

Original scientific paper

UDC: 502.51:504.5:669.35

DOI: 10.7251/afts.2015.0712.059B

COBISS. RS-ID 4988952

SORPTION OF COPPER AND ZINC BY GOETHITE AND HEMATITE

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ABSTRACT

In the present work, the abilities of natural and synthetic samples of goethite and hematite to remove copper Cu(II) and zinc Zn(II) ions from aqueous solutions were compared. Batch adsorption experiments were performed in order to evaluate the removal efficiency of iron oxide samples. The effect of initial metal ion concentration, initial pH and time on adsorption of copper and zinc onto the iron oxides has been studied. The sorption data were represented by the linearized Langmuir model. Comparing the values of adsorption capacities, there were differences between the natural and synthetic samples, natural and synthetic goethite had higher sorption capacity for both metals than hematite. The copper ions showed higher affinity than zinc ions to all samples.

Key words: *sorption, copper, zinc, goethite, hematite*

INTRODUCTION

The rapid industrialization and the increase in world population have all contributed to heavy metal pollution in ecosystems due to their high toxicities. Copper and zinc are highly toxic as they are carcinogens and mutagens in nature [1,2]. Moreover, high intakes of these metals can cause liver, kidney and pancreas damage [3]. Having in mind the adverse effects of heavy metals environmental agencies set permissible limits for their levels in drinking water and other types of waters. The maximum allowable limit for both metals in discharged water was set by the Environmental Protection Agency (EPA) to be 1.3 for copper and 5 mg/L for zinc [4]. Removal of heavy metals from industrial wastewater is of primary importance and among number of conventional treatment technologies adsorption is found to be the most effective method [5].

Iron oxides, a common constituent of soils, sediments, and aquifers, have high surface areas and are capable of adsorbing a significant quantity of metals. They are dominant adsorbents in many environments because of their capability to be finely dispersed and act as coatings on other particles [6]. Goethite (α -FeOOH), occurs in rocks and throughout the various compartments of the global system. Goethite is one of the thermodynamically most stable iron oxide at ambient temperature and is, therefore, either oxide to form or the end member of many transformations. Hematite, α -Fe₂O₃, is the oldest known iron oxide mineral and is widespread in rocks and soils. Like goethite it is extremely stable and is often the end member of transformations of other iron oxides [7].

The present work, batch adsorption experiments were conducted for the removal of copper and zinc ions from the model solution using natural and synthetic goethite and hematite. Batch experiments were designed for the sorption process and to determine the adsorption capacity of sorbents. The effect of initial metal ion concentration, pH and time on the adsorption process was investigated. The Langmuir linearized model was applied to interpret the experimental data.

MATERIALS AND METHODS

Synthesis of goethite and hematite

The iron oxides can be prepared by hydrolysis of Fe(III) acid solutions or by controlled oxidation of Fe(II) solutions. Goethite was prepared by hydrolysis of FeNO₃ by KOH. The crystallization of goethite was carried out in a closed polypropylene flask in a 70°C oven for 60 hours. Hematite was prepared by forced hydrolysis of Fe(III) solution from chlorine system (FeCl₃) at temperature close to 100°C under strongly acidic conditions (pH 1-2). The Fe-oxides samples were washed in deionized water (in order to remove impurity ions), filtered, air dried, sieved under the grain size of 40 µm and stored as a dry powders.

Natural goethite and hematite

The natural samples originated from deposit in Ukraine were obtained from Department of Geology of Mineral deposits (Faculty of Natural Sciences) in Bratislava. The samples were grinding, milling on vibrating mill and sieved under the grain size of 40 µm. The chemical composition of the natural samples is presented in table 1.

Table 1 Chemical composition of natural goethite (GP) and natural hematite (HP)

Element	Fe (%)	Al (ppm)	Si (%)	Ca (ppm)	K (ppm)	Mg (ppm)	S (%)	As (ppm)	Cu (ppm)	Zn (ppm)	Mn (ppm)
GP	54,82	770	0,79	30	110	135	0,15	< 5	40	300	8100
HP	61,94	2705	0,92	< 10	100	285	0,22	12,8	150	155	300

The surface area of both natural and synthetic iron oxide samples were determined by NOVA 1200e Surface Area& Pore Size Analyzer (Quantochrome Instruments).

The main mineral phases were confirmed by the powder X-ray diffraction and infrared spectroscopy method. Powder X-ray diffraction (XRD) patterns were recorded with a Philips PW1820 diffractometer (The Netherlands) equipped with a CuKα radiation (40 kV, 40 mA). The JCPDS PDF database was used for the phase identification.

Infrared (IR) spectra of the synthetic Fe-oxide samples were taken on a spectrometer AVATAR 330 (Thermo Nicolet Corp., USA) equipped with DGTS/KBr detector at a resolution 4 cm⁻¹. The spectra were collected with spectral resolution in the region from 4000 to 400 cm⁻¹ on potassium bromide (KBr) pellets.

Adsorption experiments

All experiments were carried out by batch adsorption technique in 100 ml Erlenmyer flasks on a rotatory shaker at 150 rpm. The model solutions of Cu (II) and Zn(II) was prepared by dissolving of CuSO₄ .5H₂O and ZnSO₄ .H₂O respectively in deionized water at concentrations 10, 20, 30, 40, 50 mg Cu, Zn/l. The concentration of added sorbents was 10 g/l. The effect of initial metal ion concentration, initial pH and time on adsorption of copper and zinc onto the iron oxides has been studied. After the adsorption, the solution was filtered and the concentrations of Cu(II) and Zn(II) ions

were measured by atomic absorption spectrophotometer (Varian AA240 Z, AA240 FS, Australia). The equilibrium adsorption capacities were calculated by the following equation:

$$Q = \frac{C_o - C_e}{C_s},$$

where Q is a sorption capacity of sorbent, C_o (mg/l) is the initial concentration of metal ion in solution, C_e (mg/l) is the equilibrium concentration of metal ion in solution and C_s (g/l) is amount of sorbent.

RESULTS AND DISCUSSION

The natural, as well as synthetic sorbents were first characterized by nitrogen adsorption method, X-ray diffraction and IR spectroscopy.

The values of specific surface area determined by BET method from the nitrogen adsorption measurement were $30.67 \text{ m}^2/\text{g}$ for synthetic goethite (GS), $5.45 \text{ m}^2/\text{g}$ for synthetic hematite (HS), $19.56 \text{ m}^2/\text{g}$ for natural goethite (GP) and $4.66 \text{ m}^2/\text{g}$ for natural hematite (HP). Whereas the value of specific surface area to a certain extent relates with the adsorption properties it can be expected, that the synthetic goethite will be the best sorbent for selected heavy metal ions. The XRD analysis of the synthetic goethite and hematite samples revealed the presence of only $\alpha\text{-FeO(OH)}$ and $\alpha\text{-Fe}_2\text{O}_3$ phase for goethite and hematite, respectively, see figures 1, 2.

Comparing the samples, higher crystallinity for the synthetic iron oxides was observed, caused probably by the method of their synthesis, than for the natural, what manifest the figures 5, 6. The IR spectra of synthetic goethite and hematite are shown in figures 3 and 4. The OH stretching and bending vibrations occurred in the spectral region of $3200 - 3600 \text{ cm}^{-1}$, resp. $793 - 891 \text{ cm}^{-1}$, confirmed the main infrared spectrum of goethite $\alpha\text{-FeOOH}$. The IR spectrum of synthetic hematite confirmed the stretching vibrations of OH groups at $3500\text{-}3200 \text{ cm}^{-1}$, and bending vibrations in the area of wavenumbers 616 and 476 cm^{-1} , typical for Fe_2O_3 phase.

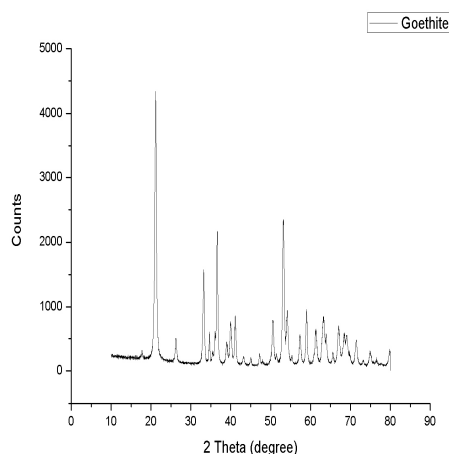


Figure 1 XRD pattern of synthetic goethite

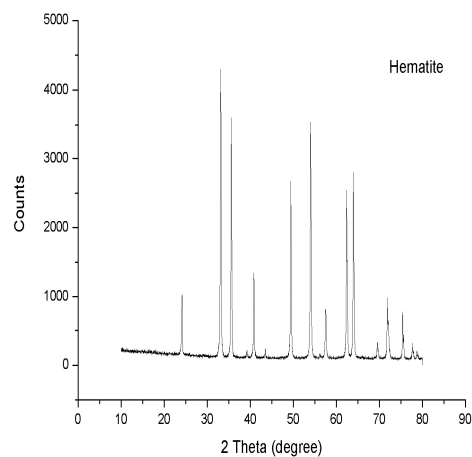


Figure 2 XRD pattern of synthetic hematite

The adsorption experiments were conducted and studied such as influence of the initial concentration of Cu(II) and Zn(II), the initial pH and time of the sorption process. Equally often like ferrihydrite, goethite and hematite have been used as model adsorbents because they have a well defined crystal structure, are widespread in nature and can be synthesized readily in the laboratory. The previous studies showed the ion adsorption on goethite in the order $\text{Cu} > \text{Pb} > \text{Zn} > \text{Cd} > \text{Co} > \text{Ni} > \text{Mn}$, the same order is followed for hematite except of the position of Cu and Pb which is reverse [8].

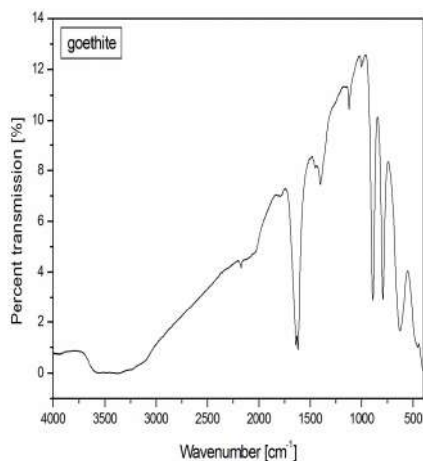


Figure 3 IR spectrum of synthetic goethite

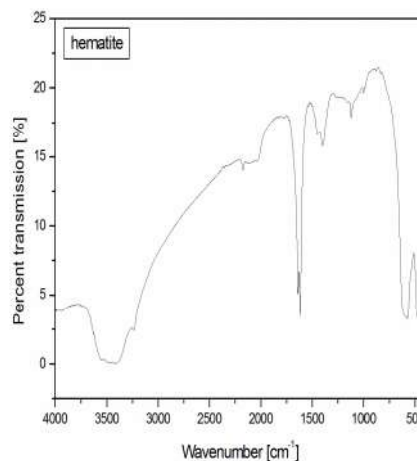


Figure 4 IR spectrum of synthetic hematite

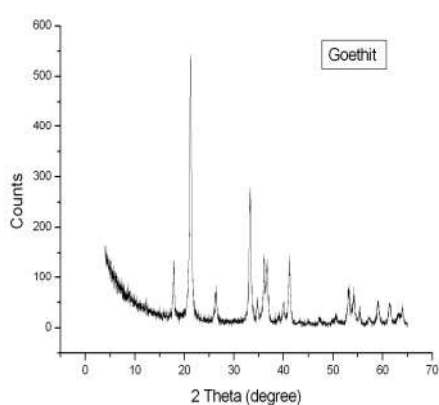


Figure 5 XRD pattern of natural goethite

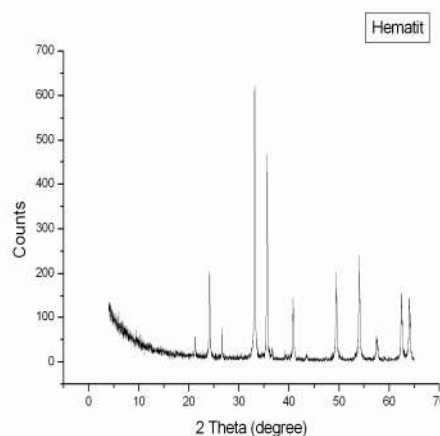


Figure 6 XRD pattern of natural hematite

The adsorption experiments were conducted and studied such as influence of the initial concentration of Cu(II) and Zn(II), the initial pH and time of the sorption process. Equally often like ferrihydrite, goethite and hematite have been used as model adsorbents because they have a well defined crystal structure, are widespread in nature and can be synthesized readily in the laboratory. The previous studies showed the ion adsorption on goethite in the order $\text{Cu} > \text{Pb} > \text{Zn} > \text{Cd} > \text{Co} > \text{Ni} > \text{Mn}$, the same order is followed for hematite except of the position of Cu and Pb which is reverse [8].

Effect of pH

The pH of the solution is perhaps the most important parameter for the adsorption. To understand the adsorption mechanism, the adsorption of Cu(II) and Zn(II) as a function of pH was measured, and the results are shown in figures 7 and 8. The influence of pH was investigated at the pH range from 3 to 7. The figures shows the increase in the adsorption capacity of sorbents with the increasing pH from 3.0 to 6.0 for Cu(II) and to 7.0 for Zn(II). The optimum pH for copper adsorption by both samples was found to be about 6.0 (1 mg/g) and zinc adsorption increased with increasing pH and not reached a maximum at this range. This related to pH value in which are individual ions soluble in solution, and above which values of pH are precipitated on insoluble compounds. At a pH value higher than 5.9 for copper and 7 for zinc are already precipitated in different species. As the pH increases, there is an increasing trend in the concentration of hydroxide ions $[\text{OH}^-]$ in solution and causing the disturbance of equilibrium. The adsorption increased very significantly with pH for both metal ions. The GS achieved the maximum adsorption capacity 2 mg/g for copper at pH 5, and GP maximum sorption capacity 1 mg/g for copper at pH 6.

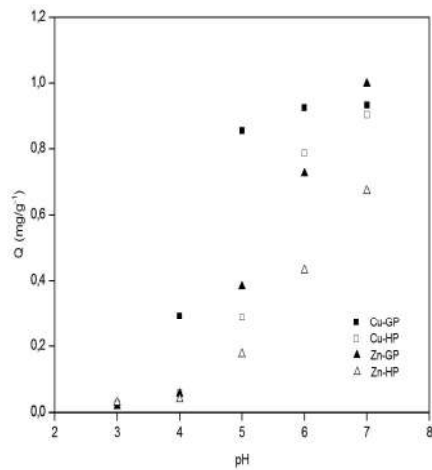


Figure 7 Effect of pH on sorption Cu(II) and Zn(II) by natural samples

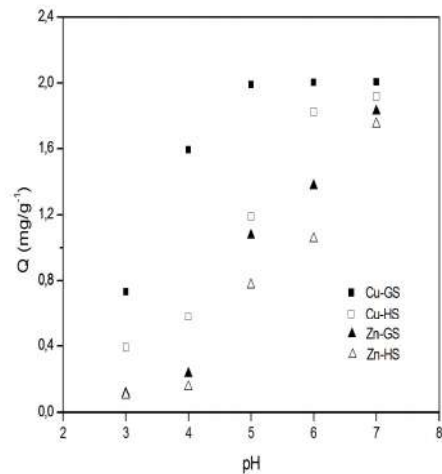


Figure 8 Effect of pH on sorption Cu(II) and Zn(II) by synthetic samples

In acidic environments the Fe-oxide surface is positively charged while in alkaline media it is negatively charged. The pH at which the net surface charge is zero is termed the point of zero charge (PZC). Pure iron oxides without sorbed ions have PZC's ranging from 8.5 to 9.3 [9]. However, adsorption of anions may shift the PZC to lower pH values, while adsorption of cations may shift the PZC to higher pH [9, 10]. Therefore, the sorption experiments were performed at pH 5, which may indicate that at higher pH values better sorption capacity of ions will be achieved (Figures 7, 8). However, many other factors can influence the sorption process. The EXAFS data suggest that on goethite zinc [11] and also copper [12] adsorb as inner sphere complexes which display Jahn Teller distortion.

The effect of contact time

The effect of contact time on copper and zinc ions adsorption onto iron oxide samples was studied and the results are shown in figure 9. It was found that the adsorptive quantity of both copper and zinc ions on Fe-oxide samples increased with the increasing contact time. The sorption of Cu(II) and Zn(II) ions was rapid for first 60 min but the equilibrium was not reached after 240 min. This slow adsorption may be explained by the rapid adsorption on the external surface at the beginning, which was followed by slow diffusion into the particles, with finally, adsorption on internal sites.

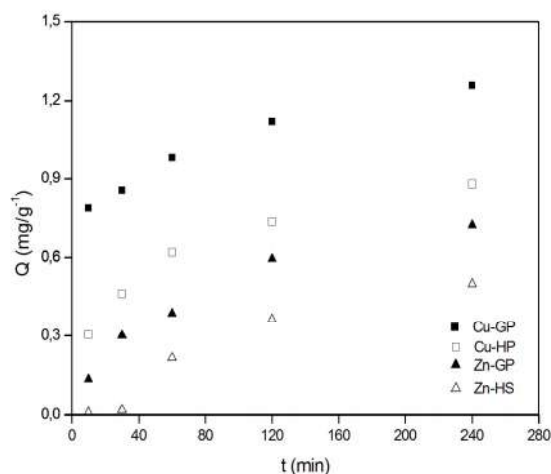


Figure 9 Effect of contact time on sorption Cu(II) and Zn(II) by Fe-oxide samples

Effect of initial metal ion concentration

The obtained results showed the differences between the natural and synthetic samples of goethite and hematite in Cu(II) and Zn(II) sorption. The values of equilibrium adsorption capacities of both natural and synthetic samples showed higher affinity of both ions to goethite compare with the hematite. Also the copper ions demonstrated higher affinity onto both samples compare with zinc ions. The adsorption of Cu(II) and Zn(II) on Fe-oxides slightly increased with the increasing initial metal ion concentration up to 20 mg/l, then the equilibrium was established, except of copper on goethite samples and also for zinc on GS sample. The figures 10 and 11 indicate, that uptake of copper ions onto both goethite samples was very fast and equilibrium was not reached, the similarly behaving was observed for zinc ions. To interpret the experimental data the Linearized Langmuir model was used and the obtained parameters are listed in table 2.

The calculated value of maximum adsorption capacity of natural and synthetic goethite was 1.4 mg/g and 2.8 mg/g for copper, respectively, figure 12. In case of natural goethite the copper ions were removed from the solution with higher efficiency than zinc ions. On the other hand, the sorption of zinc ions onto synthetic goethite was quiet effective, its value of adsorption capacity was 1.85 mg Zn(II)/g. The lowest value of adsorption capacity was obtained for the synthetic hematite: 0.28 mg Zn(II)/g, figure 13. It can be concluded that Fe-oxide samples were effective in Cu(II) and Zn(II) removal in this order: GS>GP>HS>HP, what correspond with the results obtained from the nitrogen adsorption analyses.

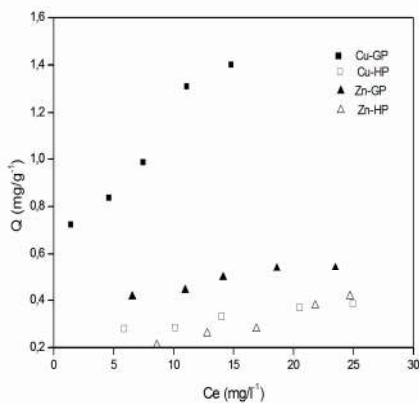


Figure 10 Effect of initial ion concentration on sorption Cu(II) and Zn(II) on natural samples

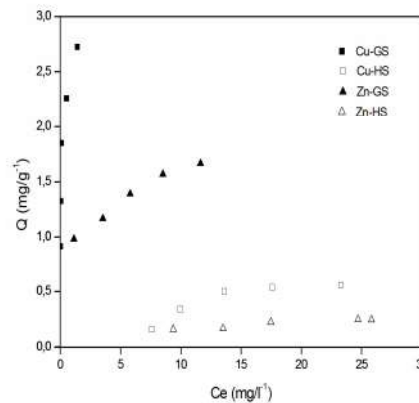


Figure 11 Effect of initial ion concentration on sorption Cu(II) and Zn(II) on synthetic samples

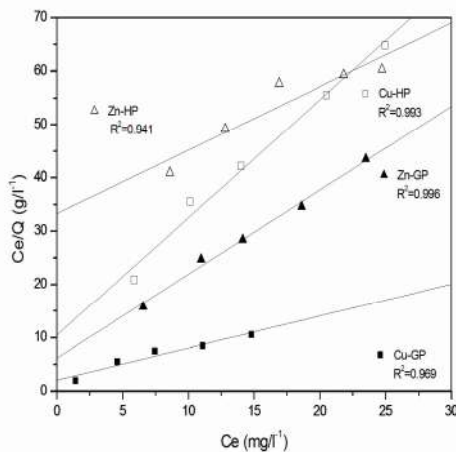


Figure 12 Linearized Langmuir model - natural samples

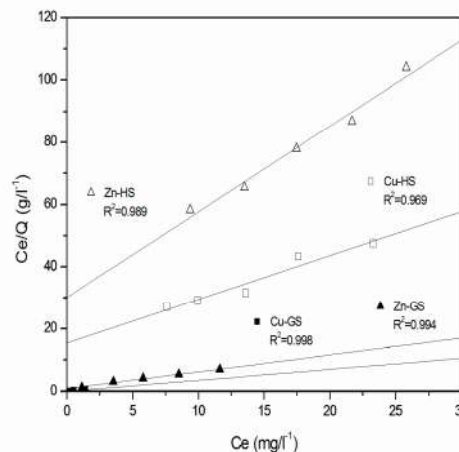


Figure 13 Linearized Langmuir model - synthetic samples

Table 2 Langmuir constants for Cu(II) and Zn(II) sorption onto natural and synthetic samples

Sample	Qm(mg/g)	b(l/mg)
GP-Cu	1,667	0,288
HP-Cu	0,452	0,212
GS-Cu	2,849	11,735
HS-Cu	0,709	0,091
GP-Zn	0,634	0,256
HP-Zn	0,839	0,035
GS-Zn	1,85	0,628
HS-Zn	0,361	0,091

CONCLUSIONS

The results obtained from this study confirmed that both natural and synthetic goethite are more suitable sorbent of Cu(II) and Zn(II) ions from the aqueous solution than hematite. The affinity of Cu(II) and Zn(II) ions to the studied samples were in the order: GS > GP > HS > HP. The highest value of adsorption capacity was achieved for synthetic goethite in sorption of Cu(II) 2.8 mg/g. The value of adsorption capacity for Zn(II) was 1.8 mg/g. The adsorption capacities of Cu(II) and Zn(II) were higher for the synthetic samples than for natural, indicating that the synthetic samples had greater specific surface area. The Cu(II) had a relatively stronger affinity to goethite than Zn(II).

It can be concluded that further investigations are still needed to make the adsorption process more effective. Therefore the next study will be focused on study of other parameters which can influence the sorption process like temperature, ionic strength and other.

ACKNOWLEDGEMENT

This work was supported by the VEGA Agency supporting the project 2/0049/15 and 2/0114/13.

(Received February 2015, accepted March 2015)

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