

Original Research Article

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Application of Flyash for the Removal of Toxic Metals from Wastewaters through Biosorption

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ABSTRACT

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Environmental pollution by heavy metal 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. The flyash was used in this work as low cost sorbent material for removal of Pb(II) and Fe(II) ions from aqueous solutions. The samples of adsorbent were sorted according to the particles diameter by standard sieves 250-500 μm . Batch experiments were carried out to study the sorption process and several parameters such as Initial pH of adsorbent, effect of contact time, effect of adsorbent amount and effect of metal concentration were conducted in these experiments. The effects of any one of those previously mentioned parameters on the sorption capacity were studied while the other parameters were kept constant. It was found that the obtained maximum sorption capacities of flyash for the removal of selected heavy metals were very high. This provide us to use flyash as a low cost material to clean up the water from toxic heavy metals studied.

Introduction

The presence of heavy metals in industrial wastewater has posed many serious environmental problems due to their non-biodegradable properties and toxicity, even at low concentrations (Vilar, *et al.*, 2007) which directly produce detrimental and toxicological impact on the biotic resources. The heavy metal ions are not only toxic to living organisms in water, but also cause harmful effects to land animals including humans through food chain transfers. In living organisms, heavy metal ions can particularly bind to nucleic acids, proteins, and small metabolites (Liu, *et al.*, 2008).

Therefore, it is necessary to eliminate such hazardous heavy metal ion in wastewater before discharging it into the ecosystem. The metals which are required to remove from the aquatic environment and need immediate concern are Zn^{2+} , Cu^{2+} , Ni^{2+} , Cd^{2+} , Pb^{2+} , and Cr^{6+} (Moradi, *et al.*, 2010; Al-Degs, *et al.*, 2006; Molinari *et al.*, 2004; Moradi and Zare, 2011). These toxic metal ions commonly exist in process waste streams from mining operations, metal plating facilities, power generation facilities, electronic device manufacturing units, and tanneries. Because of economic and

environmental factors, the removal and recovery of heavy-metal ions from industrial wastewater have been a significant concern in most industrial branches (Ngomsik, *et al.*, 2009; Yin, *et al.*, 2010). Different technologies have been used for the removal of heavy metals from wastewater. They mainly include: precipitation, ion exchange, membrane processes, evaporation, chemical oxidation or reduction, solvent extraction and biological materials. These techniques are very expensive and economically unfavorable or technically complicated, and are used only in special cases of wastewater treatment (Abdel-Halim, *et al.* 2003, Qadeer *et al.*, 2005). Relatively a new green technology for the treatment of industrial wastewater is adsorption of heavy metals and dyes from aqueous solutions by using natural material. Adsorption process has been proved to be an excellent way to treat industrial waste effluents, offering significant advantages like the low cost, availability, profitability, easy operation, and efficiency (Amuda, *et al.*, 2007; Gupta, *et al.*, 2006; Shin, *et al.*, 2005). In this study, flyash as an adsorbent was investigated for the removal of metals ions from aqueous solution under competitive adsorption conditions. The effects of initial pH, contact time, initial ion concentration on adsorption of those ions were studied. Flyash was found to be an effective adsorbent for heavy metals and it performed well in the presence of competing ions.

Material and Methods

Preparation of Binary Metal Mixtures

The applicability of the empirical Freundlich model to the biosorption of Pb(II) and Fe(II) ions from the binary metal mixtures by flyash was checked for different sets of data. The initial concentrations of Pb(II) ions were varied between 10-80 mgL⁻¹, whereas

the Fe(II) ion concentration in each metal mixture was held constant at 10, 20, 50, or 60 & 80 mgL⁻¹.

Biosorption Studies

Experiments were conducted in 100 ml flasks containing 50 ml of heavy metal solutions and 0.5 g of biomass. The pH value was selected based on reported results indicating that high sorption of copper ions is attained for pH between 4 and 6 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). Each experiment was repeated twice. 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 of 0.5g/50 ml solution 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. The suspensions were stirred for the time required to attain equilibrium, as determined from kinetic measurements. 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.

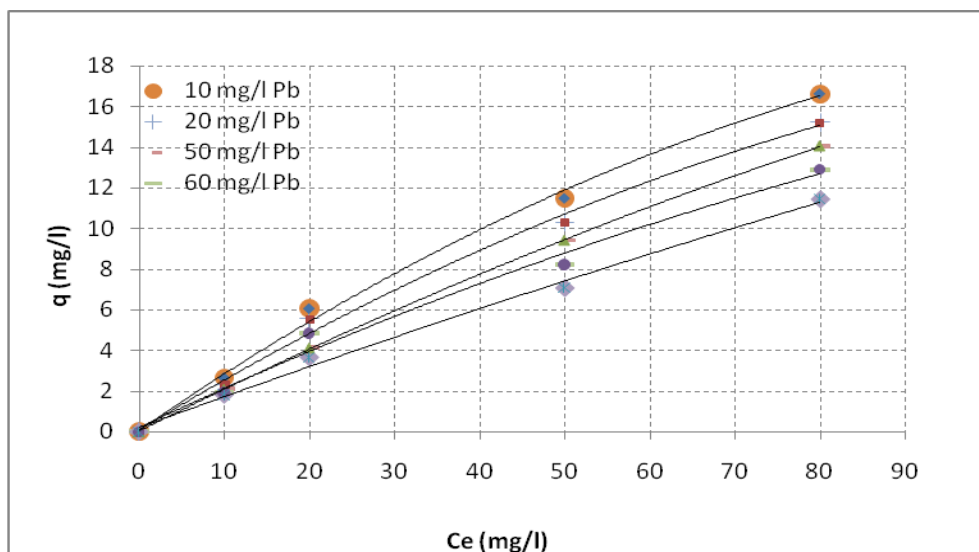
Results and Discussion

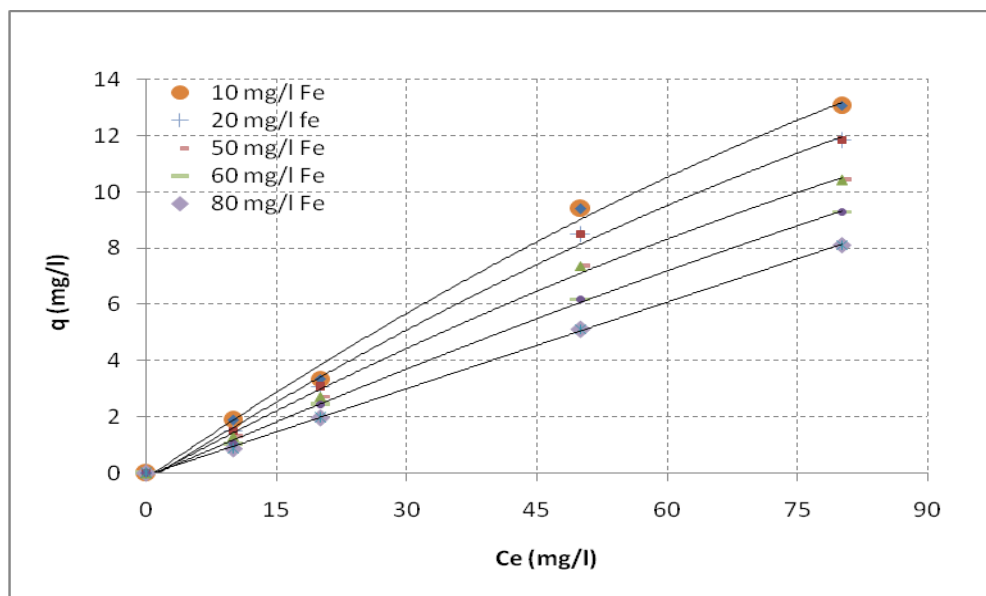
Biosorption of Pb(II) and Fe(II) in binary components of solution

In order to determine the effects of initial Pb(II) and Fe(II) ion concentrations on the equilibrium from binary metal solution, initial concentrations of Pb(II) were varied between 10 and 80 mg/l, while the initial Fe(II) concentration, in each biosorption medium was held constant at 10, 20, 50, 60 mg/l respectively at pH 5.2. The non-linearized biosorption isotherms of Pb(II) in the absence and in the presence of increasing concentrations of Fe(II) ions obtained are shown in Fig: 1. Equilibrium Pb(II) uptake increased 3.26-32.16 mgg⁻¹ by increasing the initial Pb(II) concentration from 10 to 80 mg/l. The curve-linear relationship between the amount of Pb(II) biosorbed per unit weight flyash and the residual concentration at equilibrium

suggests that saturation occurred at higher concentrations of this metal ion. When the equilibrium uptakes of Pb(II) ions by biosorbent in the presence of ions are compared with the situation, where these ions are present singly, inhibition occurred in the equilibrium uptake of the same. The equilibrium uptake of Fe(II) decreased regularly (17.04-12.08 mgg⁻¹) with increasing Fe(II) concentrations. This effect of ions on the equilibrium Pb(II) uptake was dominant at higher initial concentrations. At 60 mg l⁻¹ of initial Pb(II) concentration, in the absence and in the presence of 10 mg l⁻¹ of Fe(II) concentration, biosorbed Pb(II) quantities at equilibrium were found 48.48 mgg⁻¹ and 32.16 mgg⁻¹ respectively. Although Pb(II) was biosorbed significantly the Fe(II) ions were also biosorbed by flyash as 5.36 mgg⁻¹ at 60 mg l⁻¹. This situation shows the competition between Pb(II) and Fe(II) ions, although the initial pH plays a significant role on selective biosorption. The presence of the other ion develops a competition for the biosorption sites on the surface while some sites are captured by the second metal ion.

Fig.1 The empirical Freundlich biosorption isotherms of Pb(II) [pH:5.2] in the presence of increasing concentrations of Fe(II).





In conclusion, the present study proves the capability and effectiveness of flyash as an adsorbent for heavy metals removal. The adsorption process is a function of the adsorbent and adsorbate concentrations and contact time. Equilibrium was achieved practically in 2 h. Adsorption behavior of Pb(II) and Fe(II) were affected by experimental parameters such as pH, contact time, and initial concentration of ions solution. It was found that adsorption isotherms were better described by Freundlich biosorption isotherms model for all of those metal ions. The maximum adsorption capacity values of Pb(II) and Fe(II) ions in a mixture of binary metal ions with flyash estimated 78.5 and 80.0 mg/g, respectively.

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