

Use of nanostructured materials for Cd and Zn removal from waters

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Abstract: - The paper aims to present the synthesis, characterizations and efficiency tests for Cd and Zn removal from waters by help of iron nanostructured materials. Iron nanostructured materials such as magnetite were synthesized by classical co-precipitation technique, while for the characterization were used X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive X-ray spectra (EDS) methods. In order to establish the efficiency removal, atomic adsorption spectrometry was used. The efficiency tests indicated removal efficiencies of about 75% for Zn and 50 % for Cd removal. The adsorption equilibrium was achieved within 30 minutes for Zn(II) and Cd (II). The results indicated that the iron oxide nanoparticles could represent a valuable material for heavy metals removal from waters.

Key-Words: - heavy metals, nanostructured materials, iron oxides, removal efficiency, characterization, iron nanomaterials synthesis.

1 Introduction

Iron nanostructured materials, such as magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$), and also different ferrite compounds are known as materials used in different biological and industrial application. These materials have unique magnetic and electronic properties.

The adsorption capacity of magnetic iron oxide nanoparticles was proved by their efficiency of removing various pollutants from aqueous solutions. High efficiency rate was obtained in case of metals removal from solutions, such as Cu with magnetite, As and Cr binary system with mixed magnetite-maghemite nanoparticles. Studies regarding the hexavalent chromium from aqueous solutions were performed using adsorption tests on iron nanoparticles. The removal efficiency was high in acidic media. Recently, the organic compounds such as pentachlorophenol or an acidic dye (New Coccine) were able to be adsorbed with good results from aqueous solutions onto magnetite nanoparticles. The synthesis of nano-iron oxides is simple and highly reproducible. Among all nano-iron oxides, magnetic nanocrystals present very interesting applications.

2 Materials and methods

There are various methods for preparation of Fe_3O_4 , using different reagents for synthesis. In

our case, the nanoparticles were prepared by coprecipitation of ferrous ion (Fe^{2+}) and ferric ion (Fe^{3+}) with NaOH solution. 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 ethano [1]. All commercial reagents were pure analytical grade (Merck). Distilled water was used. 0.4 mol/L $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 0.4 mol/L $\text{FeCl}_2 \cdot 9\text{H}_2\text{O}$ were mixed at a molar ratio of 1:2 in the presence of 0.5 mol/L NaOH at room temperature. The pH of the reaction mixture was maintained at 10 for 3h. The precipitate formed was separated by centrifugation and washed several times with distilled water. The final pH was 7. The magnetite nanoparticles were dried into oven at 60° [2].

The morphology, purity, distribution and size of particles obtained were established by two different characterization methods: X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive X-ray spectra (EDS) methods.

A Panalytical X'Pert PRO MPD X-ray diffractometer with high-intensity Cu-K α radiation ($\lambda = 1.54065 \text{ \AA}$) and 2θ range from 10 to 90°, the step size was 0.001° and time per step was of 1 second, was used to obtain XRD patterns. To

evaluate the average dimension of the crystallites, the Debye–Scherrer equation was used [1]:

$$D = \frac{K \lambda_{\text{Cu-K}\alpha}}{\cos \theta \text{ FWHM}}$$

where D is the crystallite dimension, K is a coefficient (0.89), $\lambda_{\text{Cu-K}\alpha}$ is the wavelength of the radiation from the diffraction tube, FWHM is the full width at half maximum of diffraction in the 2θ scale (rad), and q is the diffraction Bragg angle. The SEM investigations were performed on a Quanta INSPECT F scanning electron microscope equipped with a field emission gun at a resolution of 1.2 nm and EDS with a resolution for Mn–K α of 133 eV.

Different levels of concentrations for target pollutants were tested under the same conditions in order to establish the maximum quantity adsorbed and removal efficiency. Target pollutants were: Zinc and Cadmium. All stock standard solutions for Zn, and Cd were prepared from Merck reagent-grade solutions by dissolving into ultrapure water. Each stock solution had an initial concentration of 1000 mg/L, and the pH was adjusted by adding HCl (0.1 mol/L). The adsorption studies were performed by measuring the initial and final concentrations of the metal on a GBC 932 AB Plus spectrometer (flame atomic absorption spectrometry) with spectral domain between 185 and 900 nm.

The values used to calculate the removal efficiency are the average values resulting from the five replicates associated with each metal. The efficiency of removal [3] was calculated as Equation (2):

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (2)$$

where C_0 is the initial concentration (mg/L) and C_e is the equilibrium concentration (mg/L). The equilibrium concentration was considered to be the final concentration when no variation occurred. The adsorbed metal amount at equilibrium is given by the ratio between the adsorbed metal (mg) and adsorbent mass (g) expressed as q_e [4] according to Equation (3):

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (3)$$

where V is the volume of the solution (L) and m is the adsorbent quantity (g).

The quantity of adsorbent used was 0.1g. The concentration of metal ions in the synthetic solutions varied between 20 and 2300 mg/L after mixing the adsorbent with each solution consisting of all metal ions at room temperature (21.5°C). The contact time between adsorbent and solution was between 10 and 120 min at pH adjusted to 2.5 using 0.1 mol/L HCl. The adsorbent samples were recovered with an external magnet.

The concentrations before and after contact with nanoparticles as adsorbed material were established by atomic absorption spectrometry (AAS) for heavy metals.

3 Results and Discussion

In Figure 1, the diffractogram obtained on the analysed sample is shown.

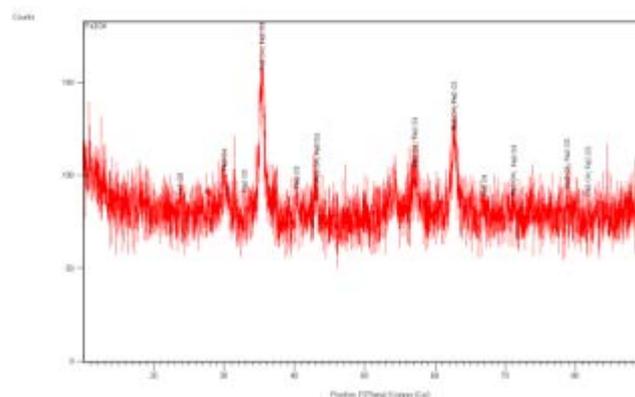


Fig. 1: XRD patterns for nanomagnetite

The crystalline structure of the sample was identified from the XRD diffractogram which has shown:

- in the sample is present as a majority phase the compound Fe_3O_4 , having a Orthorhombic crystalline system, with maximum intensity of peak diffraction at $35,536^\circ$ for 2θ , according to ICDD File 01-075-1609 (International Centre for Diffraction Data);
- as minority phases in sample are present the compounds: Fe_2O_3 , having a rhombohedral crystalline system, with maximum intensity of peak diffraction at $32,856^\circ$ for 2θ , according to ICDD File 01-088-2359 (International Centre for Diffraction Data).

- In the table 1 is presented the peak list for the sample

Table 1: Peaks list

No.	Pos. [°2Th.]	d-spacing...	Rel. Int.	FWHM [°...]	Matched by	Area [cts*°2Th]	Backgr.[cts]	Height [cts]
1	23.6639	3.75989	8.66	0.3936	01-088-2359	2.84	77.69	7.33
2	27.6330	3.22821	6.85	0.3149	01-089-2392	2.25	78.02	7.24
3	30.0100	2.97770	17.74	0.2755	01-075-1609	5.83	76.60	21.44
4	32.8735	2.72458	7.43	0.2362	01-088-2359	2.44	76.14	10.48
5	35.4185	2.53442	100.00	0.4723	01-075-1609;01-...	32.84	82.15	70.49
6	40.3207	2.23688	9.63	0.2362	01-088-2359	3.16	75.09	13.58
7	43.2144	2.09356	28.49	0.5510	01-075-1609;01-...	9.36	74.97	17.21
8	57.1262	1.61241	47.49	0.7872	01-075-1609;01-...	15.60	79.92	20.08
9	62.6940	1.48194	92.09	0.7872	01-075-1609;01-...	30.24	80.89	38.95
10	66.9649	1.39743	16.14	0.6298	01-075-1609	5.30	75.57	8.53
11	71.1296	1.32549	8.28	0.3936	01-075-1609;01-...	2.72	77.81	7.01
12	78.7364	1.21541	7.99	0.2362	01-075-1609;01-...	2.63	77.55	11.27
13	81.7669	1.17689	7.13	0.1920	01-075-1609;01-...	2.34	75.52	9.15

Making a correlation between the maximum intensities of the majority phase Fe_3O_4 for the pattern and the peaks list it can be observed a difference caused by the measurement errors. XRD patterns from Figure 2 indicates a mixture of iron oxides with nanosize dimension. From Debye-Scherrer formula, the size of crystallite dimension was about 15.75 nm. Also, from Figure 2, SEM analysis indicates nanometric dimension for analyzed samples, with agglomeration of nanoparticles. Uniform bricks can be observed with the same orientation, possible to be appeared by synthesis parameters.

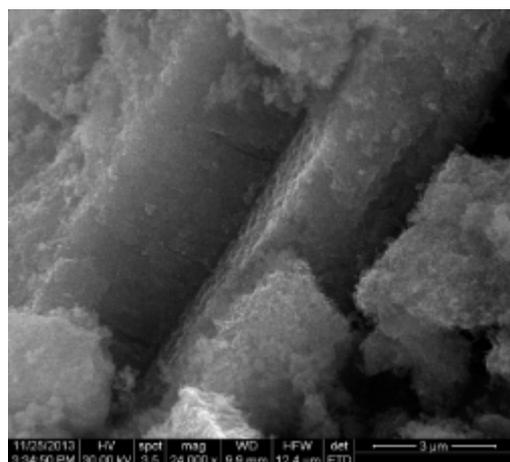


Fig 2: SEM image of the nanoparticles (nanomagnetite) at magnification of 24000x

For higher magnifications, two shape of nanoparticles can be observed: spherical and acicular, as it is shown in the Figure 3. Crystallization process and rate of precipitation are essential for these shapes.

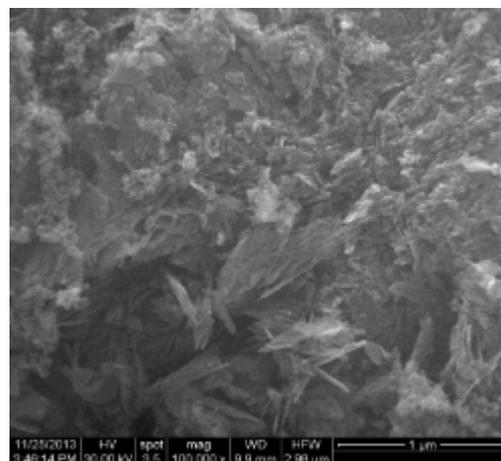


Fig 3: SEM image with acicular and spherical aspect of magnetite at 100000x magnification

In the Figure 4 nanoparticles dimensions indicate nanometric size for analyzed samples, with agglomeration of the nanoparticles at 200000X magnification.

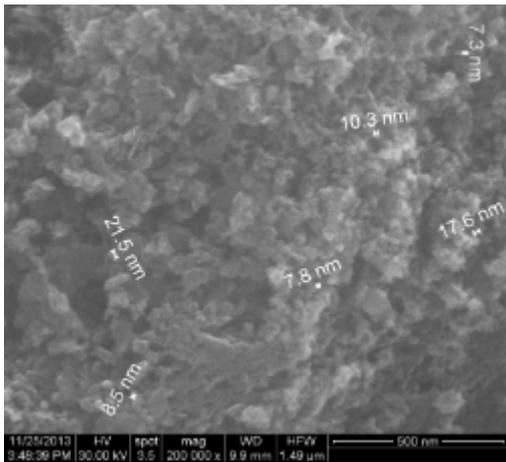


Fig. 4: SEM image with the nanoparticles dimensions for 200000x magnification

Energy dispersive spectra (EDS) indicate purity of samples. Only Fe and O as elements can be detected into sample. Cu presence is due to the copper grid for samples.

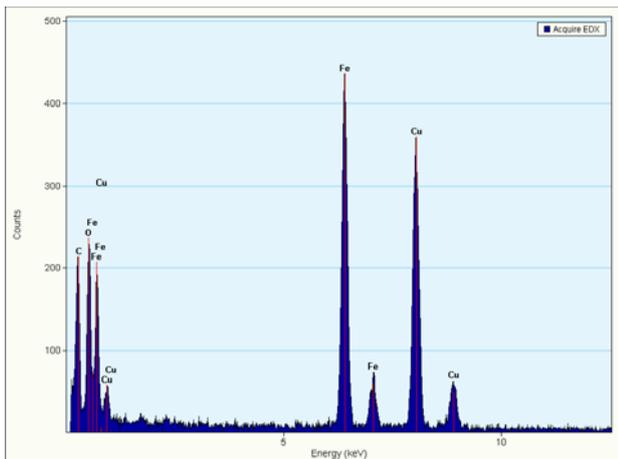


Fig. 5: EDS image for analyzed nanoparticles

According to the characterization methods (XRD and SEM with EDS), the analyzed samples have nanometric size, purity without traces of other compounds.

Based on the obtained results, the removal efficiency was established as it can be seen in Figure 6. It can be seen that the maximum efficiency was up to about 70% for Zn and 50 % for Cd. Removal of heavy metals took place after 30 minutes with good results. According to Hu et al. and Yuan et al. [5, 6], the available sites for nanoparticles are mostly present on the surface and, based on this assumption, a larger surface area will provide more sites for adsorption. The efficiency for Zn is presented in Figure 8.

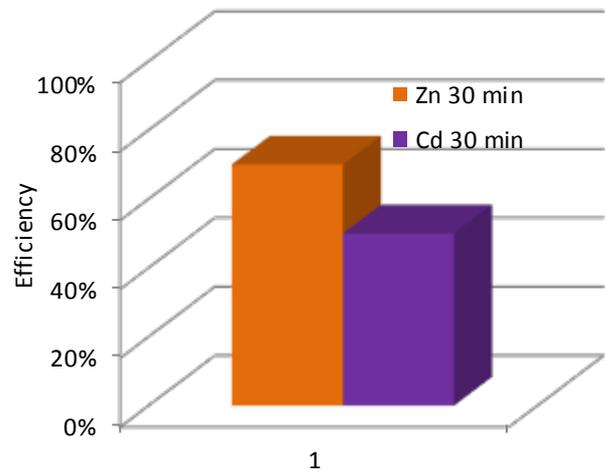


Fig. 6: Efficiency removal for Zn and Cd removal

It can be observed that for Zn, the maximum efficiency is achieved after 30 minutes at about 77%. At higher concentrations, the efficiency starts to decrease due the saturation of the adsorbent. The same tendency can be observed also for Cd(II), after 30 minutes of adsorption process (Figure 7, 8).

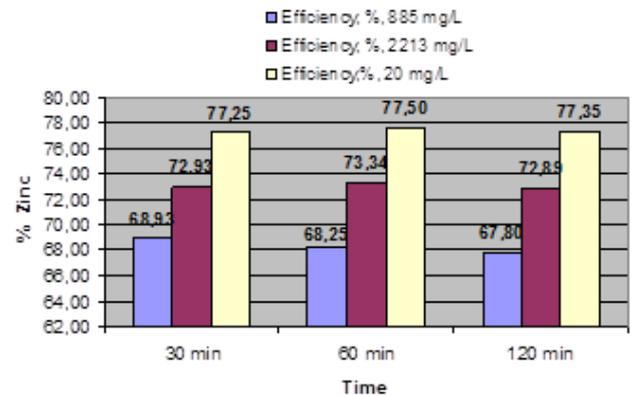


Fig. 7: Removal efficiency for Zn onto Fe₃O₄ at different concentrations

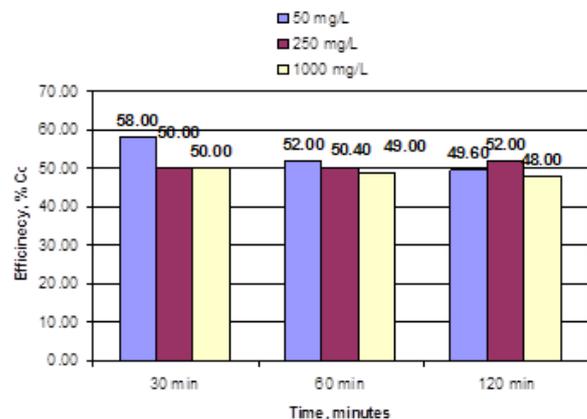


Fig. 8: Removal efficiency for Cd onto Fe₃O₄ at different concentrations

4 Conclusion

The paper presents the synthesis, characterization of iron oxide nanoparticles and efficiency tests for Cd and Zn removal from waters by help of iron nanostructured materials. Iron nanostructured materials such as magnetite were synthesized by classical co-precipitation technique, while for the characterization were used X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive X-ray spectra (EDS) methods. In order to establish the efficiency removal, atomic adsorption spectrometry was used. The efficiency tests indicated removal efficiencies of about 75% for Zn removal and 50 % for Cd removal. The adsorption equilibrium was achieved within 30 minutes for Zn(II) and Cd (II). After this time, the rate of metal uptake was the same, being independent of the adsorbent concentration. This phenomenon appears to be a result of the monolayer adsorption model [7,8], where the total available adsorption sites of adsorbents are saturated with the metal ions.

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