Remove of Humic Acid From Water Using Magnetite Nanoparticles

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ABSTRACT

Synthesis, characterization and utilization of iron oxide nanoparticles have been a subject of attention in recent years on the base of their interesting chemical and physics properties. Magnetite (Fe₃O₄) nanoparticles were synthesized by chemical co-precipitation and characterized using X ray diffraction (XDR), Fourier transmission spectroscopy (FT-IR), dynamic light scattering and (DLS). Fe₃O₄ nanoparticles were successfully removed humic acid (HA) from water. The influence of pH, contact time, adsorbent nanoparticle doses and HA concentrations were analyzed. Maximum HA removal occurred at pH 6 (89.63%), 40 mg.L⁻¹ of Magnetite (88.8%), 0.03g of HA (96.64%) and contact time of 20 min (94.37%). Sorption data fit pseudo-second order kinetics, indicated a chemical adsorption process. The Langmuir, Freundlich and Temkin adsorption isotherm models were applied to describe equilibrium data. Adsorption of HA on magnetite nanoparticles was well described by Temkin model. The maximum adsorption capacity was 128.23 mg.g⁻¹. Fe₃O₄ nanoparticles were promising potential adsorbents for HA removal from water.

Keywords: Adsorption process; Co-precipitation; Humic acid; Iron oxide nanoparticles

I. INTRODUCTION

Iron oxide nanoparticles have been previously described [1], [2]. Study reported different methods of synthesis of magnetite (Fe₃O₄) nanoparticles such as co-precipitation [3], sol-gel [4], hydrothermal [5] and decomposition methods [6]. Co-precipitation is a suitable process to produce synthetic Fe₃O₄ nanoparticles, due to its high level of efficiency [7].

Magnetite (Fe₃O₄) nanoparticles can support a diversity of applications including the development of scientific and technological functions [8]. In photocatalysis [9], biomedical [10] and adsorption for removal of heavy metals [11] or organic matters [12]. Natural humic acid (HA) are the most predominant reactive fractions of organic matter (NOM) that is present in water resources [12], [13]. Humic acid (HA) consist of a complex polymer of carbonyl, phenolic, carboxyl and hydroxyl groups [14]. Synthetic organic chemicals and trace element Humic can be and carry by HA through water treatment facilities and distribution systems [13].

Simultaneously, HA has disadvantageous effects on the taste and appearance water [15]. Mostsever , humic acid (HA) can be react with chlorine during chlorination and produce strongly carcinogenic disinfection byproducts (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs) [16]. Thus, removing of humic acid (HA) in water treatment could be paramount and essential for environmental and health reasons.]

In this paper, we reported the preparation of magnetite nanoparticles, characterization and its application to remove humic acid (HA) from a synthetic water. We chose in this study the chemical Co-precipitation method to prepare the magnetite nanoparticles, the characterization with different techniques such as XDR, FT-IR, DLS and the application was realized by studying in detail the influence of various parameters such as solution pH, contact time, solution pH,
adsorbate concentration and adsorbent dose. The adsorption procedure was also defined by kinetics and isotherm analysis.

II. PROCEDURE

A. Materials

Ferrous sulfate (FeSO₄, 6H₂O) and ferric nitrate [(Fe(NO₃)₃] were used as a source of Fe²⁺ and Fe³⁺ ions, respectively. Sodium hydroxide (NaOH) was used as a base in the synthesis of magnetite nanoparticles, PVP was used as a stabilizer in solution phase. Humic acid (HA) used in this study was purchased from Sigma.

B. Synthesis of magnetite nanoparticles

Magnetite nanoparticles were synthesized following the method [7] where we changed the triethyl amine by NaOH and the SDS by PVP.

C. Characterization of magnetite (Fe₃O₄) nanoparticles

Magnetite nanoparticles synthesized were defined by several techniques. The XRD analysis of magnetite nanoparticles was conducted on X’PERT Pro MPD PANALYTICAL with a Cu Kα source (λ = 1.54056 Å). FT-IR spectra were recorded at 400-4000 cm⁻¹ using Perkin-Elmer spectrum (FTIR2000). The size distribution and zeta potential were obtained with a zetasizer (MALVERN, NanoZS). The morphology of the particular was obtained with a scanning electron micrographs (MEB).

D. Adsorption experiments

Experiments of Adsorption were attended in triplicates and the results are reported as average. Adsorption experiments were conducted at various pH values, contact time, initial HA concentration and adsorbent dose. The solution pH was adjusted with 0.1 mol·L⁻¹ HCl or NaOH solutions. Adsorption experiments were done in flasks containing 100 ml of HA solution and 0.1 g of Fe₃O₄ at room temperature. After predetermined contact time, the aqueous solution was rapidly separated by centrifugation and the residual concentration of HA in the supernatant was measured by a Perkin-Elmer UV-Vis spectrophotometer (Lamda 25) at 260 nm. The HA adsorption capacity of Fe₃O₄ at any time t (qt, mg·g⁻¹) was calculated using the following equation:

\[ Q_t = \frac{(C_0-C_t)V}{m} \]  

where CO (mg·L⁻¹) is the initial concentration of HA, Ct (mg·L⁻¹) is the instant concentration of HA at any time t, V (L) is the volume of the solution and m (g) is the mass of Fe₃O₄.

III. RESULTS AND DISCUSSION

The FT-IR spectrum (Figure 1) of magnetite (Fe₃O₄) nanoparticles shows that the characteristics peaks at 580 cm⁻¹ relate to Fe-O stretching vibration. The bands near 3200 cm⁻¹ and 1300 cm⁻¹ refer to the O-H stretching vibration. The XRD patterns of magnetite nanoparticles samples are shown in Figure 2, which revealed the crystalline nature of magnetite nanoparticles. A series of characteristic peaks for magnetite (Fe₃O₄) (2θ = 30.15°, 35.52°, 47.17°, 53.56°, 58.23°, 64.01°) were observed and corresponding the crystal planes of (220), (311), (400), (422), (511) and (440), respectively. These peaks are consistent with standard data for magnetite phase (ASTM 89-1397). The average crystallite size calculated using the Debye-Scherrer equation was found to be 44.14 nm.

The uptake of HA by Fe₃O₄ was studied over a pH range of 4-11 and results are given by Fig.3. The plot of Fig.1 shows a noticeable increase of HA uptake by Fe₃O₄ from 11.97 to 26.88 mg·g⁻¹ when solution pH value shifts from 4 to 8. After pH = 8, the HA uptake decreases slightly and while keeping an almost constant pace. This indicates that HA uptake onto Fe₃O₄ nanoparticles is favored at higher pH values. This may be due to the charges of HA molecules and Fe₃O₄ nanoparticles [22].
The effect of adsorbent dose on adsorption of HA on Fe₃O₄ was investigated using different dose 0.01 g to 0.08 g and the results are showed in Fig.4. The adsorption capacity showed by Fig.4 decrease with an increase in adsorbent dose and this is may be caused by the higher disponible of the exchangeable sites [23].

Fig. 4. Effect of adsorbent dose on adsorption of HA on Fe₃O₄ (initial HA concentration 30 mg/L, solution pH 6, contact time 2h).

The effect of initial HA concentration was carried out at 5-50 mg.L⁻¹ as show in Fig. 5. It's well known that the initial concentration of adsorbate has almost always an effect on adsorption process. Indeed, the HA uptake onto Fe₃O₄ increased as things progress the initial HA concentration increases. This may be related to an increase driving force, which permits more HA molecules to pass from the solution to the adsorbent surface [22].

Fig. 5. Effect of initial HA concentration (solution pH 6, contact time 2h, mass 0.03g).

The effect of contact time on adsorption of onto Fe₃O₄ was carried out at 5-70 min. The results are illustrated by Fig.6.

The Fig.6 shows two phases of HA uptake rate onto Fe₃O₄. The first one occurred during the primary 20 min in which the absorption rate was elevated and the HA uptake reached the level of 80%. This high rate can be explained by the presence of a high number of vacant sites on the adsorbent surface during the initial phase. The second phase began after the primary 20 min in which the HA uptake decreases slightly and tend to be constant after 30 min. The constant rate implies that adsorption has reached an equilibrium state and this is can be explained by the presence of repulsive forces between HA molecules in the aqueous solution and those on the surface of Fe₃O₄ [24].

In order to understand how the molecules of HA interact with the adsorbent at constant temperature, many adsorption isotherms were used. The well known of them, and which often used to better describe the equilibrium adsorption, is Langmuir, Freundlich and Temkin isotherm models [25]. The Langmuir isotherm model assumes monolayer adsorption onto a surface with a finite number of identical sites with no interaction between adsorbed molecules [26].

Langmuir model is represented as follows:

$$Q_e = \frac{Q_{max}K_LC_e}{1 + K_LC_e} \quad (2)$$

Where $Q_e$ is the amount of HA adsorbed per mass unit of Fe₃O₄ at equilibrium (mg·g⁻¹), $C_e$ is the equilibrium concentration of remaining HA in the solution (mg·L⁻¹), $Q_{max}$ is the monolayer biosorption capacity of the biosorbent (mg·g⁻¹) and $K_L$ is the Langmuir biosorption constant (L·mg⁻¹).

The Linear form of isotherm can be presented as the following:

$$\frac{C_e}{Q_e} = \frac{1}{K_LQ_{max}} + \frac{C_e}{Q_{max}} \quad (3)$$

The Langmuir isotherm of HA adsorption onto Fe₃O₄ is shown in Fig.7. The Freundlich adsorption isotherm is an empirical equation based on the adsorption on the heterogeneous surface as well as multilayer adsorption [27]. The nonlinear form of the Freundlich adsorption isotherm can be defined by the following equation:

$$Q_e = K_F C_e^\frac{1}{n} \quad (4)$$

The Freundlich isotherm constant $n$ is an empirical parameter that varies with the degree of heterogeneity and $K_F$ is related to adsorption capacity. $K_F$ and $1/n$ values were determinate in using the linear form of Freundlich isotherm described by the following equation:

$$\ln(Q_e) = \ln(K_F) + \frac{1}{n}\ln(C_e) \quad (5)$$
HA adsorption process is better fitted by Temkin model than Langmuir or Freundlich models, indicating that adsorption of HA onto Fe3O4 is multilayer.

In order to identify the kinetic rate-determining step (slowest step) of adsorption process, two kinetic models were used to fit the data including pseudo-first-order and pseudo-second-order models.

The pseudo-first-order [29] is presented as follows:

$$Q_t = Q_e(1 - e^{-k_1t}) \quad (7)$$

Where $Q_e$ and $q_t$ are the HA adsorption capacities for Fe3O4 (mg.g$^{-1}$) at equilibrium and any time $t$ respectively; $k_1$ is the rate constant of pseudo-first-order kinetic model (1.min$^{-1}$). The pseudo-first-order model plots for HA adsorption onto Fe3O4 is shown in Fig.10.

The pseudo-second-order [30] is given as follows:

$$\frac{t}{Q_t} = \frac{1}{k_2Q_e^2} + \frac{1}{Q_e} \quad (8)$$

where $k_2$ is the rate constant of pseudo-second-order kinetic model (g.(mg.min)$^{-1}$). The pseudo-second-order model plots for HA adsorption onto Fe3O4 is shown in Fig.11.

Based on the correlation coefficients ($R^2$) values shown in Fig.10 and Fig.11, the pseudo-second-order kinetic model can be used to fit the adsorption process ranging the whole contact time field better than the pseudo-first-order kinetic model, indicating that the HA adsorption onto Fe3O4 is a chemical adsorption [30].
The adsorption of HA onto Fe3O4 was investigated at four different temperatures (25°C, 35°C, 45°C and 55°C). The HA adsorption for Fe3O4 at equilibrium decreases when the temperature increase from 25°C to 55°C, indicating better adsorption at lower temperature and an endothermic uptake process [31]. The values of thermodynamic parameters such as free energy (∆G°), enthalpy (∆H°) and entropy (∆S°) were determined using the following equations [32]:

$$\Delta G^0 = -RT\ln K_L$$  \hspace{1cm} (9)

$$\ln K_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$  \hspace{1cm} (10)

Where $K_L$ is the constant of equilibrium (ml.g⁻¹) and equal to $q_e/Ce$. $R$ is the universal gas constant (8.314 J.(mol.K)⁻¹) and $T$ is reaction temperature (K). The values of $\Delta H^0$ and $\Delta S^0$ are obtained from the slope and intercept of the line plotted by Ln(KL) versus 1/T, respectively (Fig.12).

![Fig. 12. LnKL versus 1/T.](image)

The obtained thermodynamic parameters for the adsorption of HA onto Fe3O4 are listed in table 1 and table 2.

**TABLE 1: ∆G VALUES.**

| T(C°) | T(K) | Co(mg/L) | Cf(mg/L) | Qe | Ln K_L | ∆G (-RTLnK) |
|------|------|----------|----------|----|--------|--------------|
| 25   | 298  | 40       | 2.27     | 125.7666 | 4.014647977 | -3756.611501 |
| 35   | 308  | 40       | 3.151    | 122.8300 | 3.660381423 | -3542.639306 |
| 45   | 318  | 40       | 3.751    | 120.8300 | 3.47262128  | -3467.223032 |
| 55   | 328  | 40       | 4.835    | 117.2166 | 3.188142376 | -3283.531596 |

**TABLE 2: ∆S AND ∆H VALUES.**

| ∆H (J/mole) | ∆S (J/mole. K) |
|--------------|----------------|
| -21722.819   | -39.687        |

The negative values of ∆G° at all temperatures and all initial HA concentrations indicate the viability of the adsorption of HA onto Fe3O4 and the spontaneous process of the adsorption. Negative ∆H° values at all initial HA concentrations indicate the exothermic of the adsorption behavior, and also its magnitude gives information on the type of adsorption, which can be either physical or chemical [33]. In fact, if ∆H° is comprised between -120 and -40 kJ.mol⁻¹, the uptake process occurred mainly by chemical bonding [34], [35]. However, the value of ∆H° obtained by the present work is -21,722 kJ.mol⁻¹, showing that adsorption process of HA onto Fe3O4 was taken place mostly via physisorption mechanism. The negative values of ∆S° indicate a decrease of the chaos at solid-solution interface during the adsorption process of HA onto Fe3O4 [32]. This can be explained by a decrease of free sites on the adsorbent area.

**IV. CONCLUSION**

Magnetite (Fe3O4) was successfully prepared by chemical co-precipitation process. The HA adsorption capacities for Fe3O4 increase with an increase in solution pH from 4 to 11 and are favored for increasing contact time and initial HA concentration. The adsorption kinetic of HA onto Fe3O4 obey a pseudo-second-order model. The equilibrium adsorption data of HA onto Fe3O4 fits better with Temkin isotherm model than Langmuir and Freundlich isotherms model. Thermodynamic parameters indicate the adsorption of HA onto Fe3O4 is spontaneous and exothermic in nature. The mechanism for the adsorption seems carried out via physisorption according to thermodynamic results. It involves electrostatic interaction and hydrogen bonding. However, chimisorption mechanism could occur but with less importance. Results of this work show that Fe3O4 is a promising adsorbent for removing HA from aqueous solution.

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