Magnetic nanopowder as effective adsorbent for the removal of Congo Red from aqueous solution

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ABSTRACT

A magnetic iron oxide nanopowder (MnP), prepared by a simple and efficient combustion synthesis technique, was tested for the removal of the anionic dye Congo Red (CR) from aqueous solution. The influence of solution pH, adsorbent dose, temperature, contact time and initial dye concentration on the adsorption of CR onto MnP were investigated. It was shown that the CR adsorption was pH dependent and the adsorption mechanism was governed by electrostatic forces. The adsorption kinetic was best described by the pseudo-second-order model and the equilibrium data were well fitted to the Langmuir isotherm, yielding maximum adsorption capacity of 54.46 mg g⁻¹. The undeniable advantages of the MnP adsorbent such as inexpensive preparation method, good adsorption capacity and easy separation using an external magnetic field, recommend it as a promising candidate for the removal of anionic dyes from polluted water.

Key words | Congo Red, dye adsorption, magnetite nanopowder

INTRODUCTION

Azo dyes are characterized by vibrant color and by the presence of one or more azo groups (-N=N-) aromatic rings in their structure. They represent over 60% of the total dyes used, being the largest and the most versatile class of dyes for commercial applications (Afkhami & Moosavi 2010; Jonstrup et al. 2011; Saratale et al. 2011; Solis et al. 2012). Azo dyes have high stability to chemical, biological and photocatalytic degradation and also to exposure to sunlight, microorganisms, water and cleaners (Jonstrup et al. 2011; Solis et al. 2012). Also, the degradation by reductive cleavage of azo linkages leads to the formation of aromatic amines which are one of the most toxic, mutagenic and carcinogenic class of compounds (Afkhami & Moosavi 2010; Jonstrup et al. 2011; Solis et al. 2012). Even at very low concentration of azo dye (10-50 mg L⁻¹), the water becomes highly colored which not only affects the aesthetic and transparency aspect of the water, but also involves environmental concerns about the toxic, carcinogenic and mutagenic effects of the azo dyes (Vandevivere et al. 1998). Therefore, the direct release into the environment of the effluents containing azo dyes, including Congo Red (CR), causes serious environmental, ecological and health problems (Jonstrup et al. 2011; Saratale et al. 2011; Solis et al. 2012), making their removal a major concern.

Among various techniques developed for removing the dye-containing wastewater including electrochemical treatment (Körbahti 2007), photocatalytic oxidation (Jiang et al. 2011), coagulation/flocculation (Wang et al. 2012a), ozone treatment (Khadhraoui et al. 2009), adsorption is the most used method due to its simplicity, high efficiency and versatility. A wide range of adsorbents were used for dyes removal including activated carbon, zeolite, clay, polymer and byproduct (Afkhami & Moosavi 2010; Ai & Zeng 2013). Recently, iron oxide magnetic nanoparticles are considered as the next generation of adsorbents for industrial scale wastewater treatment due to their high adsorption capacity, low cost, enhanced stability, extended lifecycles and easy separation by applying an external magnetic field (Kong et al. 2012; Xu et al. 2012). In recent years, several reports were published regarding the use of different adsorbents with magnetic properties for the removal of heavy metals (Huang & Chen 2009; White et al. 2009; Ge et al. 2012) and dyes (Chang et al. 2011; Madrakian et al. 2011; Xie et al. 2011; Wang et al. 2012b). Many investigations were focused on obtaining new adsorbents which possess high adsorption capacity and excellent separation by combining the properties of classical adsorbents with the magnetic properties of iron oxides (Chang et al. 2011; Madrakian et al. 2011).

The objective of the present study was to investigate the adsorption capacity of a new magnetic iron oxide nanopowder (MnP) for the removal of anionic dyes. CR, which is an important source of water pollution resulting from textiles, printing, paper, rubber, plastics industries, etc., was chosen as the model dye in this study. The iron oxide nanosorbent was obtained by a new and inexpensive technique of combustion method reported by Ianos et al. (2012), using sucrose as fuel. Unlike the literature reports regarding the synthesis of magnetite covered with different functional groups, this new method used by us has the advantage of directly obtaining, in one-step of magnetic iron oxides particles covered with some organic residues which are responsible for the adsorption capacity. The effect of different parameters including solution pH, adsorbent dose, temperature, contact time and initial dye concentration was investigated in order to optimize the adsorption process efficiency. The kinetic and adsorption isotherm were also evaluated.

METHODS

Adsorbate

CR is a benzidine-based anionic disazo dye with formula C_{32}H_{22}N_{6}Na_{2}O_{6}S_{2} and molecular weight of 696.66 g/mol. The CR structure is illustrated in Figure 1. CR has the property to change the color from blue to red at pH 3.0–5.2 and to aggregate in aqueous and organic solutions. The concentration of CR in the experimental solution was determined by measuring absorbance at 498 nm. The pH of the solution was adjusted using HCl (0.1 M) or NaOH (0.1 M) solutions.

Synthesis of magnetic iron oxide nanopowder

All the chemicals and reagents used in this work were of analytical grade. The iron oxide nanopowder was obtained by a new combustion synthesis technique, using as starting materials iron nitrate nonahydrate (Fe(NO_{3})_{3}·9H_{2}O) as oxidant agent and sucrose (D-(+)-C_{12}H_{22}O_{11}) as fuel. The reaction was conducted in the absence of air, in a round bottomed flask (Ianog et al. 2012). After water evaporation started a smouldering combustion reaction accompanied by the release of large amounts of gases which were bubbled in a large beaker filled with distilled water. The reaction product was hand grinded, washed with distilled water and dried.

Characterization

The powder was characterized in terms of phase composition (X-ray diffraction, XRD), structure, texture and carbon content. The X-ray diffraction was performed using a Panalytical XPERT-PRO diffractometer with CuKα radiation. Fourier transform infrared (FTIR) spectrum was carried out using a Shimadzu Prestige-21 spectrometer in the range 400–4,000 cm⁻¹, using KBr pellets and a resolution of 4 cm⁻¹. N₂ adsorption–desorption isotherms were performed on Micromeritics ASAP 2020 instrument, at 77 K after the sample was degassed at 100 °C under high vacuum for 24 h. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) while the pore diameter and pore volume was determined by the Barrett–Joyner–Halenda (BJH) method. The pore size distribution was computed using the BJH method from the adsorption curve. The carbon content of the powder was performed by ‘Dynamic Flash Combustion’ using an Elemental Analyzer EA 1108, according to ASTM D 5373-08 standard test procedure. The leaching of iron ions was evaluated by atomic absorption spectroscopy using a Varian SpectrAA 110 instrument.

Adsorption experiments

Adsorption experiments were performed in a thermostated shaker with a shaking speed of 200 rpm using glass flasks. The experimental solution was obtained by diluting the CR stock solution (1,000 mg L⁻¹) to desired concentrations. The adsorbent was separated from the aqueous solution by the aid of a magnet. The concentration of CR was monitored by spectrophotometric analysis using a SHIMADZU UV-VIS Spectrophotometer. The absorbance values were measured at a wavelength of maximum absorbance (498 nm). The calibration curve was made by measuring the absorbance of different predetermined concentrations of CR.
The amount of CR adsorbed, \( q_t \) (mg g\(^{-1}\)) was calculated according to Equation (1):

\[
q_t = \frac{(C_0 - C_t) \cdot V}{W}
\]

(1)

where \( C_0 \) and \( C_t \) are the initial CR concentration and the CR concentrations at any time \( t \) (mg L\(^{-1}\)), respectively; \( V \) is the volume of solution (L); and \( W \) is the weight of the MnP (g).

The removal efficiency \( R \) (%) of the adsorption process was calculated by Equation (2):

\[
R = \frac{C_0 - C_t}{C_0} \cdot 100
\]

(2)

where \( C_0 \) and \( C_t \) are the initial and the equilibrium concentration of CR (mg L\(^{-1}\)) respectively.

The investigated ranges of the experimental variables were as follows: pH 6.0–10.0, adsorbent dose 0.5–3 g L\(^{-1}\), temperature 25, 45 and 60 °C, contact time 0–300 min and initial dye concentration 20–100 mg L\(^{-1}\). The experimental data were fitted using the Lagergren pseudo-first-order and Ho and McKay pseudo-second-order equations.

The linear form of the Lagergren pseudo-first-order equation is generally expressed as follows (Zhu et al. 2011):

\[
\ln (q_e - q_t) = \ln q_e - k_1 t
\]

(3)

where \( q_e \) and \( q_t \) are the amount of solute adsorbed at equilibrium and respectively at time \( t \) per unit weight of adsorbent (mg g\(^{-1}\)); and \( k_1 \) is the adsorption rate constant (min\(^{-1}\)). The values of \( k_1 \) and \( q_e \) were calculated from the slope and intercept of the plot \( \ln (q_e - q_t) \) versus \( t \) (figure not shown).

The linear form of the Ho and McKay pseudo-second-order equation is (Chang et al. 2011):

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

(4)

where \( q_e \) and \( q_t \) are the amount of solute adsorbed at equilibrium and at time \( t \) per unit weight of adsorbent (mg g\(^{-1}\)), respectively; and \( k_2 \) is the adsorption rate constant (g mg\(^{-1}\) min\(^{-1}\)). The initial adsorption rate, \( h \) (mg g\(^{-1}\) min\(^{-1}\)) is defined as (Wang et al. 2012b):

\[
h = k_2 q_e^2
\]

(5)

The study of the equilibrium isotherms offers important information regarding the adsorption mechanism, the properties of sorbent surface and the interactions between the sorbent and sorbate. In this study, the experimental data were analyzed with the most widely used isotherms of Langmuir and Freundlich.

The Langmuir theory assumes homogeneous surface of the sorbent, monolayer coverage of adsorbent and no interactions between the adsorbed molecules. The Langmuir isotherm is represented by the equation (Yao et al. 2012; Ai & Zeng 2013):

\[
q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e}
\]

(6)

where \( q_e \) is the amount of solute adsorbed per unit mass of adsorbent at equilibrium (mg g\(^{-1}\)), \( q_{max} \) is the maximum monolayer adsorption capacity (mg g\(^{-1}\)), \( C_e \) is the equilibrium concentration of the solute in the bulk solution (mg L\(^{-1}\)) and \( K_L \) is the Langmuir sorption constant (L mg\(^{-1}\)).

The essential characteristic of Langmuir isotherm can be expressed using a dimensionless constant, the separation factor \( R_L \) (Wang et al. 2012b):

\[
R_L = \frac{1}{1 + K_L C_0}
\]

(7)

where \( C_0 \) is the initial concentration of the dye (mg L\(^{-1}\)). The value of this coefficient indicates whether the isotherm is or not favorable: for \( 0 < R_L < 1 \) the model is favorable; for \( R_L > 1 \) the model is unfavorable and for value \( R_L = 0 \) the model is irreversible.

The Freundlich isotherm presumes heterogeneous surface of adsorbent and interactions between adsorbed molecules. The Freundlich isotherm is expressed as (Yao et al. 2012):

\[
q_e = K_F C_e^{1/n}
\]

(8)

where \( K_F \) is the Freundlich constant (mg\(^{1-1/n}\) L\(^{1/n}\) g\(^{-1}\)), indicating the adsorption capacity of the adsorbent and \( n \) (dimensionless) is a constant related to the intensity of adsorption.

### RESULTS AND DISCUSSION

#### Characterization of the adsorbent

The main characteristics of the adsorbent are presented in Table 1.
The XRD pattern of MnP displays diffraction peaks at $2\theta$ values of 30.0 (220), 35.7 (311), 43.2 (400), 53.8 (422), 57.1 (511) and 62.8 (440) that correspond to magnetite according to PDF file 19-0629. The MnP isotherm is of type II with H3 hysteresis loop, according to IUPAC classification and the adsorbent structure is mainly mesoporous, as resulted on the bases of BJH analysis.

The FTIR spectrum of MnP certified the presence of some residual organic groups resulted directly from the combustion reaction. The band at 1,678 cm$^{-1}$ was assigned to C=O asymmetric stretching vibration and the band at 1,414 cm$^{-1}$ was associated with the C=O symmetric stretching and to the C–H bending vibration (Nakanishi & Solomon 1977). It was also observed the band at 3,413 cm$^{-1}$ assigned to O–H stretching vibration (Vandevivere et al. 2013) and a broadband located at 581 cm$^{-1}$, assigned to the Fe–O vibration in Fe$_3$O$_4$ (Liese 1967; Feng et al. 2012; Gong et al. 2012) confirming the presence of magnetite.

Adsorption studies

Effect of pH value

Solution pH is an important factor which significantly affects the chemistry of the dye molecules and the adsorbent (Hou et al. 2012; Mahapatra et al. 2013). The stability of the magnetic nanosorbent was evaluated by measuring the leaching of iron ions at different pH values ranging from 3 to 7 by atomic absorption spectroscopy. The leached iron concentration significantly decreased from 9.14 to 2.24 mg L$^{-1}$ with increasing the pH value from 3 to 4. Then, it decreased to 1.29, 0.87 and 0.67 mg L$^{-1}$ with the increase of the solution pH at 5, 6 and 7, respectively. These results demonstrated the good stability of the adsorbent at pH values over 6.

The effect of initial pH on CR adsorption onto MnP was studied in the range of 6–10 (Figure 2).

It can be observed that there is a sharp decrease of the adsorption capacity with increasing the pH value. This behavior can be explained by the amphoteric character of magnetite powder (Scheme 1). From the literature data (Tombácz et al. 2006), the pH$_{PZC}$ value for magnetite is 7.9. When the pH is lower than pH$_{PZC}$, the adsorbent surface is positively charged as a result of protonation, favoring the adsorption of anionic species. When the pH is higher than pH$_{PZC}$, the adsorbent surface is negatively charged as a result of deprotonation, favoring the adsorption of cationic species.

CR dye presents two sulfonic groups that ionized easily in acid media, becoming a soluble anion. This explains the high adsorption capacity of CR onto MnP at lower pH value, governed by electrostatic interactions. Correlating the results shown in Figure 2 with the concentration of leached iron ions, the pH value was set at 6 for further studies.

Effect of adsorbent dose

The effect of MnP dose ranging from 0.5 to 3 g L$^{-1}$ on CR adsorption is shown in Figure 3. The increase of dye removal efficiency from 41.12 to 94.19% with the increase of adsorbent dose can be explained by the availability of more binding sites on MnP. Given the small difference between the efficiency of the adsorption process for 2 and 3 g L$^{-1}$ MnP, the further studies were carried out using 2 g L$^{-1}$ adsorbent dose.
The effect of contact time and temperature on the amount of CR adsorbed onto the MnP is shown in Figure 4. It can be noticed that there are two stages of the adsorption process: a rapid one in the first minutes of the process followed by a slower stage as the system approaches equilibrium. At the start of the adsorption, CR removal is fast due to the high availability of vacant sites on the MnP surface which are gradually occupied in time as a result of sorption process. Figure 4 also shows the slightly positive effect of the temperature rising on the CR removal; the adsorption capacity increases as the temperature increases, suggesting that CR adsorption onto MnP is an endothermic process. On the other hand, one may notice the important decrease of the equilibrium time as the temperature increases from 25 to 60 °C. The optimum temperature was chosen as 45 °C.

Adsorption kinetics

The kinetic studies were conducted at pH 6, initial CR concentration 50 mg L\(^{-1}\), adsorbent dose 2 g L\(^{-1}\) and temperatures of 25, 45 and 60 °C.

The values of \(q_e\) and \(k_2\) were calculated from the slope and intercept of the plot \(t/q_t\) versus \(t\) (Figure 5).

The kinetic parameters and the correlation coefficients \(R^2\), determined by linear regression, are given in Table 2. According to the results presented in Table 2, the pseudo-second-order model showed a good fit with experimental data for all temperatures \((R^2 > 0.99)\); also the calculated values of \(q_e\) are very close to the experimental ones. This indicates that the pseudo-second-order model is feasible to describe the adsorption of CR adsorption onto MnP. Similar results were reported for CR adsorption onto magnetic Fe\(_3\)O\(_4@\)graphene nanocomposite (Yao et al. 2012), magnetic cellulose/Fe\(_3\)O\(_4/activated carbon composite (Zhu et al. 2014), iron oxide-alumina nanocomposites (Mahapatra et al. 2013).

Adsorption isotherms

The experimental equilibrium data were fitted to the Langmuir and Freundlich isotherms by plotting \(q_e\) versus \(C_e\) (Figure 6).
The isotherms parameters were determined using the non-linear regression analysis (Table 3). The experimental values were better fitted to the Langmuir isotherm \( (R^2 = 0.9702) \) than the Freundlich isotherm \( (R^2 = 0.9237) \) indicating the homogeneous nature of the adsorbent surface. The maximum adsorption capacity calculated from Langmuir isotherm is 54.46 mg g\(^{-1}\) and may be related to the predominately mesoporous structure of the adsorbent, with relatively small surface area \( (59.58 \text{ m}^2 \text{ g}^{-1}) \) and small total volume of pores \( (0.23 \text{ cm}^3 \text{ g}^{-1}) \). Also the values for \( R_L \) separation factor decrease from 0.329 to 0.047 with the increasing of initial dye concentration. Given that the values of \( R_L \) lie between 0 and 1, according to the Langmuir theory it can be concluded that this model is favorable for the adsorption of CR onto MnP.

The maximum adsorption capacity for the adsorption of CR onto MnP, calculated from the Langmuir isotherm \( (54.46 \text{ mg g}^{-1}) \), is higher than that of other adsorbents such as magnetic Fe\(_3\)O\(_4\)@graphene \( (33.66 \text{ mg g}^{-1}) \) (Yao et al. 2012), hollow Zn-Fe\(_2\)O\(_3\) \( (16.10 \text{ mg g}^{-1}) \) (Rahimi et al. 2011), magnetic core-manganese oxide shell nanoparticles \( (42.0 \text{ mg g}^{-1}) \) (Zhai et al. 2009), bentonite \( (19.9 \text{ mg g}^{-1}) \) (Panda et al. 2013) or activated carbon prepared from coir pith \( (6.7 \text{ mg g}^{-1}) \) (Namasivayam & Kavitha 2002).

**CONCLUSIONS**

The MnP was prepared by a facile, efficient and inexpensive combustion synthesis technique and was tested as adsorbent for the removal of CR from aqueous solution. It was shown that the CR adsorption onto MnP was pH dependent and the adsorption mechanism was governed by electrostatic forces. The kinetic studies indicated that the adsorption of CR onto MnP adsorbent followed the pseudo-second-order model and the equilibrium adsorption data were correlated by the Langmuir isotherm. The MnP presents high adsorption efficiency, can be easily manipulated and separated by using a magnetic field, suggesting that it could be used as an efficient adsorbent for the removal of anionic dyes from wastewaters and may be an alternative to more costly materials.

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