix metal ions solutions. A solution containing 0.3 mmol L<sup>-1</sup> of each metal ion was used for adsorption experiments and the pH of solution was adjusted to 5 with buffer. Using adsorbent dose of 1 g L<sup>-1</sup> with batch experimental condition, the removal efficiency observed was 23.8, 3.1, 1.1 and 43.5% for removal of Cu(II), Cd(II), Ni(II) and Pb(II) ions, respectively. Under competitive condition, the adsorption efficiency for each metal ions decreased from the maximum adsorption capacities determined using adsorption isotherms. The removal efficiency order followed Pb > Cu > Cd > Ni. This trend is in agreement with the results obtained in the study of adsorption equilibrium. The Langmuir constant ( $b$ ) for adsorption of Pb(II) ions was also higher than that of the other metal ions, indicating a higher affinity of the active sites toward Pb(II) ions.

The adsorbents were also applied to remove metal ions from wastewater collected from a laboratory. The concentration of metal ions in the mix wastewater was 19.9, 19.7, 19.5 and 51.5 mg L<sup>-1</sup> for Cu, Cd, Ni and Pb, respectively. The pH of the wastewater was adjusted to 5. The adsorption experiments were performed using adsorbent dose of 1, 5 or 10 g L<sup>-1</sup>. The results are shown in Fig. 3. The increase in adsorbent dose to 10 g L<sup>-1</sup> resulted in higher treatment efficiency and the removal efficiency for Cu(II), Cd(II), Ni(II) and Pb(II) ions from the wastewater was 99.9, 96.7, 82.2 and 100.0%, respectively. However, the removal efficiency can be altered, depending on wastewater properties (e.g. pH, interfering ions).

## 4. Conclusion

The adsorbents derived from sewage sludge were prepared. The method in surface modification with iron oxide was investigated and the suitable condition was proposed. The obtained adsorbents showed a good efficiency in metal ions removal. The parameters that affected the metal adsorption were studied, including adsorption equilibrium and adsorption kinetics. Finally, the adsorbents were successfully applied to remove metal ions from wastewater.

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