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ADSORPTION OF ZN, CU AND CD FROM WASTE WATERS BY MEANS OF MAGHEMITE NANOPARTICLES

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Nanocristale de maghemită (γ-Fe_2O_3) au fost sintetizate, la un diametru mediu de 10 nm. Ulterior, un nano-compozit format din γ-Fe_2O_3 cu răşină schimbătoare cationică de tip AMBERLITE a fost de asemenea sintetizat. Produsele au fost caracterizate prin tehnici spectroscopice ca de exemplu microscopie electronică de transmisie şi difracţie de raze X. Aceste investigaţii au confirmat formarea maghemitei prin sintetiză şi ulterior a compozitului. Acesta din urmă a prezentat o capacitate mare de adsorbţie pentru reţinerea unor metale toxice cum ar fi Zn, Cu, Cr.

Nano-sized crystals of maghemite iron oxide (γ-Fe_2O_3) were synthesized, with a size of 10 nm. Subsequently, a nano-composite from γ-Fe_2O_3 with AMBERLITE cationic exchange resin was synthesized. The products have been subjected to thorough characterization with several spectroscopic techniques as well as transmission electron microscopic measurements or X-ray diffraction analysis. These investigations confirm the formation of maghemite nanoparticles on resin surface. The nano-composite showed remarkable adsorption efficiency in removal of some toxic metal ions as Zn, Cu, Cr.

Keywords: nanomaterials, maghemite, cationic resin, heavy metal ions

1. Introduction

The industrial waste water effluents contains mainly the various heavy metals, which are a real threat to the environment and public health, because their toxicity and persistence in the environment [1]. The removal of toxic metals such as chromium, cadmium, copper, lead, nickel, mercury and zinc from waste waters became a necessity due to their toxicity and carcinogenicity. There are many removal techniques such as adsorption, chemical precipitation, ion exchange, filtration, membrane separation, and reverse osmosis in order to diminish the pollution impact of these metals. Also, due the development in nano technology, nanoscale iron oxides have became a raw material for treating the waste waters and soils, accelerating the coagulation of sewage, removing radionuclides, adsorbing organic dyes and cleaning up the contaminated soils [2]. There are

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many types of nanomaterials with these characteristics, but magnetic iron oxide nanoparticles are an efficient adsorbent, which couples magnetic separation with ionic exchange capacity for removal of heavy metals pollutants [3]. Nano-iron oxides, such as magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3), and also different ferrite compounds are known as materials used in different biological and industrial application. These materials have unique magnetic and electronic properties. Due to their chemical stability, biocompatibility and heating ability, ferrofluids of maghemite nanoparticles can be used for ferrofluids hyperthermia in tumor treatment [4].

In this paper the preparation by chemical coprecipitation and characterization of maghemite (γ-Fe_2O_3) and a nano-composite from γ-Fe_2O_3 with AMBERLITE cationic exchange resin batch adsorption/desorption studies are described.

2. Experimental

2.1. Preparation and characterization of maghemite (γ-Fe_2O_3) and nano-compsite maghemite – cationic resin (γ-Fe_2O_3 – R-H) nanoparticles

There are various methods for preparation of γ-Fe_2O_3, using different reagents for synthesis. In this paper the nanoparticles were prepared by coprecipitation of ferrous ion (Fe^{2+}) and ferric ion (Fe^{3+}) with NaOH solution. D-sorbitol was used to prevent the agglomeration between the nanoparticles [5]. The iron solutions were strongly stirred in water, after adding NaOH solution. The precipitates were separated by magnetic decantation or slow filtration after which it was washed several times with distilled water and ethanol. The magnetite nanoparticles were dried into oven at 60°C. In order to obtain maghemite (γ-Fe_2O_3), the magnetite nanoparticles was heated at 200 °C, for 3 hours and finally, red-brown maghemite nanoparticles were collected. The nanocomposite was obtained after 24 hour time contact between maghemite nanoparticles and AMBERLITE cationic resin, under mechanical stirring. After, water washing the new nanocomposite was analyzed with the same methods as initial maghemite nanoparticles.

The structure and morphology of the γ-Fe_2O_3 nanoparticles was characterized by X-ray powder diffraction, which was carried out in a SHIMADZU diffractometer with high-intensity Cu Kα radiation ($\lambda = 1.54065$ Å) with the 2θ range from 10^o to 90^o.

The particle size and distribution were detected by transmission electron microscopy (TEM). The energy dispersive X-ray (EDX) and selected area electron diffraction (SAED) spectra were recorded with a TECNAI F30 G^2 high resolution transmison electron micrsoscope with 1Å line resolution and with an EDX detector with 133 eV resolution.

2.2. Batch adsorption and recovery studies

The metal solutions were prepared from Merck stock standard solutions, consisting of dissolved metal into nitric acid, in case of zinc and copper and from potassium chromate (K_2CrO_4) salt dissolved into distilled water in case of chromium. Each initial metal standard solution concentration was 1000 mg/L. The initial standard solutions were used in order to evaluate the maximum quantity adsorbed at pH 2.5. The metal solutions with the same concentrations were mixed together for obtaining a multi-component system (Zn, Cu, Cr). The evaluation took place by analyis from 20 to 20 minutes, during 2 hours.

The time for recovery was 24 hours and all maghemite nanoparticles and nanocomposite were recycled by the magnetic separation. All samples containing hexavalent chromium were analyzed by diphenylcarbazide method with a molecular absorption spectrometer (Cintra 202 GBC) with spectral domain between 190 and 1000 nm. Total chromium quantity and the others metals were measured with an atomic absorption spectrometer (GBC 932 AB Plus) with spectral domain between 185 and 900 nm.

3. Results and Discussion

3.1. Characterization of magnetite (Fe_3O_4) nanoparticles

The obtained samples were analyzed by X-ray diffraction (XRD) using a diffractometer with high-intensity Cu Kα radiation (λ = 1.54065 Å). The diffraction pattern for maghemite is shown into Figure 1.

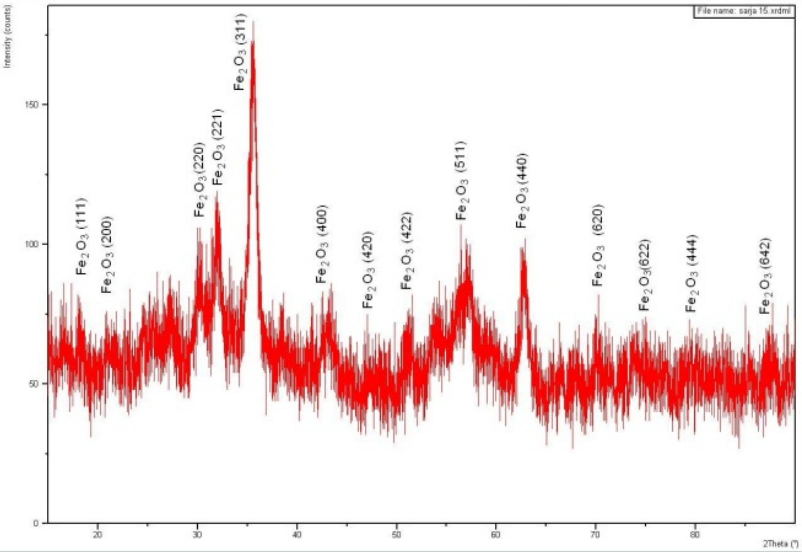
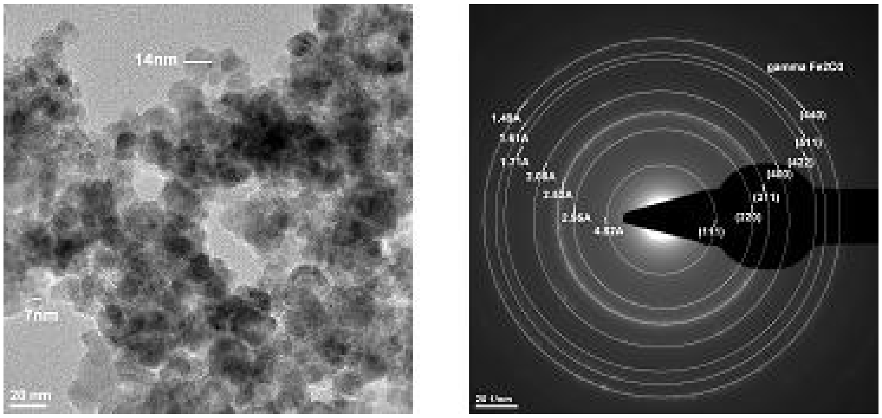


Fig. 1: XRD patterns for γ-Fe_2O_3 nanoparticles

The diffraction peaks reveal a cubic spinel structure with no other phases existing in the sample. The morphology and structure of the maghemite samples were investigated by transmission electron microscopy through bright field (TEMBF) as seen in Figure 2(a). Spherical particles with a reduced size and a good dispersion can be observed in this figure.

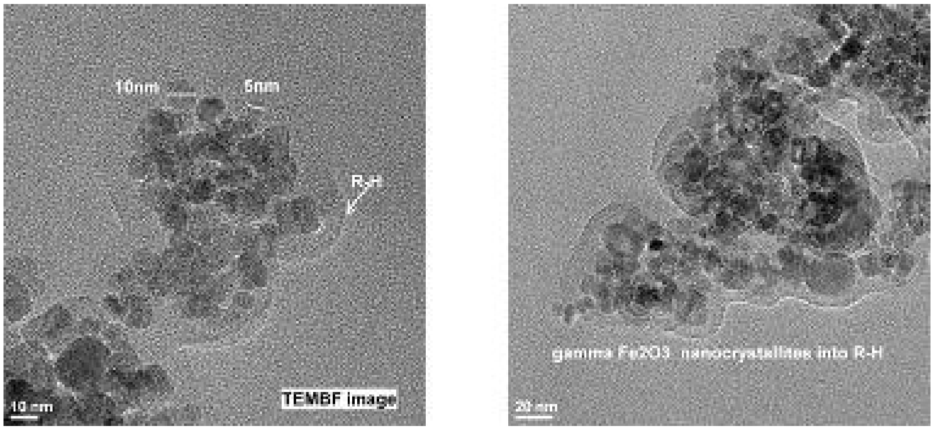


(a) (b)

Fig. 2: (a) Transmission electronic microscopy through bright field (TEMBF) for γ-Fe_2O_3; (b) Selected area electron diffraction (SAED) image associated to the sample from figure (a)

In order to identify the planes associated with the maximum values for the nanoparticles a selected area electron diffraction (SAED) image was recorded (Figure 2(b)). The SAED diffraction peaks corresponding to the (440), (511), (422), (400), (311), (220) and (110) planes for γ-Fe_2O_3 match with the XRD pattern. The SAED image confirmed the formation of the γ-Fe_2O_3 nanoparticles. These nanoparticles have been used as adsorption material for pollutants from wastewaters, in accordance with their small particle size and high specific surface area.

The morphology and structure of the maghemite incorporated into cationic resin samples were investigated by transmission electron microscopy through bright field (TEMBF). The TEMBF image is presented in the Figure 3(a). Spherical particles with a reduced size and a good dispersion can be observed in this figure, covered by a layer of resin (R-H). Also, another image at about 20 nm for maghemite nanoparticles into resin is shown in the Figure 3(b).



(a) (b)

Fig. 3: (a) Transmission electronic microscopy through bright field (TEMBF) for Fe_3O_4; (b) Selected area electron diffraction (SAED) image associated to the sample from figure (a)

3.2. Batch adsorption and recovery studies

Fifty milliliters out of 1000 mg/L multi-component solution and 1 g/L γ-Fe2O3 nanoparticles were mixed at pH of 2.5. Also, the same concentration was used for mixture with 1 g/L γ-Fe2O3-R-H. An important characteristic for maghemite was the value for the surface charge which is 6.3 at the zero point of charge (pHpzc) [6]. This value was not obtained as experimental data, instead it was taken from literature. Below this value, the adsorbent surface is positively charged and the anions are adsorbed by electrostatic attraction. Above this value of pHpzc, the adsorbent surface is negative by charged and the cations are adsorbed on the maghemite [6]. For example, with the increase in pH, the uptake of Cr (VI) ions decreased, because in the aqueous phase, the surface of the metal oxides is covered with hydroxyl groups that vary at different pH values. Hexavalent chromium in wastewaters is present in forms as chromates (CrO_4^{2-}), dichromates ($Cr_2O_7^{2-}$) and bichromates ($HCrO_4^-$). In these conditions, the OH^- groups from the mixture will compete with the chromium species for adsorptions sites. Also, if the adsorption surface is negatively charged, the electrostatic repulsions increase between negatively charged Cr (VI) species and negatively charged nanoparticles, leading to the removal of some adsorbed species such as bichromates ($HCrO_4^-$) or chromates (CrO_4^{2-}) [6]. In the environment, at acidic pH value, the metal ions can appear in the following oxidation states: Ni^{2+}, $NiSO_4^0$, Cu^{2+}, Zn^{2+}. With these information, regarding the distribution of the ions one can make an assessment on the metal species present into water environment.[7] For the analyzed aqueous solutions the samples were analyzed during of 120 minutes, from 20 to 20 minutes. The evolution in time of the removal efficiency using γ-Fe_2O_3 is presented in Figure 4.

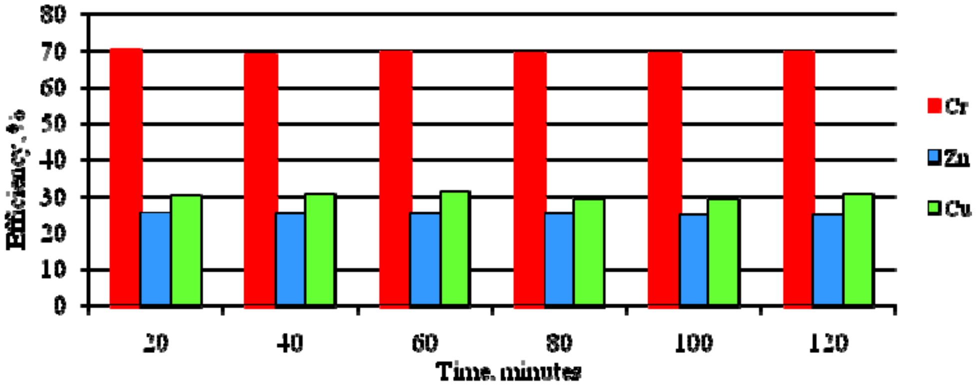


Fig. 4: The removal efficiency using γ-Fe_2O_3 as adsorbent for metal ions, at pH 2.5

It was observed that after the first minute of reaction, about 70% from hexavalent chromium is removed and the quantity remains almost the same at 120 minutes. In case of the others metal ions, the efficiency was lower due the presence of the metals as cations (Cu^{2+}, Cd^{2+}) which is diminished by the pH pzc value for maghemite. In this case, the removal efficiency is not higher than 35%. The variation of the removal efficiency remains the same in the case of the nano-composite consisting of maghemite and AMBERLITE cationic resin (γ-Fe_2O_3-R-H) but the removed quantity of the metals is significantly higher compared with the maghemite nanoasorbent. This situation is due the double effect of the exchange resin and the adsorption of the maghemite. The high efficiency for all metal ions can be observed in Figure 5.

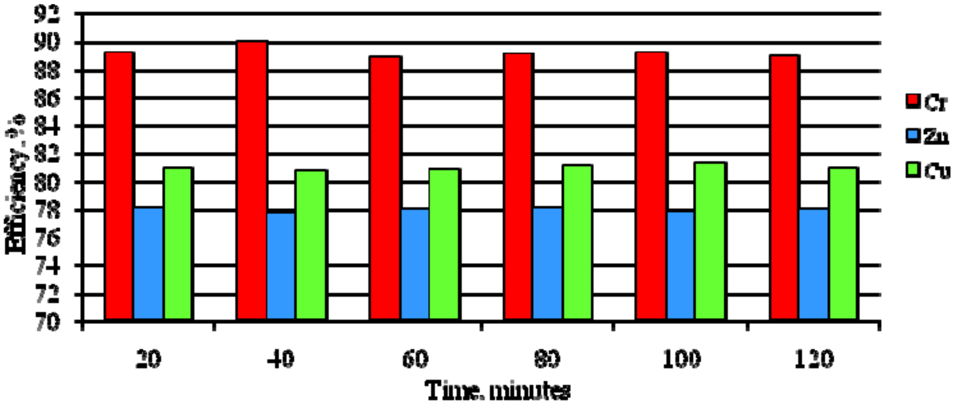


Fig. 5: The removal efficiency using γ-Fe_2O_3-R-H as adsorbent for metal ions at pH 2.5

The amount adsorbed at equilibrium, q_e, was calculated with the following formula expressed as:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \qquad (1)$$

where: C_0 – initial concentration, mg/L; C_e – equilibrium concentration, mg/L; V – volume of solution, L; m – adsorbent quantity, g.

The effect of time as function of adsorbed quantity is shown in Figure 6, for maghemite nano-adsorbent. It can be seen the rapid adsorption of metal on maghemite nanoparticles, initially quite high, followed by a much slower removal rate this leading to an equilibrium state. It can be assumed that after the first 20 minutes the adsorbed quantity reaches a maximum. The quantity is quite different function of the type of metal. The highest quantity is for hexavalent chromium 55mg/g, a high value compared with common adsorbents from the literature: 11.5 mg/g for diatomite and 15.47 mg/g for activated carbon, respectively [6].

For the remaining metals, the adsorbed quantities are different: 15.9 mg/g for Cd and 15 mg/g for Cu.

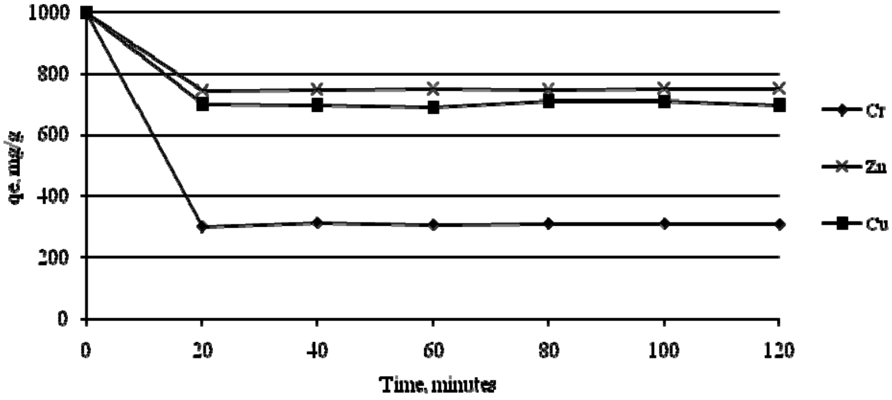


Fig. 6: Effect of time on the removal of metal ions on maghemite nanoparticles

In case of maghemite incorporated in AMBERLITE cationic resin, the adsorbed quantities significantly increase, as a result of the exchange effect of the resin. The adsorbed quantity as function of time is shown in Figure 7.

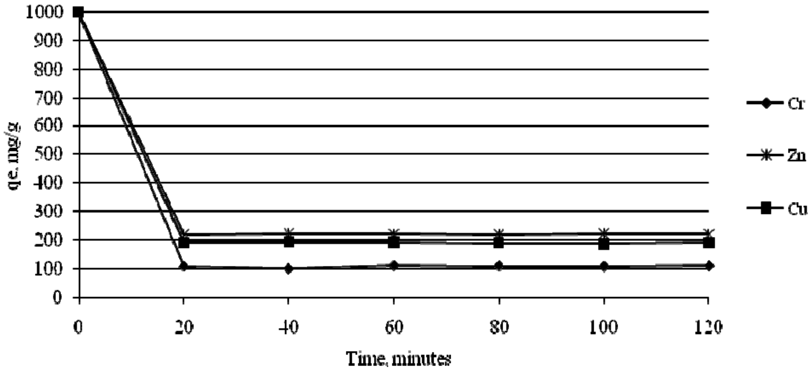


Fig. 7: Effect of time on the removal of metal ions on maghemite nanoparticles

The trend of the adsorption remains the same as in case of the maghemite nanoparticles, but the adsorbed quantities are higher. In this case, the adsorbed quantity of the hexavalent chromium onto 1 g of γ-Fe_2O_3-R-H nano-adsorbent is 44.6 mg/g. Lower quantities are adsorbed for Cd: 42 mg/g, Cu: 40.5 mg/g. All values are higher than in case of adsorption onto maghemite nanoparticles. All measurements for metals, before and after the adsorption process, were made by flame atomic absorption spectrometry (FAAS). The presented results are an average of 10 measurements. For hexavalent chromium, two analysis methods were chosen: FAAS for total chromium and molecular absorption spectrometry for hexavalent state. Comparing the results, it can be observed that the oxidation state of the hexavalent chromium remains the same, this indicating that no redox reaction occurs during the adsorption process. The chromium valence in solution never changes after the adsorption process. Dissolved hexavalent chromium formed a color complex with diphenylcarbazide detected by absorbance at 530 nm. For sake of comparison, in Figure 8 the difference between initial and final concentration, after the adsorption onto maghemite and maghemite incorporated in cationic resin, can be observed.

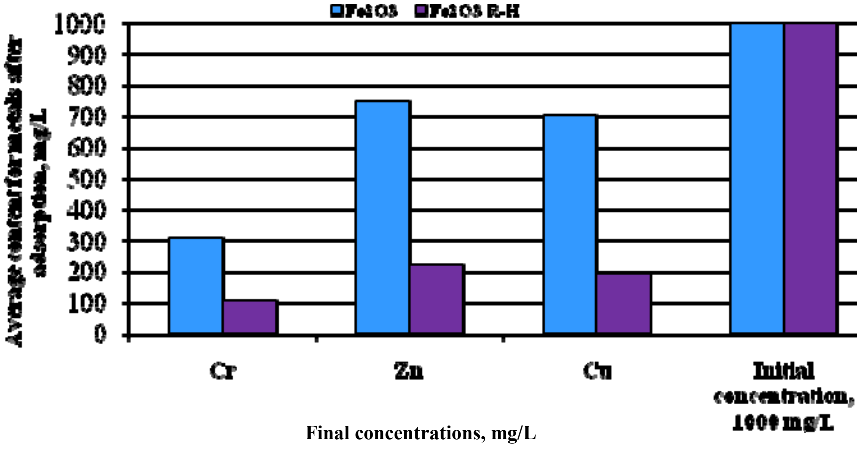


Fig. 8: Comparison between the initial and final concentration of the metals adsorbed onto nanoaparticles as maghemite and maghemite incorporated in cationic resin

It can be observed the highest efficiency for hexavalent chromium adsorbtion in case of the two nano-adsorbents and a higher tendency of adsorption for maghemite covered by cationic resin. The later composite behaves as a new material showing its own exchange capacity and adsorption characteristics. The adsorption is a reversible process, making possible the reuse of the adsorbent, after the regeneration. By washing the adsorbents with NaOH (1 N) solution, after magnetic separation of the maghemite and maghemite with cationic resin, followed by washing with ultrapure water, the recovered quantity was 0.96 g (the rate of recovery was 96%) for the two adsorbents. These are only preliminary results and future experiments will be made in order to evaluate the regeneration capacity for these adsorbents.

4. Conclusions

The maghemite nanoparticles with an average diameter of 10 nm were synthesized using a coprecipitation method. Also, a nanocomposite with average diameter for maghemite of 10 nm was obtained by covering the maghemite nanoparticles with AMBERITE cationic resin. These nanoparticles were successfully tested for the removal of some toxic metals from synthetic aqueous solutions, such as hexavalent chromium, copper and cadmium. The adsorption process was conducted into acidic environment, at pH 2.54. The obtained adsorption data indicated a good adsorption capacity for metal ions removal especially in case of maghemite into cationic resin (γ-Fe_2O_3-R-H) and a higher adsorption tendency for hexavalent chromium in comparison with the other metal ions. The regeneration of the adsorbents was investigated with good results, in presence of sodium hydroxide solution. The adsorption study showed that the electrostatic attraction was responsible for the metal removal in case of maghemite nanoparticles and a double effect of electrostatic attraction during the adsorption process and ionic exchange was observed for maghemite covered cationic resin (γ-Fe_2O_3-R-H).

The obtained data represents only the preliminary result obtained for achieving a systematic study regarding the removal of heavy metals from wastewaters using as adsorbents the nanoparticles with high capacity of adsorption due theirs high surface area.

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