Adsorption of Cd(II) from aqueous solution onto pyrite

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Abstract

The physicochemical factors such as equilibrium time, solution pH, initial concentration of Cd(II), particle size and temperature that control the adsorption of Cd(II) from aqueous solutions onto pyrite has been investigated through batch experiments. Prior to this study, pyrite was characterized through chemical and XRD-analysis. The point of zero charge, pH_{pzc} was determined using the batch equilibrium technique and was found to be 6.4. The equilibrium time was 30 min at the solution pH of 6.0. The pH influence of Cd(II) adsorption was remarkable and maximum metal uptake was observed at 6.0 which is closer to pH_{pzc}. Under this weakly acidic condition Cd(II) ions are responsible for adsorption. Concentration dependence of metal uptake indicates that saturation of pyrite surface by adsorbate occurs at an initial Cd(II) concentration of 350 mg/L and the corresponding metal uptake was 576.5 mg/L of −150 mesh size pyrite at pH 6.0 and 30 °C. Particle size affects the adsorption capacity to a great extent and a decrease in particle diameter enhances metal uptake. The effect of temperature on adsorption performance reveals that the effective temperature for Cd(II) adsorption is 30 °C. The empirical Freundlich isotherm was applied to represent the adsorption process, which fits the experimental data quite well. The work reveals that natural pyrite is a very good choice as an adsorbent for the removal of toxic metals from industrial wastewater and bears significant industrial implications.
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Keywords: Pyrite; Characterization; pHpzc; Cd(II) adsorption; Isotherm

1. Introduction

Adsorption of ion on solid surfaces plays a very important role in both technological and natural processes. The adsorption of metal ions on minerals, soil and suspended matter may be responsible for the distribution of metals in aquatic systems [1–3], the defiencies in animals diets of trace metals and for the retention of micronutrients, cations and pollutants in soils [4–6]. Adsorption also provides an effective way to curtail pollution and is extensively used in the treatment of industrial wastewaters [7–12]. Industrial wastewaters can contain large amounts of different types of heavy metals; some of which are extremely toxic to animals and human beings [13–15]. Abatement of these heavy metal pollutants is a great concern worldwide and currently much attention is devoted in this regard.

Heavy metal removal by the usual adsorption processes involves various types of adsorbent such as fungus [16], synthetic polymers [17–19], activated carbon [20,21], ash [22], coal [23], char [24], clays [4,25], soils [6,26], oxides [27–29], hydroxides [26,30], oxyhydroxides [31,32], metal sulphides [33,34] etc. The usefulness of these adsorbents depends upon their selectivity, efficiency, availability and cost effectiveness.

Pyrite (FeS_2) is naturally abundant sulphide mineral and occurs in different environments viz. mineralizing solution of shear zone in metamorphic rocks, vein minerals and placed in fracture metamorphic rocks, igneous bodies—intrusive and nonintrusive, peat, coal, sediment, soil, etc. which reveals that variation of its formation and deposition might attribute varying physical properties. Sulphide minerals are known to have some unusual surface properties [35] and the adsorption of metal ions on pyrite surface has been found to be similar to those of oxide surface in many respects [36].

The present investigation was concentrated on removing Cd(II) from aqueous solution by mineral pyrite in single ion situation through the batch equilibrium technique. The objectives of choosing a natural pyrite were—(a) it is widely available in the north eastern part of India and (b) its surface properties and hence adsorption behaviour are very much similar to oxide surfaces in a number of aspects. Prior to this

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study, pyrite was purified and characterized by chemical and XRD-analysis. The point of zero charge of pyrite was determined. Effects of various factors which include equilibrium time, solution pH, initial concentration of Cd(II), particle size and temperature on adsorption performance were evaluated. Freundlich adsorption model was applied to represent the adsorption phenomenon.

2. Experimental

2.1. Adsorbent preparation

The adsorbent chosen for the present investigation is a hard rock mineral pyrite and was collected from East Khasi Hills of Meghalaya (India). The golden yellow pyrite portion was removed and ground to fine powder with a mortar. The pyrite sample was initially purified to remove the adhering minerals and silicates with the objective to minimize their influence on adsorption performance. The sample was first soaked overnight in hot HF to expel the intergrown silicates and washed several times with double distilled water. This was followed by treatment with 2 N HCl at 30 °C (laboratory temperature) for 60 min, washed repeatedly with double distilled water, vacuum dried and immediately stored under N_2. The sample was split into three different size fractions viz. -100, -150 and -200 mesh using Standard Tyler mesh sieves. Portion of -150 mesh size pyrite powders was dissolved in 2 N HNO_3 keeping the mixture at ~ 110 °C for 2 h and then filtered. The filtrate was collected for chemical analysis to detect the presence of adhering metals using atomic absorption spectrometry. The XRD-profile was recorded using Fe-filtered Cu K$_\alpha$ radiation. The BET specific surface area of the -150 mesh size pyrite was measured from the nitrogen adsorption isotherm.

2.2. Determination of pH_{pzc}

Both potentiometric titration method and batch equilibrium technique are used to determine the point of zero charge, but in the present study it was estimated by the latter process. A definite amount (50 mg) of -150 mesh size pyrite was treated with 50 mL 0.1 M $NaNO_3$ solution which is used as an inert electrolyte. The initial pH of the solution was adjusted at 3.0 using 0.01 M HNO_3 or 0.01 M NaOH. The suspension was allowed to equilibrate for 6 h in an isothermal shaker bath fixed at 30 °C. After completion of the equilibration time the admixture was filtered and the final pH value of the filtrate was measured. This set of experiments was performed at a pH interval of 0.5 and on each occasion the solution pH was adjusted at the desired value using 0.01 M HNO_3 or 0.01 M NaOH. In all of the experiments the ionic strength was kept constant.

2.3. Determination of equilibration time

Initially a stock solution of 2000 mL of strength 1000 mg/L Cd(II) ion was prepared by dissolving an appropriate amount of $Cd(NO_3)_3 \cdot 4H_2O$ (analytical grade) in double distilled water.

Solutions of other strengths were prepared from this stock solution.

The batch equilibrium technique was used to determine the equilibrium time of the Cd(II) adsorption. The experiments were performed with -150 mesh size pyrite at a solution pH of 6.4. In each experiments 100 mg of pyrite was suspended in a 100 mL of 100 mg/L strength solution of Cd(II) ion and thermostated in a shaker bath at 30 °C for an appropriate time and then filtered and washed repeatedly. The filtrate was collected for Cd(II) analysis. The ionic strength of the solution was adjusted to 0.1 M using $NaNO_3$ solution. The final volume of the solution was made up to 250 mL by adding double distilled water.

2.4. Adsorption of Cd(II) ion

The influence of pH was studied by batch experiments in the pH range of 2.0–8.0 with -150 mesh size fraction at a pH interval of 0.5. Each experiment was carried out by suspending 100 mg pyrite in 100 mg/L Cd(II) solution at a definite pH and allowing the suspension to equilibrate for 1 h in an isothermal shaker bath at 30 °C. The pH and ionic strength were adjusted to the desired level in each experiment as stated above. The final volume of the mixture was raised up to 250 mL by adding double distilled water. After the desired equilibration time the suspension was filtered, washed several times with double distilled water and the collected filtrate was analysed for Cd(II) ion.

The concentration dependence of Cd(II) adsorption onto pyrite was studied by batch experiments in which the initial concentration was varied between 20 and 500 mg/L using 100 mg of -150 mesh size pyrite suspended in 100 mL of appropriate strength Cd(II) solution at a solution pH of 6.0. The pH and ionic strength were adjusted as before. The final volume of the admixture was made up to 250 mL. The entire mixture was equilibrated for 1 h in an isothermal shaker bath at 30 °C. The process involved in the metal analysis was the same as described above.

The effect of particle size of pyrite was studied with -100, -150 and -200 mesh size in a similar manner through batch experiments at a solution pH of 6.0 and a temperature of 30 °C. Identical procedures were involved in the investigation of the influence of temperature where four temperatures were considered viz. 30, 32, 35 and 40 °C with -150 mesh size pyrite at a solution pH of 6.0. In these two sets of experiments the equilibration time and the initial concentration of Cd(II) were 1 h and 100 mg/L, respectively.

2.5. Calculations

The adsorption performance, i.e. the amount of Cd(II) adsorption onto pyrite is expressed as metal uptake, q (mg/g) which is calculated by using the following relation

$$q = (C_0 - C_e) \times V/m$$

where C_0, initial concentration of Cd(II) ion (mg/L); C_e, concentration of free Cd(II) ion at equilibrium; V, volume of