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ORIGINAL ARTICLE

Decolorization of Congo red from Aqueous Solutions using Fe_3O_4 Nanoparticles

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ABSTRACT
Present work is focused on structural and magnetic properties of magnetite nanoparticles for removal of Congo red which is a recognized contaminant in wastewater of different industries such as paper and textiles. Magnetite (Fe_3O_4) nanoparticles were synthesized via Sol–Gel method by using Ferric nitrate and Ethylene glycol as precursors with different annealing temperatures. This procedure was preferred because of being affordable, producing high purity materials and using less toxic iron salts, compared to other procedures. The prepared nanoparticles were characterized by X-ray energy dispersive spectrometer (EDS) which shows the compositional analysis, Vibrating Sample Magnetometer (VSM) to prepare magnetic properties and Transmission Electron Microscopy (TEM) to indicate phase structure, particle size, and morphology. The adsorption capacity of magnetite nanoparticles and removal efficiency of Congo red were evaluated using effects of pH, concentration, time, and two isotherm models: Langmuir and Freundlich. The magnetite nanoparticles showed remarkable high adsorption capacity compared to some other adsorbents.
Keywords:*Congo red adsorption, Magnetite nanoparticles, Sol-Gel method, Structural analysis*

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INTRODUCTION

Iron oxide nanoparticles have diameters between about 1 and 100 nanometers. The important forms of iron oxides are magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) [1]. Magnetite is one of the common magnetic iron oxide on earth and has an inverse spinel structure [2] with oxygen forming a face centered cubic crystal system [3]. The nanoparticles of magnetite are super paramagnetic at room temperature [4]. The magnetic properties of nanoparticles cause to use simple magnetic methods to separate them from solutions which make them special compared to other nanoparticles. The iron oxide nanoparticles were widely used in different industrial fields like gas sensors [5], catalysts [6], semiconductors [7], and also environmental applications because they are biocompatible and potentially non-toxic to human [8].

The discharge of waste to the environment creates more pollution such as organic dyes which are released to the environment from dyeing industries [9]. The removal of these dyes is very important from health and hygiene point of view. Congo red is a dye with two azo groups [10] and defined as a Synthetic dye which is difficult to biodegrade due to their complex aromatic structures [11].

Magnetite nanoparticles exhibit high surface area to volume ratios, depending on the particle size, which associated with their ability for surface chemical modification [12]. There are different methods to synthesis the Iron oxide nanoparticles such as Sol-gel [13], Micro emulsion [14], and Co-precipitation [15]. Sol–Gel method has several advantages, including low cost, high purity and easy to control the size. In this work, magnetite nanoparticles were synthesized by Sol–Gel method using ferric nitrate and ethylene glycol as precursors which were annealed at different temperatures. Then, the nanoparticles were used for removal of Congo red from waste water as an effective adsorbent.

MATERIAL AND METHODS

Materials and Reagents

Ferric nitrate (Fe $(NO_3)_3.9H_2O$) and ethylene glycol ($C_2H_6O_2$) were used to synthesize magnetite nanoparticles. Congo red ($C_{32}H_{22}N_6Na_2O_6S_2$) was used to prepare a stock solution by distilled water and the stock solution was used to obtain different concentrations of Congo red. Hydrochloric acid (HCl) and Sodium hydroxide (NaOH) were used to adjust the pH of Congo red solutions. The materials were of analytical purity and obtained from Finar Chemicals Corporation.

Synthesizing Method of Fe_3O_4 Nanoparticles

The Sol–Gel method for synthesizing magnetite nanoparticles was as below: Ferric nitrate was dissolved in ethylene glycol in proper ratio with stirring around 2 h at 40 °C. Then, the prepared sol was heated to 80 °C to obtain brown gel. The gel was aged at room temperature for about 1 h and then the xerogel was annealed at 200 °C, 300 °C, and 400 °C in furnace. Finally, magnetite nanoparticles in different sizes were synthesized [16].

Instruments

Compositional analysis was obtained by SEM S-3400N. Magnetic properties of samples were obtained by using Lake Shore's Vibrating Sample Magnetometer (model 7410). The JEOL JEM-2100 was used for preparation of Transmission Electron Microscopy (TEM) images. Digital pH meter (model 2001) was used for pH measurements. The DOUBLE BEAM UV-VIS Spectrophotometer (2202) was used to determine Congo red concentration in the solutions. A mini rotary shaker (RS12) and REMI MAGNETIC STIRRER (model: 1MLH) were used.

RESULTS AND DISCUSSION

Characterization of Fe_3O_4 Nanoparticles

Compositional Analysis

Figure 1 shows the EDS image of obtained nanoparticles. It indicates that the nanoparticles consist of good amount of Fe and O elements.

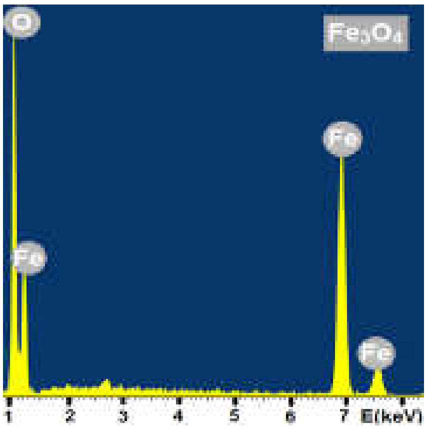


Figure 1. EDS image of Fe_3O_4 nanoparticles with Fe and O elements of nanoparticles

Magnetic Properties

The magnetization loop of magnetite nanoparticles was measured at room temperature, as shown in Figure 2. This hysteresis loop indicates that nanoparticles are super paramagnetic. It can be explained that in sufficiently small nanoparticles, the influence of temperature change the direction of magnetization of the single domain magnetic particles which is related to the anisotropy energy of the particles and the magnetization of the particles in the absence of an external magnetic field is in average zero [17].

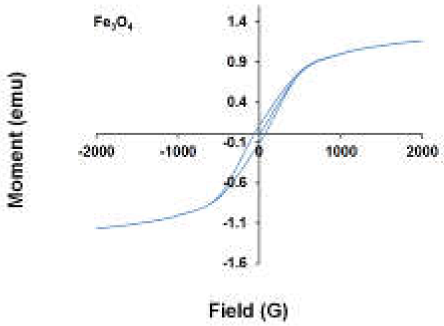
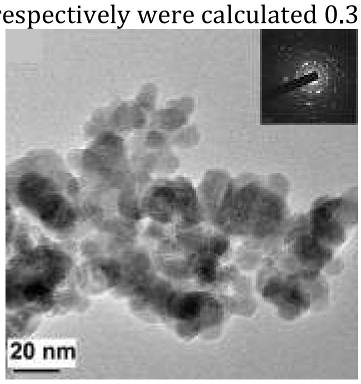


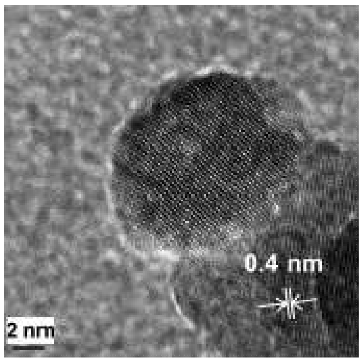
Figure 2. Hysteresis loop of Fe_3O_4 nanoparticles

Structural Analysis

The obtained sizes of nanoparticles from TEM analysis are around 21 nm, 24 nm, and 27 nm respectively at 200°C, 300°C, and 400°C. TEM image of synthesized Fe_3O_4 at 300°C is presented in Figure 3. According to Figure 3 (a), the nanoparticles have a semi spherical shape with homogenous particles size distributionand the SAED area on the corner of figure shows that nanoparticles have FCC structure. Figure 3 (b) indicates that the average d-spacing is 0.4 nm at 300 °C. The average d-spacing of nanoparticles at 200 °C and 400 °C, respectively were calculated 0.35 nm and 0.7 nm.



(a)



(b)

Figure 3. TEM image of Fe_3O_4 nanoparticles at 300 °C: a) with semi spherical shape and SAED area of FCC structure, b) with d-spacing of 0.4 nm

Adsorption Reaction of Congo red

In all experiments, adsorption investigations were performed by adding magnetite nanoparticles to 50 mL of Congo red solutions with different concentrations (10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L, and 50 mg/L). The pHs of the Congo red solutions were adjusted by HCl and NaOH. The absorbance wavelength of Congo red is 498 nm [18].

The pH of zero point charge (pH_{zpc}), in which the surface charge is neutral, is around 7.33 for magnetite nanoparticles. At pH lower than pH_{zpc}, magnetite surface which is covered with hydroxyl groups, has positive charges and it can adsorb dye anions. By increasing the solution pH the adsorption decreases as there is a separation for hydroxyl groups' protons of adsorbent [11, 19].

pH Studies

The pH studies were performed in the range of 4-7 for removal of Congo red. The percentage of adsorption was appropriate in the pH range of 5.5-5.9. Around 0.05 g of magnetite nanoparticles was added into solutions at different pH which were stirred for 30 min. Efficiency was calculated by using the following equation:

$$Efficiency(\%) = \left(\frac{C_0 - C_e}{C_0} \right) \times 100 \quad (1)$$

Where C_0 and C_e are initial and equilibrium concentration of the Congo red in the solution (mg/L). The best removal efficiency was for the solution with 30 mg/L concentration in which the adsorption percentage increased by increasing pH and reached maximum at pH 5.9, as shown in Figure 4. In other concentrations, there are no significant changes of efficiency at different pHs.

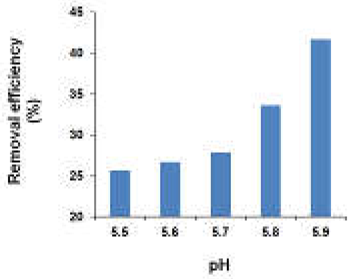


Figure 4. Removal efficiency of Congo red as a function of pH at 30 mg/L using 0.05 g magnetite nanoparticles

Adsorbent Concentration Studies

The effect of adsorbent dosage was studied on the solution with 30 mg/L concentration at pH 5.9 and different adsorbent dosage (0.016 g, 0.025 g, 0.05 g, 0.1 g, and 0.15 g). Figure 5 indicates that the percentage of removal efficiency increased with increasing in adsorbent dosage. There are little changes of efficiency in lower dosages but in higher dosages the efficiency difference between 0.05 g and 0.1 g is more than obtained difference between 0.1 g and 0.15 g. Hence, work was focused on 0.05g and 0.1g adsorbent dosages which were selected to try the removal efficiency.

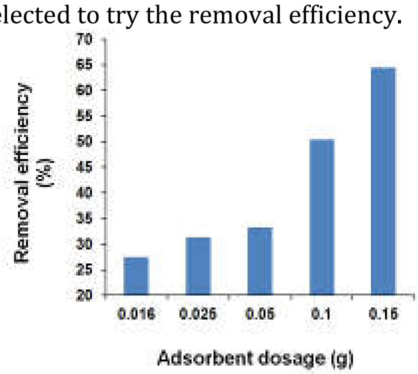


Figure 5. Removal efficiency of Congo red as a function of adsorbent dosage at 30 mg/L and pH 5.9

Contact Time Studies

The studies about contact time were performed to define the time needed for magnetite nanoparticles to remove Congo red from solutions with different initial concentrations of Congo red (10-50 mg/L) at pH 5.9. Around 0.05 g of magnetite nanoparticles was added into solutions. The solutions were stirred for about 30 min. Figure 6 shows that the rate of adsorption is rapid up to about 15 min and after that the slope of decreasing is constant up to 30 min. It means in about 30 min, appropriate amount of Congo red can be adsorbed by nanoparticles. Furthermore, it can be detected that the removals of Congo red at lower concentrations are more appropriate.

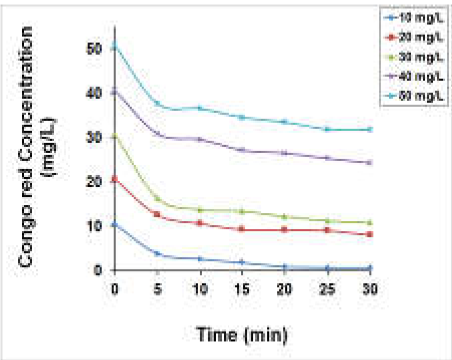


Figure 6. Adsorption levels of Congo red onto magnetite nanoparticles as a function of time at different concentrations (10-50 mg/L) and pH 5.9 using 0.05 g magnetite nanoparticles

Isotherm Models Studies

The equilibrium adsorption isotherm model is the mg of adsorbate which is adsorbed per gram of adsorbent (q_e) as a function of the equilibrium concentration of adsorbate. The adsorption capacity of the adsorbent can be determined by isotherm results. Two isotherm models were used to describe the adsorption behaviour: Langmuir and Freundlich. The Langmuir equation studies monolayer adsorption with no interactions between adsorbed molecules which shows the maximum adsorption capacity. Furthermore, there are homogeneous adsorption sites distributed over the coverage surface [20]. The linearized form of the Langmuir equation is:

$$C_e/q_e = C_e\left(a_L/K_L\right) + \left(1/K_L\right) \quad (2)$$

Where q_e is the amount of Congo red adsorbed per unit mass of adsorbent (mg/g) at equilibrium concentration, a_L (L/mg) and K_L (L/g) are the Langmuir constants. a_L is related to the adsorption energy. q_m (K_L/a_L) shows the maximum adsorption capacity (mg/g) which depends on the number of adsorption sites. Equation (2) shows that a plot of C_e/ q_e (g/L) as a function of C_e (mg/L) yields a straight line if the Langmuir equation is followed by the adsorption equilibrium, as shown in Figure 7. The amount of adsorbed Congo red (mg/g) was calculated by using the following equation [21]:

$$q_e = V(C_0 - C_e)/m \quad (3)$$

Where V is the volume of experimental solution (L) and m is the dry weight of nanoparticles (g).

The Freundlich equation studies the behavior of multilayer adsorption with the interactions between adsorbed molecules. In this model, the adsorption sites are distributed heterogeneously [11]. The linearized form of the Freundlich equation is:

$$\ln q_e = \ln K_f + \left(1/n\right)\ln C_e \quad (4)$$

Where K_f ($mg^{1-1/n}.L^{1/n}.g^{-1}$) and 1/n are Freundlich constants related to the adsorption capacity and adsorption intensity of the adsorbent, respectively. 1/n values are within the range 0-1. Equation (4) shows that a plot of Ln q_e as a function of Ln C_e gives a straight line, same as the plot of Langmuir equation shown in Figure 7.

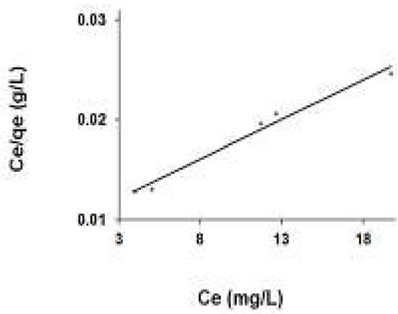


Figure 7. Langmuir isotherm as a function of equilibrium concentration of the Congo red at pH 5.9

Equilibrium isotherms were studied with different initial concentrations of Congo red (10-50 mg/L) at pH (5.5-5.9) by adding 0.05 g of magnetite nanoparticles. Table 1 indicates that q_m and K_f are highest at pH 5.9. Correlation coefficient (r) values are in the range between -1 and 1 [22] which indicate the experimental data to isotherm equations by using the values of regression coefficients [23]. The values of r for Langmuir isotherm are more close to 1 than those for Freundlich equation, as shown in Table 1. Therefore, the Langmuir isotherm represents the better fitted experimental data.

Table 1 Maximum adsorption capacity and correlation coefficient of magnetite nanoparticles for Langmuir and Freundlich equation at pHs (5.5-5.9)

	Langmuir equation	Langmuir equation	Freundlich equation	Freundlich equation
pH	q_m (mg/g)	r	K_f ($mg^{1-1/n}.L^{1/n}.g^{-1}$)	r
5.5	112.21	0.9402	78.29	0.4756
5.6	239.79	0.9690	1.06	0.9317
5.7	355.29	0.9833	36.85	0.9980
5.8	214.75	0.9835	49.75	0.8507
5.9	1322.43	0.9904	135.49	0.9965

Comparison of several adsorbents

There are some other adsorbents of Congo red which already have shown proper adsorption capacity such as CTAB modified chitosan beads [11], N, O-carboxymethyl chitosan [24], maghemite nanoparticles [21], mesoporous activated carbons [25], bentonite [26], and Ca-bentonite [27]. The values of q_m for them respectively are 352.5 (mg/g), 330.6 (mg/g), 208.3 (mg/g), 189 (mg/g), 158.7 (mg/g), 107.4 (mg/g). Magnetite nanoparticles showed significantly higher adsorption capacity (1322.43 mg/g) compared to Congo red adsorbents which mentioned above.

CONCLUSIONS

Magnetite (Fe_3O_4) nanoparticles were obtained by Sol–Gel method combined with annealing temperature of 200 °C, 300 °C, and 400 °C. Compared to other methods, Sol-Gel process has some advantages such as being environmental friendly and being easy to control the size of nanoparticles. The characterization results show that Fe_3O_4 nanoparticles consist of Fe and O and they have semi spherical shape. Also, they are super paramagnetic and the adsorption capacity of nanoparticles increases as there is a decrease in size of them. Magnetite nanoparticles were used to adsorb the Congo red from waste water and the adsorption capacity was evaluated by Langmuir and Freunlich models. Langmuir model showed better results.

NOMENCLATURES

C_0 Initial concentration of the Congo red in the solution ; C_e Equilibrium concentration of the Congo red in the solution ; q_e mg of adsorbate per gram of adsorbent; a_L Langmuir constant; K_L Langmuir constant; q_mMaximum adsorption capacity; V Volume of experimental solution; m Dry weight of nanoparticles; K_f Freundlich constant; 1/n Freundlich constant; r Correlation coefficient

REFERENCES

1. Wikipedia .The Free Encyclopedia Web, (2015). Iron oxide nanoparticles".May. See also URL http://en.wikipedia. org /wiki/Iron_oxide_nanoparticles.
2. Wikipedia The Free Encyclopedia Web, (2015). "Magnetite". May. See also URL https://en.wikipedia.org /wiki/Magnetite.
3. Wang, B., Wei, Q., Qu, S., (2013). Synthesis and characterization of uniform and crystalline magnetite nanoparticles via oxidation-precipitation and modified co-precipitation methods". *International Journal of Electrochemical Science*, 8(3), March, pp. 3786-3793.
4. Teja, A.S., Koh, P.Y., (2009). Synthesis, properties, and applications of magnetic iron oxide nanoparticles". *Progress in Crystal Growth and Characterization of Materials*, 55(1-2), March, pp. 22-45.
5. Zdansky, K., Kacerovsky, P., Zavadil, J., Lorincik,J., Fojtik, A., (2007). Layers of metal nanoparticles on semiconductors deposited by electrophoresis from solutions with reverse micelles". *Nanoscale Research Letters*, 2(9), August, pp. 450-454.
6. Khedr, M.H., Halim, K.S.A., Soliman, N.K., (2009). Synthesis and photocatalytic activity of nano-sized iron oxides. *Materials Letters*, 63(6-7), March, pp. 598-601.
7. Schaadt, D.M., Feng, B., Yu, E.T., (2005). Enhanced semiconductor optical absorption via surface plasmon excitation in metal nanoparticles. *Applied Physics Letters*,86(6), February, pp. 063106.

8. Markides,H., Rotherham,M., El Haj, A.J., (2012). Biocompatibility and toxicity of magnetic nanoparticles in regenerative medicine. *Journal of Nanomaterials*, July, Paper number 614094.
9. Senan, R.C., Abraham, T.E., (2004). Bioremediation of textile azo dyes by aerobic bacterial consortium. *Biodegradation*, 15(4), August, pp. 275-280.
10. WIKIPEDIA The Free Encyclopedia Web, (2015). Congo red".May. See also URL http://en.wikipedia.org /wiki/Congo_red.
11. Chatterjee, S., Lee, D.S., Lee, M.W., Wooa, S.H., (2009). Enhanced adsorption of Congo red from aqueous solutions by chitosan hydrogel beads impregnated with cetyl trimethyl ammonium bromide. *Bioresource Technology*, 100(11), June, pp. 2803-2809.
12. Dalali,N., Khoramnezhad,M., Habibizadeh,M., Faraji, M., (2011). Magnetic removal of acidic dyes from waste water using surfactant-coated magnetite nanoparticles: Optimization of process by Taguchi method". International Conference on Environmental and Agriculture Engineering, Chengdu, China, July.
13. Albornoz, C., Jacobo, S.E., (2006). Preparation of a biocompatible magnetic film from an aqueous ferrofluid. *Journal of Magnetism and Magnetic Materials*, 305(1), October, pp. 12-15.
14. Chin,A.B., Yaacob, I.I., 2007. "Synthesis and characterization of magnetic iron oxide nanoparticles via w/o microemulsion and Massart's procedure". *Journal of Materials Processing Technology*, 191(1-3), August, pp. 235-237.
15. Sun, Y.K., Ma, M., Zhang, Y., Gu, N., (2004). Synthesis of nanometer-size maghemite particles from magnetite". *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 245(1-3), September, pp. 15-19.
16. Xu,J., Yang, H., Fu, W., Du, K., Sui, Y., Chen, J., Zeng, Y., Li, M., Zou, G., (2007). Preparation and magnetic properties of magnetite nanoparticles by sol–gel method. *Journal of Magnetism and Magnetic Materials*, 309(2), February, pp. 307-3011.
17. Qi,H.Z., Yan,B., Li, C.K., Lu, W., (2011). Synthesis, characterization of water-soluble magnetite nanocrystals via one-step sol-gel pathway. *Science China Physics, Mechanics and Astronomy*, 54(7), July, pp. 1239-1243.
18. Sladewski,T.E., Shafer,A.M., Hoag, C.M., (2006). The effect of ionic strength on the UV-vis spectrum of congo red in aqueous solution. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 65(3-4), November, pp. 985-987.
19. Wang, X.S., Ren, J.J., Lu, H.J., Zhu,L., Liu, F., Zhang, Q.Q., Xie, J., (2010). Removal of Ni(II) from Aqueous Solutions by Nanoscale Magnetite. *Clean Soil Air Water*, 38(12), December, pp. 1131-1136.
20. Afkhami, A., Madrakian,T., Amini, A., (2009). "Mo(VI) and W(VI), removal from water samples by acid-treated high area carbon cloth". *Desalination*, 243(1-3), July, pp. 258-264.
21. Afkhami, A., Moosavi, R., (2010). Adsorptive removal of congo red, a carcinogenic textile dye, from aqueous solutions by maghemite nanoparticles. *Journal of Hazardous Materials*, 174(1-3), February, pp. 398-403.
22. Finding Your Way around table of contents Web, (2015). Correlation Coefficient". May. See also URL http://mathbits.com/MathBits/TISection/Statistics2/correlation.htm.
23. R-Bloggers R news and tutorials contributed by (573) R bloggers, 2015. "Grumble10, Interpreting regression coefficient in R". May.See also URLhttp://www.r-bloggers.com/interpreting-regression-coefficient-in-r/.
24. Wang, L., Wang, A., (2008). Adsorption properties of congo red from aqueous solution onto N, O-carboxymethly-chitosan. *Bioresource Technology*, 99(5), March, pp. 1403-1408.
25. Grabowska, E.L., Gryglewicz, G., (2007). Adsorption characteristics of congo red on coal based mesoporous activated carbon. *Dyes and Pigments*, 74(1), pp. 34-40.
26. Bulut, E., Ozacar, M., Sengil, I.A., (2008). Equilibrium and kinetic data and process design for adsorption of Congo Red onto bentonite. *Journal of Hazardous Materials*, 154(1-3), June, pp. 613-622.
27. Lian, L., Guo, L., Guo, C., (2009). Adsorption of congo red from aqueous solutions onto Ca-bentonite. *Journal of Hazardous Materials*, 161(1), January, pp. 126-131.