Biosorption of Lead (II), Nickel (II) Iron (II) and Zinc (II) on Flyash from Dilute Aqueous Solution

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ABSTRACT

Nowadays environmental pollution by heavy metals is arising as the most endangering tasks to both water sources and atmosphere quality. The treatment of heavy metals is of special concern due to their recalcitrance and persistence in the environment. To limit the spread of the heavy metals within water sources, flyash as biosorbent was studied with the aim of removal of aggressive heavy elements including Zn(II), Pb(II) and Ni(II) & Fe(II) . The results indicated that sorption capacity of metal ion by flyash is favoured. Affinity and efficiency sorption parameters including contact time, initial concentration of metal ions, the dosage and competitive biosorption behaviors were studied. The results showed that the Pseudo second-order reaction fits the reduction of metal ions studied and also showed linear relationship with a high correlation coefficient.

Introduction

Heavy metals include lead (Pb), cadmium (Cd), zinc (Zn), mercury (Hg), arsenic (As), silver (Ag) chromium (Cr), copper (Cu) iron (Fe), and the platinum group elements. The presence of these metal ions in drinking water can cause severe diseases such as anemia, encephalopathy, and hepatitis etc. Heavy metals can be emitted into the environment by both natural and anthropogenic causes. The major causes of emission are the anthropogenic sources specifically mining operations, municipal solid waste, waste oil, metal plating facilities and tanneries (Slacka et al., 2005; Amara-
by suitable desorption processes for multiple use (Pan et al., 2009). In addition, many desorption processes are of low maintenance cost, high efficiency, and ease of operation. So, the adsorption process is considered as one of the major suitable technique for heavy metals removal from water/wastewater sources. Activated carbon as an adsorbent is currently being used extensively for the removal of toxic metal ions from liquid phases. The problems associated with this adsorbent are the high regeneration cost, intraparticle resistance in adsorption process and poor mechanical strength (Aravindhan et al., 2006). In this regard coal fly ash is a very attractive alternative because it is cheap, widely available and has been reported to have good mechanical stability (Potgiester, 2009). Coal fly ash, is obtained from the combustion of powdered coal as waste product. This adsorbent requires little processing to increase its sorption capacity. The fly ash is influenced by the origin of the coal and burning condition under which it was formed (Potgiester, 2009). In this study, we report the investigation on the feasibility of fly ash to remove heavy metal ions (Zn$^{2+}$, Pb$^{2+}$) from water, modeling the adsorption process of heavy metal ions and investigation of the interactive effects of process parameters such as sorbent dose, contact time, solution pH, and initial concentration on the adsorption capacity of coal fly ash towards the metal ions.

**Materials and Methods**

**Preparation of Biosorbent**

The biomass was collected from a Local Coal processing plant, washed several times with distilled water, and then dried in a vacuum drying in an oven at 100°C for 3 hours. The dried biomass was grounded with a mortar and pestle. The powdered form was stored in a sealed bottle with a silica gel to prevent re-adsorption of moisture.

**Stock Solutions**

Lead (II), Nickel (II), Iron (II) and Zinc (II) solutions and standards were prepared by dissolving analytical grade Pb (NO$_3$)$_2$, Zn(NO$_3$)$_2$, Fe (SO$_4$)$_2$ and Ni (NO$_3$)$_2$. Stock solutions of these metal ion (1000 mg/l) was prepared with deionised distilled water. The solutions of varying concentrations were prepared by diluting the stock solutions with deionised water.

**Selection of Optimum Contact Time**

The sorption process is strongly influenced by the contact time. For study of effect of contact time, 50ml of 10 mg/l Lead(II), Nickel(II), Iron(II) and Zinc(II) solutions of varying pH were mixed with 50mg of flyash and stirred at different contact times. Then filtrate was analyzed for remaining metal ions.

**Determination of Optimum Dosage of Biosorbent**

To determine the optimum dosage of flyash, it was added to conical flask in different dosage containing known concentration of metal ion dosage. The solution in the conical flask was subjected to striving for optimum contact time, filtered and analyzed for residual metal concentrations. The dosage that gave minimum residual concentration was chosen as optimum dosage.

**Biosorption Studies**

Experiments were conducted in 100 ml flasks containing 50 ml of heavy metal solutions and ad the different biomass. The pH value was selected based on reported results indicating that high sorption of metal
ions is attained for different pH values. The pH range chosen for the sorption is also based on avoiding metal precipitation and was adjusted to the required value with 0.1 mol/L HNO₃ or 0.1 mol/L NaOH hourly, throughout the experiment. The mixtures were shaken on a rotary shaker (agitation rate, 200 rpm) for 2.5 hours, and then set still 1 hour to reach equilibrium. Then the biosorbent was filtered through an acid-cleaned 0.45μm Millipore filter and the concentrations of heavy metal ions in the filtrates were analyzed by flame atomic absorption spectrometer (Model GBC 932 Plus Australia). For the kinetic experiments, 25-200 mg of biomass was contacted with 50 ml of the metal ion solutions of initial concentration between 10-100 mg/l, keeping the same conditions as described above. At scheduled time intervals, 8 ml solution samples were drawn out and the concentrations of the residual heavy metals were analyzed. The depleted metal solutions were then analyzed to assess the metal concentration decline. Equilibrium isotherms were obtained using sample doses and a range of initial metal concentrations between 10 and 100 mg/l. The general procedure depicted above was followed, applying the same experimental conditions. Duplicate experiments were carried out for all the experiments. Average values are reported. In all the tests, metal and sorbent free blanks were also used for control.

Kinetic Experiments

Kinetic experiments were conducted in order to determine the equilibration time and binding rate of metal ions binding by flyash. Sampling times ranged from as low as15 minutes to as high as 2.5 hours, based on preliminary experiments. Eight-milliliter samples were taken periodically using a syringe and filtered. Data were modeled using both first and second-order kinetic models. The pseudo-first-order model assumes that the rate of change of surface site concentration is proportional to the amount of remaining unoccupied surface sites:

\[ \frac{dq}{dt} = k_1(q_e - q) \]

where \( q \) and \( q_e \) are adsorbed amounts (mg/g) at time \( t \) (min) and equilibrium, respectively, and \( k_1 (1/min) \) is the first-order Lagergren adsorption rate constant (Lagergren, 1898). This model can be linearized as:

\[ \log(q_e - q) = \log q_e - k_1 / 2.303 t \]

The pseudo-second-order model assumes that the rate is proportional to the square of the number of remaining free surface sites (Ho, et al., 1998):

\[ \frac{dq}{dt} = k_2(q_e - q)^2 \]

where the second-order adsorption rate constant is \( k_2 \) (g/meq.-min). This model can be linearized as:

\[ t/q = 1/ k_2q_e^2 + t/q_e \]

Isotherms

Isotherms were obtained by varying the initial metal ion concentration from 10 to 100mg/L. An equilibration time of 2.5 hours was allowed. Equilibrium sorption was done by using the Langmuir and the Freundlich isotherms because of their ease of interpretation. The Langmuir model considers that the sorbent surface contains only one type of binding site and sorption of one ion per binding site is taking place (Lagergren, 1898). This can be described as:
\[ q_e = q_{\text{max}} C_e / (1 + k C_e) \]

where \( q_e \) is the metal uptake, \( q_{\text{max}} \) is the maximum biosorption capacity, \( k \) is a constant related to adsorption energy, and \( C_e \) is the equilibrium concentration of metal ions. The Langmuir parameters can be determined from the slope and intercept when plotting \( C_e / q_e \) versus \( C_e \), based on a linearized form can be written as:

\[ C_e / q_e = 1 / k q_{\text{max}} + C_e / q_{\text{max}} \]

The empirical Freundlich model considers no surface saturation and can be expressed as:

\[ q_e = k_f (C)^{1/n} \]

where \( k_f \) and \( n \) are model constants that can be determined from the slope and intercept when \( \log q_e \) is plotted versus \( \log C_e \) according to the linearized form:

\[ \log q_e = \log k_f + 1/n \log C_e \]

**Results and Discussion**

**Effect of Contact Time and Kinetic Modeling**

Agitation time is one of the primary aspects while designing batch sorption systems for optimization of wastewater treatment plant. Fast sorption is among the main required parameters for successful usage of the biosorbent for practical application. Fig.1, 3, 5, & 7(a) indicates the metal uptake by flyash as a function of time. An uptake capacity 60mg/g (30 min) of biosorbent was observed and then the sorption capacity increased constantly with increasing time. Beyond 90 min, the percentage of biosorption is almost constant indicating the attainment of equilibrium conditions. The presence of sufficient external surface area on flyash may have increased the rate of biosorption in the initial stages, which was followed by a slower internal diffusion process, and may be the rate determining step. The equilibrium time was reached in 150 min 32mg/g for Fe(II), 38mg/g for Zn(II), 13mg/g for Ni(II) & 48mg/g for Pb(II) respectively which was fixed as the optimum equilibrium time for the experimental runs. The increase observed in the uptake capacity with increase of contact time was due to availability of active sites on the biosorbent surface. In order to better understand the kinetics of metal ion biosorption on flyash, the Lagergren’s Pseudo-first-order model and pseudo-second-order model were used to describe the experimental data. The experimental data and the models obtained in the present study can be used in designing a large-scale batch biosorption system for wastewater containing Fe(II), Pb(II), Zn(II) and Ni(II). For a given initial metal concentration and a defined liquid quantity and in order to achieve a required removal of heavy metal ions, the amount of biosorbent to be used and the residence time of the liquid in the batch needs to be calculated. These values along with the corresponding correlation coefficient \( r^2 \) were found as: \( K_1 = 0.062 \text{ min}^{-1}, q_{\text{cal}} = 29.83 \text{ mg/g for Zn(II) & 32.74 mg/g for Fe(II), 25.67 mg/g for Pb(II) & 14.08 mg/g for Ni(II)} \). The uptake value calculated from the Pseudo-first-order model do not agreed well with the experimental values \( q_{\text{exp}} = 14.82 \text{ mg/g for Zn(II), 11.31 mg/g for Fe(II), 13.43 mg/g for Pb(II) & 8.81 mg/g for Ni(II)} \) respectively. Therefore the Pseudo-first-order model is not suitable for the biosorption of the metals studied onto the biosorbent and the Pseudo-second-order model is more appropriate for the description of the kinetic behavior of biosorption in which the chemical sorption process is the rate-controlling step.
Effect of Initial Metal Concentration and pH on Biosorption

The initial concentration of a metal is one of the main aspects for the evaluation of biosorption of toxic metal ions within an aqueous system and provides an important driving force to overcome the hindrances faced while molecules are transferred between the liquid phase and solid phase. In this study, metal uptake capacity of Zn(II), Pb(II), Fe(II) and Ni(II) were investigated at biosorbent loading of 1.2 g/l for Zn(II), 1.0 g/l for Pb(II) & Fe(II) and 1.5 for Ni(II) respectively. The metal removal using flyash as biosorbent corresponding to different initial metal concentrations 10-100 mg/l for Zn(II), 10-80mg/l for Pb(II)& Fe(II) mg/l and 10-50 mg/l for Ni(II) are shown in Fig. 2.(b). The increase in initial concentration of various metals mentioned above resulted in the increased uptake capacity (q_t) (20.32 to 46.58 mg/g, 29.56 to 48.48 mg/g, 14.86 to 33.18 mg/g and 4.58-12.92 mg/g) and decreased percent removal (68.82-46.58 mg/g, 39.42-60.85 mg/g, 73.22-41.46 mg/g and 52.16-36.18 mg/g) respectively. The required driving force to counter the mass transfer hindrance of metal ions studied (Pb, Zn, Fe & Ni) between the liquid and the solid phase may be provided by the initial concentration of metal ions. An increase in heavy metal ion concentration also increases the interaction between the ions in the aqueous phase and the fly ash surface, which further resulted in higher uptake for the given mass of fly ash. The results revealed that at lower initial concentrations, all the ions interacted with the binding sites on the surface of biosorbent. At high initial concentrations, binding sites on the surface of flyash were saturated, with no further biosorption. A decrease in the biosorption capacity was observed which was taken into consideration due to the repulsive forces between metal ions at related nearly sites on the surface of biosorbent. The percentage removal of toxic metal ions by flyash was found to decrease with increase in initial metal concentration. The observed behavior can be correlated to the increase in the amount of toxic metal ions to the non-alteration of available active sites on the surface of biosorbent, but some metal ions were left in aqueous solution. Thus, it can be said that removal of metal ions studied are highly concentration dependent. Generally, the biosorbate forms a thin layer over the surface, whose thickness is only about of one molecule. When this mono-molecular layer covers the surface, the capacity of the biosorbent gets exhausted. The maximum percent removal is attained after 90-120 min of stirring. From the figures 1(a) to 4(a) it can be seen that initially the uptake capacity increases in a linear way with rising equilibrium concentration until it is limited by the fixed number of uptake active sites on the flyash and resulting plateau can be observed, which represents the maximum uptake capacity of the biosorbent, for each metal ion. pH is an important factor controlling the process of biosorption. There was a change in the quantity of sorbed metal ions on the solid phase of flyash by increasing pH of the medium up to a maximum value of pH 5.2. for Pb(II), 5.2 for Zn(II), 4.2 for Fe(II) and 5.9 for Ni(II). At low pH values, the sorbent is positively charged, as the pH is lower than the point of zero charge or isoelectric point. Hence the removal of metal ions was very low due to the electrostatic repulsion forces between positively charged H_3O^+ and takes it metal ions.

Thereafter, the biosorption percentage decreased in alkaline medium, perhaps due to the formation of metal hydroxides and soluble hydroxyl complexes. Low pH depresses biosorption of metal ions (Pb, Fe, Zn, & Ni) which is due to competition of
metal ions with hydrogen ions bound to the biosorbent for forming part of the surface.

**Effect of Biosorption Loading**

The effect of biosorbent dosage on the biosorption of metal ions (Pb(II), Fe (II), Ni(II), & Zn(II)) was investigated and was found that the percentage removal increases sharply with increasing dosage to a certain limit: 1.0g for Pb(II) & Fe (II), 1.2 g for Zn(II) and 1.5 g for Ni(II) respectively. Beyond these values, the percentage did not increased significantly. This phenomenon can be contributed to the larger availability of active sites on surface area of biosorbent making easier penetration of the metal ions to the biosorption sites of flyash. The dependence of Pb(II), Zn(II), Fe(II) and Ni(II) sorption on dose was studied by varying the amount of biosorbents. The initial metal concentration (100, 80, 60 and 50 mg/l), shaking speed (120 rpm) and temperature (22°C) were kept constant. The maximum uptake capacity for the metals under study by flyash was found to be 29.83, 25.67, 17.84 and 12.4 mg/g respectively. The dose of biosorbent has a significant impact on biosorption process. This suggests that after a certain dose of biosorbent, the maximum biosorption occurs in and therefore the amount of toxic metal ions attached to the biosorbent and the amount of free ions, do not change even with further addition of the dose. For dose of biosorbent used, there was an increase in percentage removal [43.52 to 59.66% for Zn(II), 48.48 to 64.17% for Pb(II), 23.47-44.62% for Fe(II) and 26.66-49.62% for Ni(II)]. The quantity of biosorbent added to the aqueous solution evaluates the number of binding sites available for sorption of toxic metals. The decrease in the sorption capacity (34.82-29.83 mg/g, 53.86-25.67 mg/g, 27.16-17.84 mg/g and 16.44-12.46 mg/g) with the increasing biomass dose suggests that at constant concentration on increasing sorbent amount, the number of binding sites increases. Thus the effect of biosorbent dosage on percentage biosorption and uptake is considered to be an essential aspect. This forms an impact of partial aggregation, which occurs at higher dose of biosorbent & hence giving raise to decrease of active sites.

**Figure.1** Effect of Initial metal concentration on removal of Fe(II) ions from Aqueous solutions by flyash. Experimental Conditions: [pH: 4.2, biomass loading metal: 1.0 gl-1, T: 22°C, shaking speed: 120 rpm, contact time: 2.5 hrs].

![Figure 1](image-url)
Figure 2 Comparison between Experimental kinetic data and predictions of (a) Pseudo-second-order model (b) Pseudo-first order model for the biosorption of Fe(II) ions by flyash. [pH: 4.2, T: 22°C, Biosorbent loading: 1.0 g/l].
Figure 3 Effect of initial metal concentration on removal of Zn(II) ions from aqueous solutions by flyash. Experimental Conditions: [pH: 6.4, biomass loading metal: 1.2 gl-1, T: 22°C, shaking speed: 120 rpm, contact time: 2.5 hrs].
**Figure 4** Comparison between experimental kinetic data and predictions of (a) Pseudo-second-order model (b) Pseudo-first order model for the biosorption of Zn(II) ion by flyash. [pH: 6.4, T: 22o C, Biosorbent loading: 1.0 g l⁻¹].
Figure 5 Effect of Initial metal concentration on removal of Ni(II) ions from aqueous solutions by flyash. Experimental Conditions: [pH: 5.9, biomass loading metal: 1.5 gl-1, T: 22°C, shaking speed: 120 rpm, contact time: 2.5 hrs].

**Graph (a)**
- q (mg/g) vs. Time (min)
- Lines represent different metal concentrations (10 mg/l, 20 mg/l, 30 mg/l, 40 mg/l, 50 mg/l)

**Graph (b)**
- % removal vs. Time (min)
- Lines represent different metal concentrations (10 mg/l, 20 mg/l, 30 mg/l, 40 mg/l, 50 mg/l)
Figure 6 Comparison between experimental kinetic data and predictions of (a) Pseudo-second-order model (b) Pseudo-first order model for the biosorption of Ni(II) ion by flyash. [pH: 6.4, T: 22o C, Biosorbent loading: 1.5 g/l].
Figure 7 Effect of initial metal concentration on removal of Pb(II) ions from aqueous solutions by flyash. Experimental Conditions: [pH: 5.2, biomass loading metal: 1.0 gl-1, T: 22°C, shaking speed: 120 rpm, contact time: 2.5 hrs].
Figure 8 Comparison between Experimental kinetic data and predictions of (a) Pseudo-second-order model (b) Pseudo-first order model for the biosorption of Pb(II) ion by flyash. [pH: 5.2 T: 22o C, Biosorbent loading: 1.0 g/1].
Figure 9 Langmuir plots (a) Freundlich plots (b) for the equilibrium biosorption of Zn(II) ions onto flyash. Comparison between the experimental data (points) and model predictions (lines); [Co: 10-80 mg/l, pH: 6.4, T: 22°C, Time: 2.5 hrs, M=1.2 g/l, Rate of agitation: 120 rpm].
Figure 10 Langmuir plots (a) and Freundlich plots (b) for the equilibrium biosorption of Fe(II) ions onto flyash. Comparison between the experimental data (points) and model predictions (lines); [Co: 10-80 mg/l, pH: 4.2, T: 22°C, Time: 2.5 hrs, M=1.0 g/l, Rate of agitation: 120 rpm].

Fig 10(a)

Fig 10(b)
Figure 11 Langmuir plots (a) Freundlich plots (b) for the equilibrium biosorption of Ni(II) ions onto flyash. Comparison between the experimental data (points) and model predictions (lines); [Co: 10-50 mg/l, pH: 5.9, T: 22°C, Time: 2.5 hrs, M=1.5 gl-1, Rate of agitation: 120 rpm].

Figure 12 Langmuir plots (a) Freundlich plots (b) for the equilibrium biosorption of Pb(II) ions onto flyash. Comparison between the experimental data (points) and model predictions (lines); [Co: 10-80mg/l, pH: 5.2, T: 22°C, Time: 2.5 hrs, M=1.0 gl-1, Rate of agitation: 120 rpm].
Effect of Equilibrium biosorption/Modeling

Adsorption isotherms are very useful for analyzing the nature of sorbate-sorbent interaction. That’s why in order to optimize the design of a successful sorption unit for the removal of toxic metal ions from industrial discharge, it is necessary to establish the maximum correlation for the equilibrium isotherms. In this study, the equilibrium data for the biosorbed metal ions [Pb(II), Fe(II), Zn(II) & Ni(II)] onto flyash was expressed using two of the isotherms, namely, Langmuir and Freundlich isotherms. The purpose of the biosorption isotherms is to exhibits the correlation between the sorbate concentration and the sorbed amount at the interface. Several models are often used to interpret equilibrium data. Results obtained for each sorbate (q_{eq}, mg g^{-1}) starting at different initial concentrations versus residual sorbate concentration at the equilibrium (C_{eq}, mg l^{-1}) were fitted to the linearized sorption isotherms of Langmuir and Freundlich. The value for Langmuir Constant (b) were found to be 0.33/mg for Zn(II), 0.204/mg for Pb(II), 0.507/mg for Fe(II) and 0.248/mg for Ni(II) respectively. The values of Freundlich Constant (k_f) & 1/n were found to be 7.35/g and 0.411 for Zn(II), 8.51/g and 0.525 for Pb(II), 8.78/g and 0.414 for Fe(II), and 4.18/g and 0.332 for Ni(II) respectively. The sorption constants together with the correlation coefficients ($r^2 > 0.9$) were found for both the models. The studied values of correlation coefficient reach near to unity indicating a good fit of experimental data to models studied. The calculated value of Freundlich constant is within the range (0.1 < 1), showing that biosorption process is favorable.

However, the linearized equation did not give a good correlation for the removal of toxic metal ions studied onto flyash, indicating that sorption fits better to the Langmuir model than to the Freundlich model. Inspection of the isotherm fits indicates that both empirical models (Langmuir & Freundlich) were in good agreement with the experimental results, although it appears that the Langmuir model gave a somewhat more accurate fit of the data and can be observed from Figure 9-12. An important factor in evaluating sorbent performance is the initial gradient of the sorption isotherm, because it indicates the sorbent affinity at different toxic metal concentrations.
Conclusions

The ability of flyash as biosorbent was investigated for sorptive removal of Pb(II), Zn(II), Fe(II) & Ni(II) ions from aqueous solutions. Various physio-chemical parameters such as pH, initial metal ion concentration and equilibrium contact time were studied. The optimum solution pH for adsorption of metal ions from aqueous solutions was found to be pH 5.2 for Pb(II), 5.2 for Zn(II), 4.2 for Fe(II) and 5.9 for Ni(II) and the optimum contact time was found to be 90-120 min. The sorption isotherms were obtained using concentrations of the metal ions ranging from 10 to 100 mg/l. The process followed pseudo-second-order reaction kinetics, as well as Langmuir and Freundlich sorption isotherms. The maximum capacity of flyash is 48.66, 39.8, 32.6 & 12.14 mg/g respectively for the metal ions studied. This study revealed that flyash was an effective adsorbent for removal of metal ions from aqueous solutions.

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