Journal of University of Science and Technology Beijing
Vol.7(2000), No.4, p.237

Copper Adsorption on Olivine

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(Received 1999-11-18)

Abstract: Copper adsorption on olivine supplied by the A/S Olivine Production Plant at Aheim in western Norway was studied. The factors were evaluated which affect the uptake of copper. It is shown that the equilibrium pH of aqueous solution has the greatest influence on copper adsorption thanks to the competitive adsorption between proton and copper ions, and the adsorption of copper to olivine increases rapidly with pH increasing from 4 to 6. Moreover, initial copper concentration and olivine dose possess significant effect on copper adsorption, for the adsorption rate of copper increases with olivine dose increasing or initial copper concentration decreasing at the same pH. In addition, the ionic strength effect on the adsorption was also investigated, but it owns little effect on the adsorption process of copper due to the formation of inner sphere adsorption of copper on olivine. The experimental data show that olivine has a high acid buffer capacity and is an effective adsorbent for copper.

Key words: copper; adsorption; olivine; ionic strength; acid mine drainage

Acid mine drainage is the most common pollution problem in water environment [1]. The oxidation of pyrite and other sulfide minerals by oxygen plays a key role in acid mine drainage, which is highly acidic and heavy-metal rich solution via the reactions of protons with carbonates, silicates, oxyhydroxides or even sulphides [2,3]. The treatment of acid mine drainage has long been the study object of environmental chemists. Many materials like activated carbons, low cost carbons, zeolites, iron and aluminium oxides, apatite as well as blast furnace sludge have been deeply studied in the adsorption and desorption process for the elimination of heavy metals from industrial wastewater [4,5]. Certain low cost natural materials display the ability of ion exchange due to their composition and crystallographic structure, and their utilization for removing heavy metals is very promising [6].

The main purpose of this study is to investigate the solidification of copper ions by olivine dust from the mining industry and its potential utilization as a geochemical barrier at the base of landfills and waste depots in addition to the traditional hydrological ones. The present paper discusses the adsorption of copper ions on olivine in the sub-neutral pH region since the major mechanism responsible for removing Cu^{2+} under such conditions is probably adsorption of copper ions to the mineral surface. The adsorption of copper ions to olivine as a function of equilibrium pH and the amount of acid added, initial copper concentration, adsorbent doses and ionic strength has been reported in this paper.

1 Experimental

1.1 Mineral adsorbent

Olivine dust was supplied by the A/S Olivine production plant at Aheim in western Norway. A/S Olivine produces over 2 million tonnes of olivine material each year, which is used primarily in metallurgical industry. Olivine used in this study consists of dust retrieved from the dust removal system of the plant and was given no additional treatment prior to their use in the adsorption experiments.

Mineral phase composition of olivine was determined by X-ray powder diffraction (XRD) using a Philips diffractometer and monochromatized CuK_α radiation (the generator tension is 70 kV, and current is 50 mA). The XRD pattern was recorded from 5° to 70° (2θ) with a step size of 0.02° and a counting time of 0.4 s per step. Chemical composition of olivine was analyzed by X-ray fluorescence technique (XRF) using a Philips 1480 PW X-ray spectrograph. Both the XRD and XRF analyses were performed by the Norwegian Geological Survey (NGU).

The size distribution of olivine was obtained by a Coulter LS 230 Particle Size Analyzer, while specific surface area was determined by the N_2-adsorption technique (BET) with a Flow Sorb II 2300 volumetric gas adsorption analyzer. The results are shown in **table 1**.

Table 1 Material characteristics of olivine

Mineral phase composition / %				Chemical composition / %				Size distribution / μm			Specific surface area / $m^2 \cdot g^{-1}$
Forsterite	Serpentinite	Augite	Pyrotite	MgO	SiO_2	Fe_2O_3	NiO	d_{90}	d_{50}	d_{10}	
>95	—	—	—	50.3	43.5	7.7	1.3	<67	<21	<3.5	3.4

1.2 Reagents

All chemicals used in the study were of analytical reagent grade. Deionised water was used throughout the study. All glasswares and other containers were thoroughly cleaned by soaking in detergent (Deconex) followed by soaking in 10% HNO_3 for 24 h and finally rinsed with deionised water several times prior to use.

- 0.01 mol/L Cu solution: the solution was prepared by dissolving 0.6043 g of copper nitrate ($Cu(NO_3) \cdot 4H_2O$) in a volumetric flask containing 5 mL of 0.5 mol/L nitric acid and diluting to 250 mL with deionized water.

- 0.5 mol/L nitric acid solution: the solution was prepared by diluting 17.3 mL of 65% nitric acid to 500 mL with deionized water.

- 1 mol/L sodium nitrate electrolyte solution: the solution was prepared by dissolving 42.495 g of $NaNO_3$ in deionized water and diluting to 500 mL.

1.3 Adsorption experiments

Batch adsorption experiments were conducted in 100 mL polyethylene bottles by firstly equilibrating an accurately weighed amount of olivine with a defined volume of solution containing deionized water, a chosen amount of 0.5 mol/L nitric acid and a required amount of 1 mol/L sodium nitrate to keep the ionic strength in the final solution fixed at 0.05 mol/L. Based on the results of the leaching experiments olivine was assumed to release predominately divalent ions when exposed to the initially acidic solution, and the required amount of electrolyte ($NaNO_3$) was calculated according to the formula

$$V_{el}=\frac{I V_t}{N_{el}}-\frac{F V_{acid} c_{acid}}{2N_{el}} \tag{1}$$

where V_{el} is the required volume of sodium nitrate electrolyte, I is the desired ionic strength, V_t is the total solution volume (100 mL), N_{el} is the normality of the electrolyte (1 mol/L), F is the ionic strength factor and the value is 3 for olivine, c_{acid} is the initial concentration of nitric acid, V_{acid} is the volume of nitric acid. A pH-drift experimental technique was adopted due to the difficulty to control pH of the aqueous phase during the experiment. In order to obtain the data from the desired pH interval different amounts of acid were added to each bottle. The suspensions were then equilibrated by a thermostatic agitator's orbital agitation at a speed of 145 r/min at (25±0.1)℃ for 24 h.

After the initial equilibration, a defined volume of copper solution was added to each bottle to reach a suspension volume of 100 mL and to obtain the desired initial copper concentration. In order to attain the equilibrium between the solute and the solid phase, the thermostatic agitation process was repeated at the same temperature and speed as before for an additional 24 h.

Each suspension was eventually sampled by extracting and filtering a volume of 10 mL by using a syringe and a 0.45 μm syringe filter. Simultaneously the final pH of the suspensions was measured by using a Metrohm 744 pH Meter, which was calibrated prior to each series of measurements. The filtrates were collected in small bottles and acidified by using 20 μL of 65% nitric acid, if not analysed immediately.

The filtrates were then analysed for the copper concentration using the atomic absorption spectrometry (AAS) method. The degree of copper adsorption on olivine was calculated from the measured equilibrium copper concentration in the aqueous phase. The difference between the initial and equilibrium copper concentrations, *i.e.* the amount retained by the solid phase, is then taken to represent the amount adsorbed by olivine.

2 Results and discussion

2.1 Effect of pH

The adsorption of copper ions on olivine was studied over the pH range 3–6 for the initial copper concentration of 0.1 mmol/L and a fixed olivine dose of 10 g/L. The pH was adjusted by 0.5 mol/L HNO_3 solution and measured after the solution had been in contact with olivine for 48 h. Graphical representation of the adsorption rate for copper over the studied pH range is shown in **figure 1**. Compared with the precipitation curve of copper ions, it is concluded that the disappearance of copper in the aqueous solution is mainly due to the precipitation of copper ions in the pH range of above 6 and the adsorption of copper on olivine in the pH range of below 6. A general increase in adsorption with the increase of pH in solution has also been observed. The similar behavior has been reported by other authors for the adsorption of heavy metal ions on various adsor-

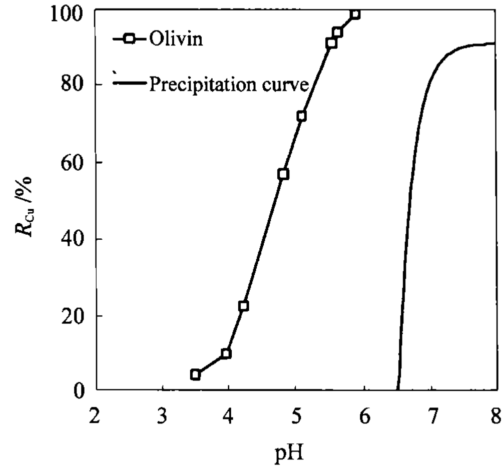

Figure 1 Relations of the Cu adsorption rate on olivine, R_{Cu} with the equilibrium pH. Olivine dose: 10 g/L; Initial Cu concentration: 100 μmol/L.

bents [7]. The adsorption is regarded as surface complex formation of cations by hydrous oxides involving the coordination of the metal ions with the oxygen donor atoms and the release of protons from the surface,

$$S—OH + Cu^{2+} = S—OCu^{+} + H^{+} \quad (2)$$

the process is strongly pH dependent since the complex formation is a competitive adsorption process between copper ions and H^+ [8].

pH and adsorption rate of copper on olivine as a function of HNO_3 added is shown in **figure 2**. The pH decreases from 5.9 to 3.5 and copper adsorption rate from 98.5% to 4.6% with the acid amounts increasing from 2.5 to 11 mL. It shows that olivine possesses a high acid neutralisation or buffer capacity which is very important in the acid mine drainage treatment.

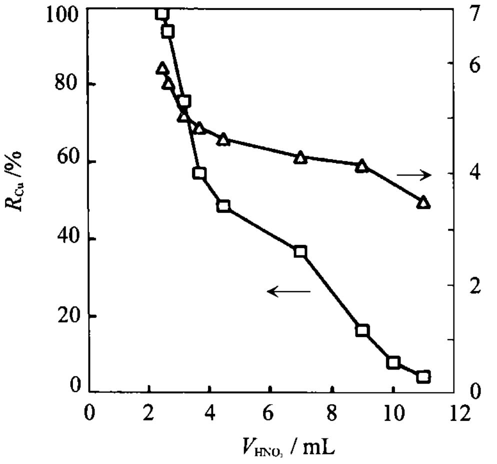

Figure 2 Relations of the Cu adsorption rate on olivine, R_{Cu}, with the equilibrium pH with the 0.5 mol/L HNO_3 amount added, V_{HNO_3}. Olivine dose: 10 g/L; Initial Cu concentration: 100 μmol/L.

2.2 Effect of initial copper concentration

Based on the studies carried out with initial copper concentration of 20, 50, 100, 200 and 400 μmol/L as well as a fixed olivine dose of 10 g/L, the influence of varying copper concentration on its adsorption as a function of equilibrium pH is presented in **figures 3 and 4**. These figures reveal that for the same equilibrium pH, the copper adsorption rate decreases and the adsorption on unit mass of olivine increases with the increase of the initial copper concentration. It is assumed that more efficiently utilizing the adsorptive capacities of the adsorbent is expected due to a greater driving force by a higher concentration gradient [9].

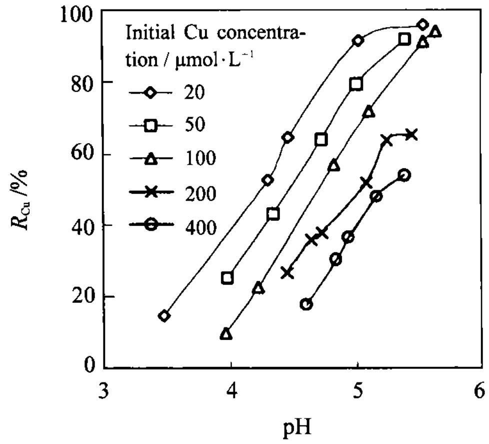

Figure 3 Relations of the Cu adsorption rate, R_{Cu}, with the equilibrium pH under various initial Cu Concentration. Olivine dose: 10 g/L.

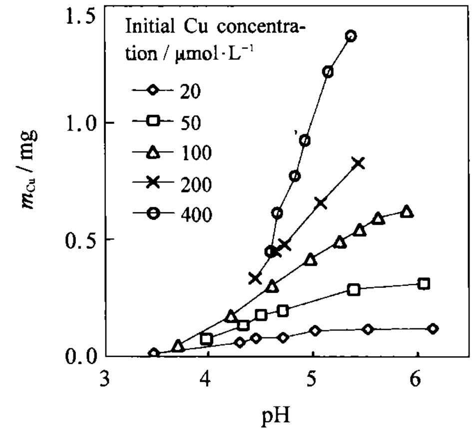

Figure 4 Relations of the Cu adsorption mass on 1 g olivine, m_{Cu} with the equilibrum pH. Olivine does: 10 g/L.

2.3 Effect of olivine dose

The effect of olivine dose on its adsorption properties was studied with different olivine doses of 2.5, 5, 7.5, 10, 12.5 g/L at a fixed initial copper concentration of 100 μmol/L and HNO_3 amount of 2 mL (**figures 5**

and 6). The adsorption rate of Cu increases from 22.8% to 99.9% and the pH from 4.77 to 6.54 with olivine dose increasing from 2.5 to 12.5 g/L because olivine offers larger surface area and greater buffer capacity with higher dose. But the copper adsorption on unit mass of olivine experiences three stages. It decreases with olivine dose increasing from 2.5 to 5 g/L, increases with olivine from 5 to 7.5 g/L and finally decreases again with olivine from 7.5 to 12.5 g/L. Since the copper adsorption process is highly pH dependent, this phenomenon can be explained that the copper adsorption on unit mass of olivine decreases on the first stage due to the slow increase of pH and increases on the second stage thanks to the rapid increase of pH. The adsorption decreases on the third stage as the copper in the solution has almost been adsorbed to olivine.

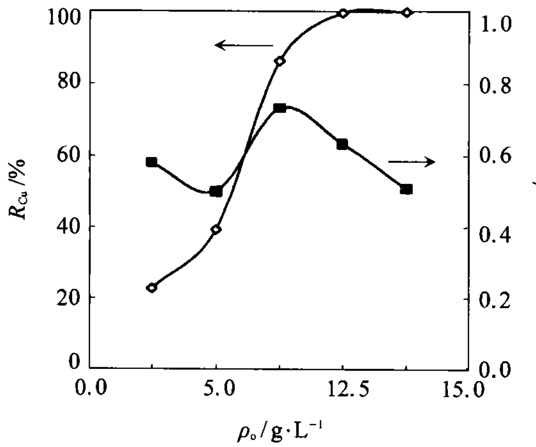

Figure 5 Relations of the Cu adsorption rate on olivine, R_{Cu} and the Cu adsorption mass on 1 g olivine, m_{Cu} with the olivine dose, ρ_o. Initial Cu concentration: 100 μmol/L; HNO_3 amount: 2 mL.

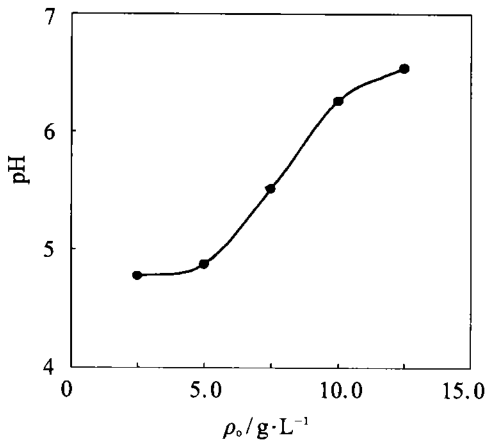

Figure 6 Relation of the equilibrium pH with the olivine dose, ρ_o. Initial Cu concentration: 100 μmol/L; HNO_3 amount: 2 mL.

2.4 Effect of ionic strength

The ionic strength (denoted *I*) effect on the adsorption of copper on olivine was studied with *I*=0.05 and 0.50 mol/L (**figure 7**) at a fixed initial copper concentration of 100 μmol/L and olivine dose of 10 g/L. The curves show that the adsorption rate of copper on olivine just decreases slightly with the increase of ionic strength from 0.05 to 0.5 mol/L. The insensitivity to ionic strength is taken as an indication for inner sphere surface complexation, where a change in the value of ionic strength does not visibly change the adsorption of a certain ion on a certain oxide under otherwise equal conditions [10].

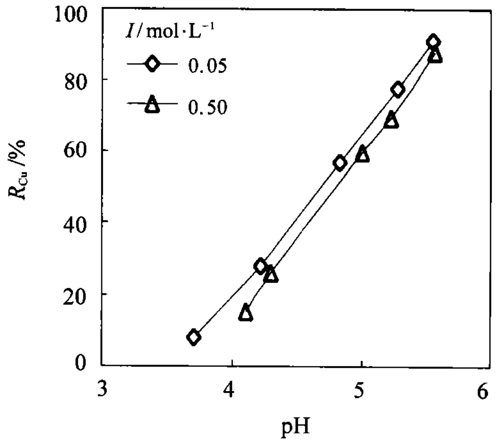

Figure 7 Relations of the Cu adsorption rate on olivine, R_{Cu} with the equilibrium pH under different ionic strength. Initial Cu concentration: 100 μmol/L; Olivine dose: 10 g/L.

3 Conclusions

The present paper studied the utilization of olivine dust as an adsorbent for removing copper from the aqueous solution in sub-neutral pH range. The effect of pH, initial copper concentration, olivine dose and ionic strength on the adsorption of copper on olivine is also investigated. As a result, the adsorption process is highly pH dependent due to the competitive adsorption between copper ion and proton. Moreover, the initial copper concentration and olivine dose also possess significant influence on the copper adsorption. It is assumed that the copper ion forms inner sphere adsorption on olivine since ionic strength has almost no effect on the adsorption.

The results also indicate that olivine is an effective adsorbent for eliminating copper from acid mineral drainage due to its high acid buffer capacity. However, its capacity to remove other heavy metals from multicationic aqueous effluents, its behavior on real wastewater samples and the adsorption/desorption equilibrium in the natural system need further investigating.

Acknowledgements

The authors would like to thank the Research Council of Norway and A/S Olivine for funding the project. Thanks should also been extended to SINTEF in Norway for the analyses of some samples.

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