

A study on the use of nano/micro structured goethite and hematite as adsorbents for the removal of Cr(III), Co(II), Cu(II), Ni(II), and Zn(II) metal ions from aqueous solutions.

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Abstract

Numerous adsorbents for the removal of heavy metals from aqueous solutions are in various stages of research. The main goal for most of this research is to develop low-cost and environmentally friendly materials for the removal of heavy metals from contaminated groundwater, surface water, and drinking water.

Materials that have ion exchange sites are expected to be able to efficiently remove heavy metals from water. Iron oxides, especially in the micro/nano structured forms, are good candidates for the removal of toxic heavy metal ions from water due to their structural properties. In the present work the efficiency of synthesized micro/nano particles of goethite and hematite for the removal of Cr(III), Co(II), Cu(II), Ni(II) and Zn(II) ions from water was compared. The adsorbent capability of goethite as a function of pH, contact time, and initial metal ion concentration was studied.

The results showed that maximum absorption for all metal ions using goethite occurred at a pH=5.3, which was a common trend for all metal ions. At this pH and after one hour contact time goethite was able to adsorb about 100% of the Cu ions (50mg/g), 85% (42.5 mg/g) of the Ni ions, 70% (35mg/g) of the Cr and Co ions and 60% (30 mg/g) of Zn ions from the solutions. Whereas and under the same conditions hematite was able to adsorb 20% (10mg/g) of the Cu ions, 85% (42.5mg/g) of the Ni ions, 95% (47.5mg/g) of the Cr ions, 80% (40mg/g) of the Zn ions, and 70% (35mg/g) of the Co ions. Both oxides are equally efficient for the removal of Co(II) and Ni(II) from water. However, goethite is a much more efficient candidate than hematite for the removal of Cu(II), while hematite is more efficient adsorbent for Zn(II) and Cr(III). The adsorption affinity of the five metallic cations to goethite is Cu > Ni > Co ~ Cr > Zn, whereas the adsorption affinity of the cations to hematite is Cr > Ni > Zn > Co > Cu. Under the conditions used in the batch experiments (mass of goethite 2g/l) maximum adsorption of the metal ions onto the goethite particles occurred when the initial metal concentration for Ni(II),

Cu(II), and Cr(III) was 100ppm, (0.05g/g of adsorbent), 200ppm for Zn(II), (0.1g/g), and 50 ppm for Co(II), (0.025g/g) . Although the rates and the extent of absorption vary for the different metal ions, the findings indicate that they are both effective materials and may be used for the removal of heavy metal ions from aqueous streams. They present low cost adsorbents for the fast, convenient, and highly efficient removal of metals from contaminated water.

Keywords: nano-goethite; nano- hematite; adsorption; heavy metals; contaminated water

Introduction

It is well known that chemical contaminants in water sources have increased as a result of their production in the industrial and agricultural activities. These contaminants include heavy metals which when consumed in relatively high amounts are toxic to human health and may cause many serious problems upon long term exposure. Many studies have found that heavy metals such as arsenic, cadmium, copper, cobalt, chromium, nickel, and zinc, exist in variable amounts in drinking water as well as in ground water [Oulabi, (1999); Acra, (1981); Alam, (1989)]. This makes the removal of these toxic contaminants from water sources, efficiently and within reasonable costs, an important issue.

Many adsorption materials have been investigated for the removal of heavy metal ions from water. Sorbents that have been studied include natural and artificial materials such as clay mineral [Gu et al., (2010); Yavuz et al., (2003); Abollino et al., (2003)], carbon-nanomaterials [Li et al., (2002), Li et al., (2003); Gao, (2009)], biosorbents (Guo et al., (2008)), and micro/nano structured metal oxides [Debnath and Ghosh (2009); O'Reilly and Hochella (2003)]. Recently the emphasis is on the use of efficient, yet low cost and environmentally friendly adsorbents. Micro/nano iron oxides such as goethite (α -FeOOH) and hematite (α -Fe₂O₃) fall under this category. The benefits of using these micro/nano materials may derive from their increased affinity due to their high surface area and the presence of surface functional groups which makes them appropriate to interact with heavy metal ions. Theoretically, materials that have high surface area and ion exchange sites are expected to be able to efficiently remove heavy metal ions from water. Iron oxides are ideal for the removal of heavy metal ions from water due to their strong mechanical structure that can sustain water flow for extended periods of time and their low cost.

A few recent studies have investigated the adsorption of some toxic metal ions onto goethite and hematite in aqueous solutions [Chen and Li, (2010); Mustafa et al., (2004); Mohapatra et al., (2010)]. One study have indicated that nano-particles of goethite and hematite have a high removal capacity of Cu(II) ions from aqueous solutions [Chen and Li, (2010)] . Mustafa et al., (2004) studied the kinetic and thermodynamic aspects of cadmium adsorption onto synthesized goethite. Adsorption behavior of nano-structured goethite was also studied for Pb(II), Cd(II), Cu(II) and Co(II) from single and binary aqueous solutions on nano-structured goethite [Mohapatra et al., (2010)]. The maximum loading capacities were estimated as 109.2, 86.6, 29.15, and 37.25mg/g of goethite for Pb(II), Co(II), Cd(II) and Cu(II) respectively from single cation containing solutions. Although there have been few studies on the use of goethite and hematite for the removal of toxic heavy metals from water sources, comparative comprehensive reports on all heavy metals are not available yet. In This study, batch adsorption experiments were performed with synthesized nano/micro goethite and hematite to investigate their use as adsorbents for Cu(II), Co(II), Cr(III), Ni(II), and Zn(II) cations in water. The objective of the study was to examine the absorbance affinity of the five metallic cations into the two iron oxides to obtain the optimal

conditions for adsorption and to compare the effectiveness of goethite with that of hematite. Experiments were conducted for both hematite and goethite in order to compare the adsorption behavior of Cu(II), Co(II), Cr(III), Ni(II), and Zn(II), onto these two iron oxides as a function of contact time. In addition, the adsorption of the five metal ions onto goethite as a function pH of the solution and the initial metal concentration was studied. The main goal for investigating the use of such materials is to develop low-cost and environmentally friendly materials for removal of heavy metals from contaminated water. Moreover, the understanding of these patterns is necessary to come up with practical solutions for designing or operating the removal of heavy metals from contaminated water sources.

Materials and Methods

Synthesis of goethite and hematite for use as adsorbents:

All chemicals $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, KOH, and CTA used for synthesis were of an analytical grade and were obtained from BDH. The goethite and hematite particles were synthesized based on published methods [Wainippee et al., (2010); Mohapatra et al., (2011)] as follows: 18 ml of 5M KOH were added to 10 ml of 1M Iron (III) nitrate under stirring. The mixture was diluted with 200 ml water then kept in an oven at 70 °C for 60 hours where a yellow brown precipitate of goethite was formed. After that, the precipitate was washed 5 times with 0.06 M acetic acid, separated by centrifugation, and dried in an oven at 95 °C for 24 hours. The powder was collected and characterized. The hematite particles were synthesized by the addition of 5 ml of 10 % CTA to 100 ml of 0.88 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and stirred for two hours. The pH value was adjusted to 10 by the drop wise addition of 1M NaOH solution under stirring followed by stirring for 24 hours. The precipitate was filtered, washed with distilled water, transferred to a 500 ml beaker and diluted with distilled water to the 500 ml line mark. The obtained solution was kept at 60°C for 12 hours in an oven, filtered, washed with distilled water and dried at 100°C for another 24 hours in an oven. X-ray diffraction (XRD) of the synthesized goethite and hematite was obtained by using an (XRD Bruker AXS D8 Focus) diffractometer. The particle size and the frequency distribution of the particles were determined by a dynamic light scattering (DLS) laser granulometer (Horiba laser scattering particle size distribution analyzer LA-950V2).

Adsorption experiments:

The adsorption batch experiments were done using Cu(II), Co(II), Ni(II), Cr(III) and Zn(II) solutions. The metal ion stock solutions were prepared from their respective nitrate or chloride salts. The pH of the initial metal ion solutions was adjusted, when needed, either by addition of hydrochloric acid (0.1N) or NaNO_3 (0.1 N). The pH measurements were done using a pH meter (Hanna PH 211 microprocessor PH meter). All reactions were carried out at room temperature.

Effect of pH:

To study the pH effect, 100 mg/l solutions of the metal ion and 2 g/l of the goethite were mixed at different pH values ranging from 3 to 6 and kept under stirring for one hour. After that the solutions were filtered. The filtrates were collected and the amount of the remaining metal ion was measured using a UV-visible spectrophotometer (VWR 2000 UV/SP).

Effect of contact time:

The capacity of adsorption of the metal cations onto the two iron oxides was investigated by adding 2 g/l of the adsorbent to 100mg/l solution of the metal ion. The pH value was adjusted to 5.3 using 0.1 N NaNO_3 . The solutions were kept under stirring for two hours, while samples were collected every 5 min., filtered with a 0.45-mm filter, and the absorbance of the remaining metal ions was measured by using a UV-visible spectrophotometer (VWR 2000 UV/SP).

Effect of initial metal concentration:

The effect of the initial concentration of the metal ions was investigated by varying the metal ion concentrations from 50 ppm to 500 ppm. 2g/l of the goethite were added to these solutions followed by adjusting the pH value to 5.3. The mixtures were kept under stirring for one hour, filtered and the absorbance of the remaining metal ion in the filtrate was measured.

Results and Discussion

Characterization of the goethite and hematite particles:

Figures 1 and 2 show x-ray diffraction patterns of nanogoethite and nanohematite respectively. The patterns reveal peaks at d- values of 6.8571, 4.55, 4.64, 4.16, 3.75, 3.44, 3.021, 2.66, 2.33 and 2.15 corresponding to the nano-goethite ($\alpha\text{-FeOOH}$) and peaks at d-values of 3.67, 2.69, 2.51, 2.20, 1.84, 1.69, 1.48 and 1.45 corresponding to the nano-hematite. The intense and sharp peaks indicate that the samples are highly crystalline [Nidin et al., (2008)]

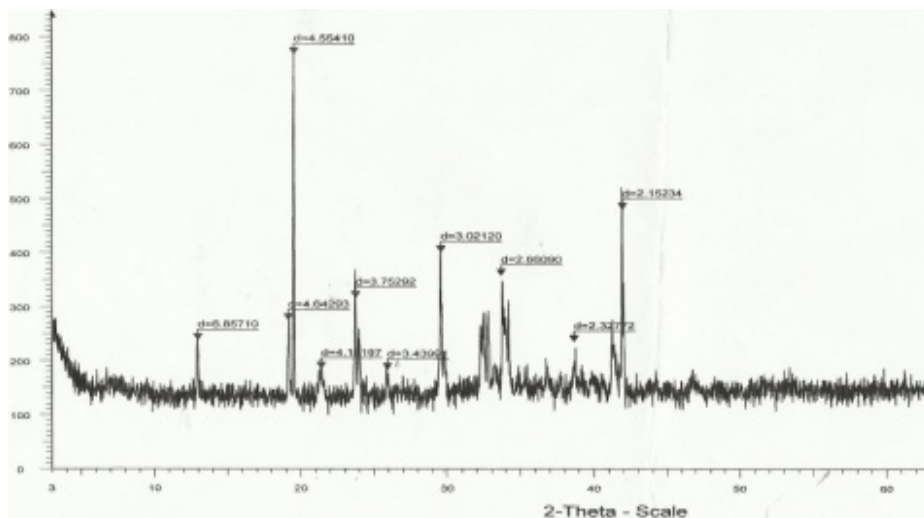


Fig.1: X-ray diffraction pattern of nano-goethite

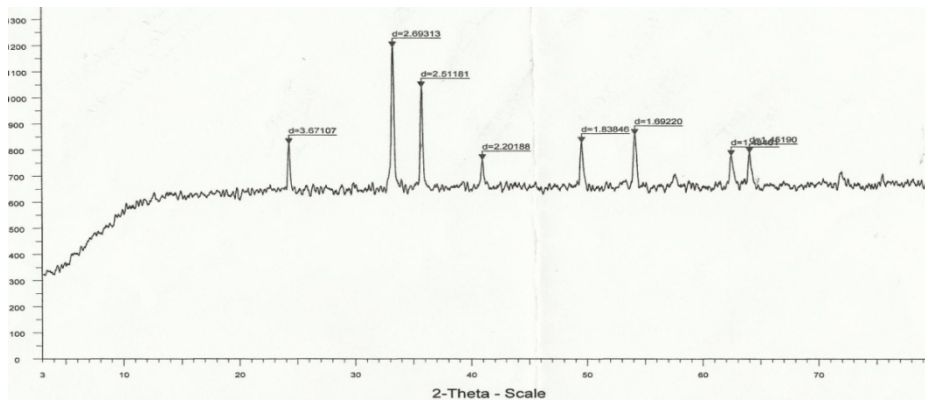


Fig. 2: X-ray diffraction pattern of nano-hematite

Figure 3 gives the DLS results of the size distribution of goethite and hematite. Goethite particle's size ranges from 87 nm to 669 nm with an average value of 259 nm. The DLS result of the hematite particle distribution ranges from 51 nm to 584 nm with an average particle's size of 197 nm.

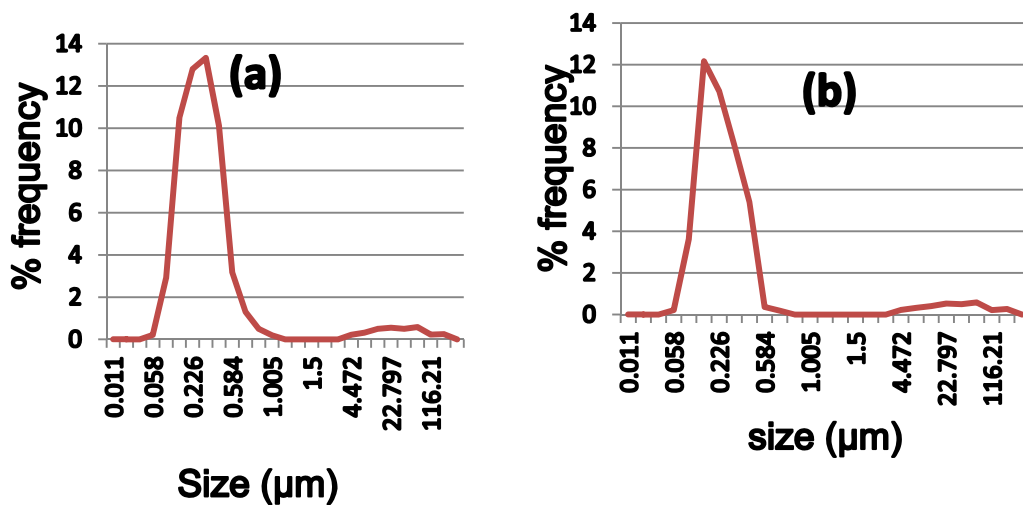


Fig. 3: The size distribution of goethite (a) and hematite (b)

Effect of pH of the solution:

The adsorption of the five metal ions onto nano/micro goethite was examined over a pH range of 3 to 6. This pH range was chosen because it has been found in a previously published work that maximum adsorption of metal ions onto goethite occurs in an acidic medium [Mohapatra, (2010)]. The initial concentration of the metal cations was 100ppm and the goethite concentration 2g/l. As shown in Figure 4, a general increase in the adsorption with the increase of pH of the solution was observed for all the metal ions up to a pH value of 5.3. A decrease in adsorption occurred when the pH value of the solution exceeded 5.3. This was a common trend for all metal ions. Similar results have been reported for other metal ions by many authors [Zhang et al., (2001) ;

Benjamin and Leckie (1981)]. All previously reported work found that the pH of the solution is an important factor that controls the extent of the cations adsorption. At low pH, the amount of metal ions adsorbed are small, this is due to large quantities of proton ions that compete with metal cations for the adsorption sites. The goethite (α -FeOOH) possesses oxygen functional groups (S-OH is the formalism of the oxide surface site) and the surface charge in goethite is neutral at pH 6.9, positive at lower pH, and negative at basic pH values [Yannick Mamindy, (2009)]. In the batch experiments carried out, HCl was used to adjust the acidic pH value; this is done by the titration of the oxygen groups of the goethite surface as follows:



The presence of large amounts of protonated sites would lead to competition between the metal ions and H^+ . Consequently the percentage of metal ion removal may decrease at low pH. The positive charge on the adsorbent surface, however, gradually decreases as pH increases due to lower amount of H^+ which leads to the increase in the absorbance of remaining metal ion. As seen in Figure 4 a decrease in adsorption occurs as the pH approaches 6 indicating that when the surface charge is neutral adsorption decreases significantly. It is anticipated that at highly basic pH the presence of OH^- ions may lead to the formation of the complexes $[\text{M}(\text{OH})_n]^{2-n}$ which in turn may decrease the adsorption of metal ions onto the goethite particles.

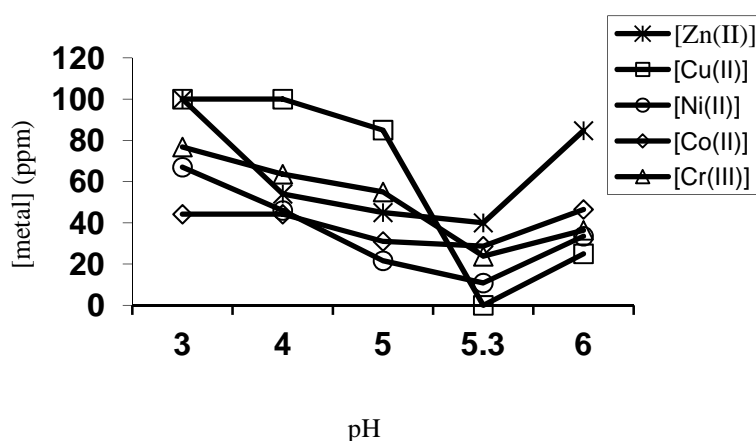


Fig. 4. Effect of pH on the adsorption of the five metallic cations onto goethite
Conditions: Goethite [2g/l], initial metal concentration 100 ppm, contact time 1hr.

Effect of contact time

The removal of Cr(II), Co(II), Cu(II), Ni(II), and Zn(II) ions from aqueous solutions using goethite and hematite was monitored for two hours and the results are illustrated in figures 5-9. The results indicated that maximum adsorption for all five metal ions occurred within one hour. Further increase in contact time did not increase the amount of metal ion adsorbed. This indicates that equilibrium is reached after one hour contact time. Similar results have been reported for Pb(II), Cd(II), Cu(II), and Co(II) metal ions [Mohapatra et al., (2010)]. The adsorption of Cr(III) onto goethite and hematite is shown in figure 5. It seems to be fast where after 10 minutes contact time about 70% of Cr(III) were adsorbed onto goethite. Whereas after 15 minutes contact time with hematite 95% of Cr(III) were adsorbed. From the results obtained hematite proved to be a more efficient adsorbent for Cr(III) than goethite since the maximum amount adsorbed by hematite is 47.5mg/g, whereas the

maximum amount adsorbed by goethite is 35mg/g of Cr(III). Goethite and hematite are equally efficient adsorbents for Co(II) and Ni(II) (figures 6 &7). The concentration of Co(II) in the solution decreased gradually as the contact time with the goethite and hematite increased, after 20 to 40 minutes approximately 70% of Co(II) were removed. The maximum adsorption capacity of Ni(II) onto goethite and hematite was 85% which was attained with both iron oxides after 30 minutes of contact time. The maximum loading capacity of both iron oxides is 35, and 42.5mg/g of adsorbent for Co(II) and Ni(II) respectively

The absorption affinity of goethite and hematite for Cu is quite different as seen in figure 8, the concentration of copper in the solution decreased gradually with increasing contact time. The adsorption of Cu(II) into the goethite was complete as it reached zero ppm after 60 min of contact time. This means that the adsorption capacity of Cu (II) ion into goethite is 50 mg/g. In a previously reported work, the maximum loading capacity of Cu(II) ions into nano structured goethite, where the size of the particles ranged from 2-10 nm, was 37.25mg/g which is less than the amount obtained in this study [Mohapatra et al., (2010)]. These experimental results indicate that the particle size of the adsorbent has an important effect on the adsorption capacity which has to be further investigated for confirmation. The maximum adsorption capacity of Cu(II) onto hematite was 20% which means that goethite is a much more efficient adsorbent for Cu(II) ions than hematite. Figure 9 shows that after 20 minutes of contact time of Zn(II) with goethite the maximum adsorbed amount of Zn(II) was 60%, Whereas with hematite the maximum adsorbed amount of Zn(II) was 80%.

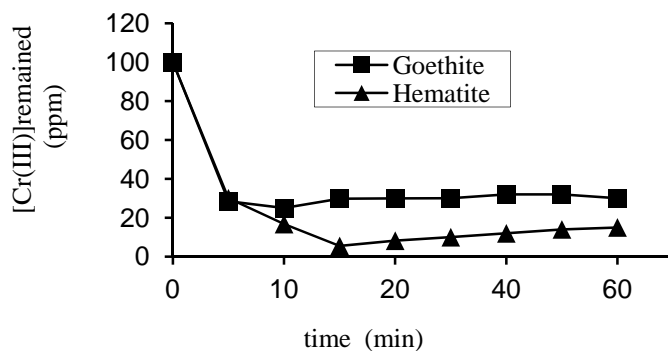


Fig. 5. Effect of contact time on the adsorption of Cr(III) ions into goethite and hematite. Conditions: adsorbent [2g/l], initial metal concentration 100ppm, pH 5.3, temperature 25°C

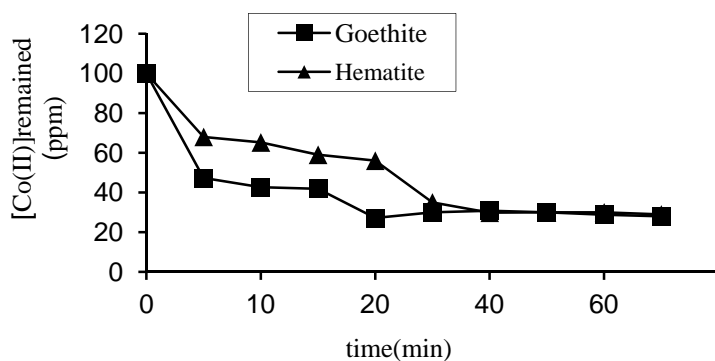


Fig. 6. Effect of contact time on the adsorption of Co(II) ions into goethite and hematite. Conditions: adsorbent [2g/l], initial metal concentration 100ppm, pH 5.3, temperature 25°C

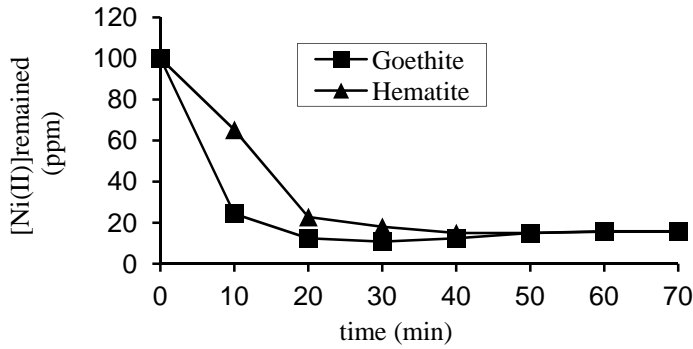


Fig.7. Effect of contact time on the adsorption of Ni(II) ions into goethite and hematite. Conditions: adsorbent [2g/l], initial metal concentration 100ppm, pH 5.3, temperature 25°C

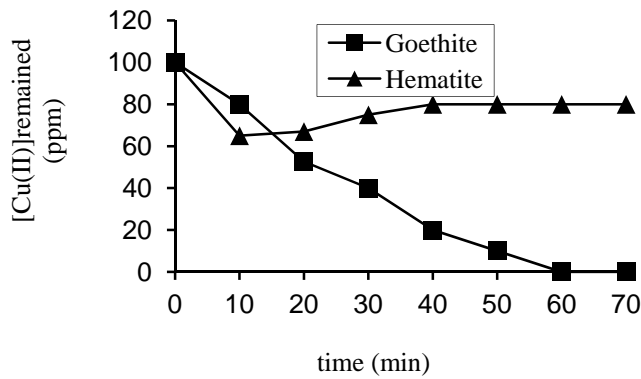


Fig. 8. Effect of contact time on the adsorption of Cu(II) ions into goethite and hematite. Conditions: adsorbent [2g/l], initial metal concentration 100ppm, pH 5.3, temperature 25°C

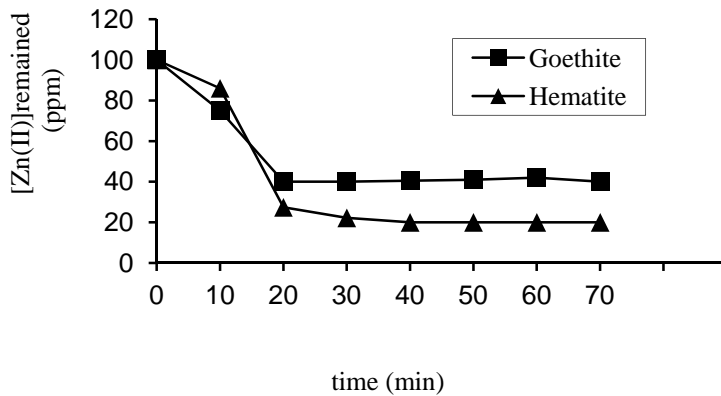


Fig. 9. Effect of contact time on the adsorption of Zn(II) ions into goethite and hematite. Conditions: adsorbent [2g/l], initial metal concentration 100ppm, pH 5.3, temperature 25°C

The experimentally obtained maximum adsorbed amounts of the metal ions were estimated as 50, 42.5, 35, 35, and 30 mg/g of goethite for Cu(II), Ni(II), Cr(III), Co(II), and Zn(II) ions respectively, and 10, 42.5, 47.5, 40, and 35mg/g of hematite for Cu(II), Ni(II), Cr(III), Zn(II) and Co(II) ions respectively. The adsorption affinity of the five metallic cations to goethite is Cu > Ni > Co > Cr > Zn, (figure 10), whereas the adsorption affinity of the five cations to hematite is Cr > Ni > Zn > Co > Cu (figure 11).

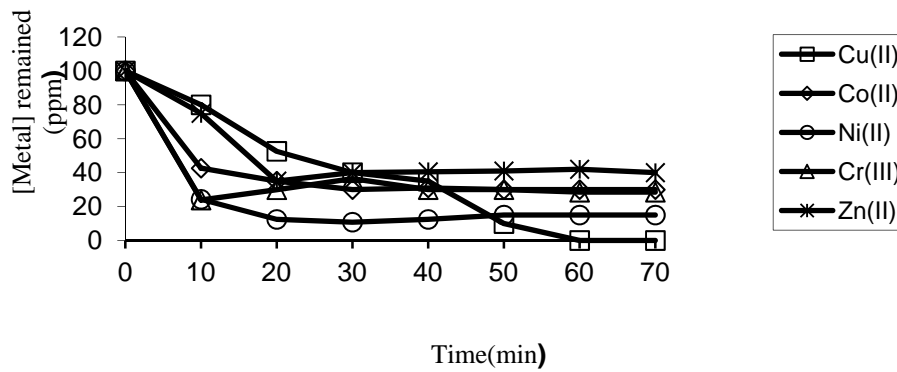


Fig. 10. Effect of contact time on Cu(II), Ni(II), Cr(III), Zn(II) and Co(II) ions adsorption onto goethite. Conditions: adsorbent [2g/l], initial metal concentration 100ppm, pH 5.3, temperature 25°C

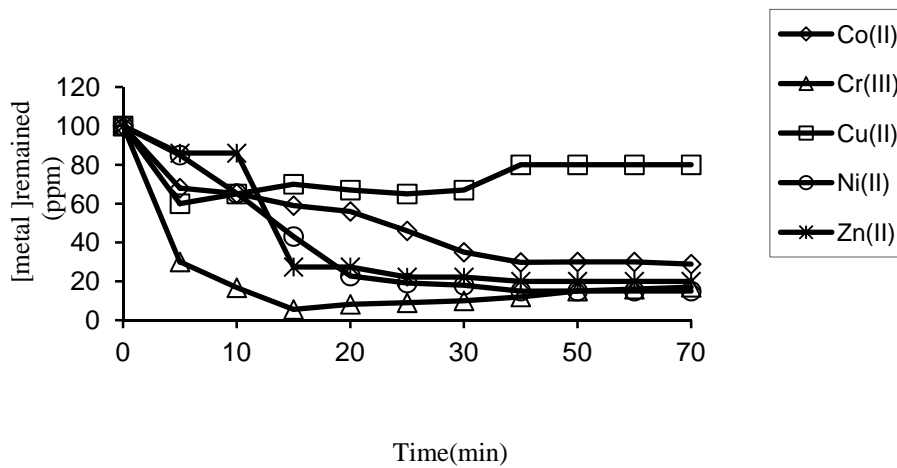


Fig. 11. Effect of contact time on Cu(II), Ni(II), Cr(III), Zn(II) and Co(II) ions adsorption onto hematite. Conditions: adsorbent [2g/l], initial metal concentration 100ppm, pH 5.3, temperature 25°C

from the above reported results it is concluded that it is quite complicated when it comes to try to explain the relation between the metal ion properties and their adsorbent affinities

In order to find a correlation between the metal ion uptake, metal ion properties, and physicochemical properties of the adsorbent, several parameters have to be considered. Such as the size of the metal ion, the stability of the metal hydroxo complex formed, the preferred adsorption site on the adsorbent are responsible for the preferential adsorption of one metal ion over other, the size of the adsorbent particles, and the surface area of the adsorbent.

In this study our experimental results indicated that the adsorption affinity of the metal cations onto goethite nano/micro particles increased as the size of the metallic cation decreased. The adsorption became more complete for Cu(II) ions, as all Cu(II) ions in the solution were adsorbed after 60 minutes of contact time with the goethite. Moreover, bigger cations such as Cr(III) underwent many adsorption and desorption before it attained equilibrium.

Effect of metal ion concentration:

The initial metal concentration was varied from 50 to 400 mg/l for all the metal ions and their adsorption onto goethite was studied. The results shown in figure 12 indicated that the maximum amounts of Cu(II), Ni(II), and Cr(III) adsorbed were 50mg/g, 42.5 mg/g and 35mg/g respectively with the initial metal concentration was 100 mg/l. After that saturation occurred as there was no increase in the amount adsorbed. For Co(II) maximum amount adsorbed occurred was 40mg/g with the initial metal concentration was 50mg/l, whereas the amount adsorbed decreased as the concentration of the Co(II) ion increased. For Zn(II) adsorption of the metal ion onto goethite increased up to 35mg/g until saturation was reached with the initial metal concentrations of 200 mg/g. One explanation as to the relation between the metal ion and saturation of goethite could be explained as due to the size of the metal ion. Zn(II) is a smaller ion than Co(II) that is probably why it reaches saturation with a higher initial metal ion concentration .

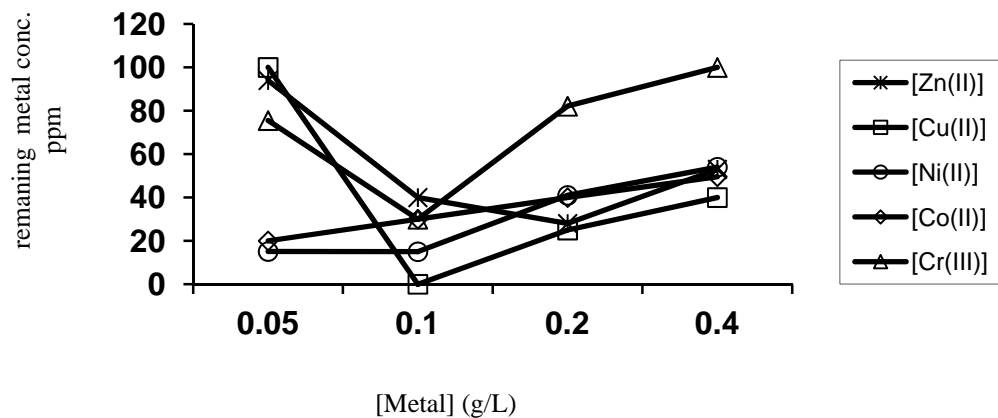


Fig. 12. Effect of initial metal ion concentration on the adsorption of the five metallic cations onto goethite.

Conclusion

In this study nano/mico goethite and nano/micro hematite particles were synthesized and the efficiency of adsorption of Cr(III), Co(II), Ni(II), Cu(II), and Zn(II) ions onto these particles was studied. Both iron oxides were compared as low cost, environmentally friendly adsorbents of heavy metals from contaminated water sources.

Both iron oxides proved to be efficient with variable capabilities in the removal of the five metal ions from aqueous solution. The goethite was able to adsorb 50, 42.5, 35, 35, and 30mg/g of Cu, Ni, Cr Co, and Zn ions respectively, whereas and under the same conditions hematite was able to adsorb 10, 42.5, 47.5, 40, and 35mg/g of Cu, Ni, Cr, Zn, and Co ions respectively from the aqueous solutions.

The results showed that maximum adsorption for all metal ions using goethite occurred at a pH of the solutions of 5.3.

Moreover comparing the efficiency of the two iron oxides, goethite proved to be more efficient for the adsorption of Cu(II), Co(II), and Ni(II) and hematite is more efficient for the adsorption of Zn(II) and Cr(III) ions .

For Cu(II), Ni(II), and Cr(III) ions saturation occurred with the initial metal concentration was 100 mg/l. For Zn(II) the maximum amount adsorbed onto goethite was found to be 35mg/g with the initial metal concentration of 50 mg/l. For Co(II) saturation occurred with the initial metal concentration of 200 mg/l and the amount adsorbed onto goethite reached 40mg/g.

Goethite and hematite can be used in various environmental applications and for water treatment from heavy metals contamination.

References

- [1] Abollino, O. ; Aceto, M. ; Malandrino, M. *et al.* (2003) : Adsorption of heavy metals on Na-montmorillonite. Effect of pH and organic substances. *Water Res.*, 37, pp. 1619-1627.
- [2] Acra, A. ; Milki, R. ; Karahagopian, Y. (1981) :Changes in quality of thermal groundwater from unique resources in Lebanon.. *Int. J. Environ. Studies*, Vol. 19, pp. 63-68
- [3] Alarm, I. ; Sadiq, M. (1989) : Metal contamination of drinking water from corrosion of distribution pipes. *Environ. Pollut.*, Vol 57, pp. 167-168
- [4] Benjamin, M. ; Leckie, J. (1981): Multiple-site adsorption of Cd, Cu, Zn and Pb on amorphous iron oxide. *J. Colloid Interf. Sci.*, Vol.79, pp. 209–221.
- [5] Chen, Y-H. ; Li, F-A. (2010): Kinetic study on removal of copper(II) using goethite and hematite nano-photocatalysts . *Journal of Colloid and Interface Science* , 347, pp. 277-281.
- [6] Debnath, S. ; Ghosh, U. C. (2009): Nanostructured hydrous titanium (IV) oxide: Synthesis, characterization and Ni(II) adsorption behavior. *Chem. Eng. J.*, 152, pp. 480-491.
- [7] Gao, Z. ; Bandosz, T. j. ; Zhao, Z. *et al.* (2009) : Investigation of factors affecting adsorption of transition metals on oxidized carbon nanotubes. *J. Hazard. Matter.*, 167, pp. 357-365.
- [8] Gu, Xueyuan ; Evans, Les j. ; Barabash, Sara J. (2010): Modeling the adsorption of Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) onto montmorillonite. *Geochimica et cosmochimica Acta*, 74, pp. 5718-5728.
- [9] Guo, X. ; Zhang, S. ; Shan, X. Q. (2008): Adsorption of metal ions on lignin. *J. Hazard. Matter.*, 151, pp. 134-142.
- [10] Li, Y. H. ; Ding, J. ; Luan, Z. *et al.* (2003): Competitive adsorption of Pb²⁺, Cu²⁺ and Cd²⁺ ions from aqueous solutions by multiwalled carbon nanotubes. *Carbon*, 41, pp. 2787-2792.
- [11] Li, Y. H. ; Wang, S. ; Wei, J. *et al.* (2002): Lead adsorption on carbon nanotubes. *Chem. Phys. Lett.*, 357, pp. 263-266.
- [12] Mohapatra, M. ; Rout, K. ; Singh, P. S. ; Anand *et al.* (2011) : Fluoride adsorption studies on mixed-phase nano iron oxides prepared by surfactant mediation-precipitation technique. *Journal of Hazardous Materials*, 186, pp. 1751–1757.
- [13] Mohapatra, M. ; Mohapatra, L. ; Singh, p. ; Anand, S. ; and Mishra, B.K (2010): A Comparative study on Pb(II), Cd(II), Cu(II), Co(II) adsorption from single and binary aqueous solutions on additive assisted nano-structured goethite. *International journal of Engineering, Science and technology*, Vol. 2, No. 8, pp. 89-103.
- [14] Mustafa, Ghulam ; Singh, Balwant ; Kookana, Rai S. (2004): Cadmium adsorption behavior on goethite at low equilibrium concentrations: effects of pH and index cations, *Chemosphere*, 57, pp. 1325–1333.
- [15] Nidhin, M. ; Indumathy, R. ; Sreeram, K. J. ; and Balachandran, U. (2008): Synthesis of iron oxide nanoparticles of narrow size distribution on polysaccharide templates, *Bull. Mater. Sci.*, 31, pp. 93–96.
- [16] O'Reilly, S. E. ; Hochella, M. F. (2003): Lead sorption efficiencies of natural and synthetic Mn and Fe-oxides. *Geochim. Cosmochim. Acta.*, 67, pp. 4471-4487.
- [17] Oulabi, M. ; Saad, Z. ; Slim, K. (1999) :*Journal Europeen D'Hydrologie*, tome, 30, fasc. 2, pp. 245-260
- [18] Wainipiee , wimolporn ; Weiss, Dominik ; Sephton, Mark A. ; Coles, Barry j. *et al.* (2010): The effect of crude oil on arsenate adsorption on goethite. *Water research*, 44, pp. 5673-5683
- [19] Yannick Mamindy-Pajany Y. ; Charlotte Hurel ; Nicolas Marmier ; Michele Romeo (2009): Arsenic adsorption onto hematite and goethite . *C. R. Chimie*, 12, pp. 876-881
- [20] Yavuz, Omer ; Altunkaynak, Yalcin ; Guzel Fuat (2003): Removal of copper, nickel and Manganese from aqueous solutions by Kaolinite. *Water research*, 37, pp. 948-952.
- [21] Zhang, G. ; Dong, Y. ; Li, X. (2001): Effects and mechanisms of oxalate on Cd(II) adsorption on goethite at different pH and electrolyte concentration (In Chinese). *Plant Nutrition and Fertilizer Science*. Vol.7, pp. 305–310.