Synthesis of Magnesium Ferrites for the Adsorption of Congo Red from Aqueous Solution Using Batch Studies

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Abstract. A sol gel method with citric acid as an anionic surfactant was used to fabricate nano magnesium ferrites (MgFe$_2$O$_4$) under different calcination temperatures for 2h, respectively. The microstructure and surface morphology of magnesium ferrite powder were characterized by FTIR, XRD, SEM, and BET. The results of this study are useful for adsorption Congo red. The results showed that increasing solution pH and extending contact time are favorable for improving adsorption efficiency. With initial Congo red concentration of 50 mg/L and 100 mg/L, Adsorption data fits well with the Langmuir isotherm models with a maximum adsorption capacity (qm) and a Langmuir adsorption equilibrium constant (K) of 65.1 mg/g and 0.090 L/mg, respectively. The adsorption kinetic agrees well with pseudo second order model with the pseudo second rate constants (K2) of 0.0468 and 0.00189 g/mg/min for solutions with initial congo red of 50 and 100 mg/L, respectively.

1. Introduction.

The fabrication of nano ferrites has attracted much greater interest because of their large surface-to-volume ratio yielding remarkable material properties. A number of methods have been developed to fabricate ferrites including electrospinning [1], sol gel [2], coprecipitation [3], high energy ball milling [4], solid state reaction [5], and oxidative thermal decomposition [6]. Among the various methods, the sol–gel method yields more promising results in the fabrication of ferrites particularly at a fairly low temperature [7]. The sol gel method for preparing ferrites has many advantages with respect to good stoichiometric control and particle size distribution at a lower temperature [3].

Previous publications reported that ferrites were used for magnetic separation technology, as a rapid and effective technology for adsorption (Rashad, 2006). Due to large specific surface area, excellent physicochemical characteristics and easy separation under external magnetic fields, spinel ferrite magnetic nanoparticles have been regarded as a promising adsorbent and widely used for dye removal from wastewaters.

Zui Ding, et al [8] synthesized CoFe$_2$O$_4$ ferrite nanoparticles for removal Congo red from aqueous solution by an ethanol-assisted hydrothermal method, where the ethanol is mixed with water as the solution. The maximum adsorption capacity for CR of CoFe$_2$O$_4$ nanoparticle is 190.5 mg g$^{-1}$ when the volume ratio of ethanol to water is 4/3. In this work, magnesium ferrite was directly prepared by a sol gel method, and they were employed to absorb Congo red in water. The adsorption efficiency has been investigated in details.
2. Methods

2.1 Synthesis of magnesium ferrites

The fabrication of magnesium ferrites by a sol gel method using a solution of citric acid as an anionic surfactant included several steps: (i) a solution of ferric nitrate, magnesium nitrate, and citric acid was mixed; (ii) the mixture was constantly stirred and heated up to 100°C for 24h to form the gel; (iii) the brown, fluffy gel was calcinated at different temperatures (300°C, 600°C and 800°C) for respective 2h.

2.2 Adsorption experiments

Into the CR solution is inserted a magnesium ferrite. Agitation rate was held constant at 120 rpm, filter, and concentration in supernatan was analyzed spectrophotometrically (Shimadzu UV 160) at 540 nm. The amount of CR adsorbed onto the compounds (%) was calculated as:

\[
\text{Amount (\%)} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100\%
\]

where \(C_o\) is the initial CR concentration (mg/L), \(C_t\) is the concentration of CR (mg/L) at equilibrium time, t,. All the experiments were carried out in duplicates.

3. Results and Discussion

3.1 The FTIR and XRD Spectra

The absorption peaks of the FTIR spectra at 3393 cm\(^{-1}\), 1624 cm\(^{-1}\) and 1384 cm\(^{-1}\) of the fabricated magnesium ferrites disappeared as the calcinations increased from 300°C to 800°C indicating the removal of the OH-, CO- and NO groups from the material of interest, which is shown in Figure 1. The absorption peak of the FTIR spectra (400 cm\(^{-1}\) to 800 cm\(^{-1}\)) was more obviously shown as the calcination temperatures were getting increased (from 300°C to 800°C) that indicated the formation of tetrahedral – octahedral structures of the metals oxide after the removal of all volatile matters. Pradeep et al. (2008) investigated the vibration of the tetrahedral and octahedral structures of metal complexes at 561 cm\(^{-1}\) and 437 cm\(^{-1}\) of the FTIR spectra of magnesium ferrite that was attributed to the shorter bond length of tetrahedral complex producing more stable structure.

![Figure 1. The FTIR spectra of magnesium ferrites at 100°C, 300°C, 600°C and 800°C.](image-url)
Figure 2. The XRD spectra of magnesium ferrites at 100°C, 300°C, 600°C and 800°C

Figure 2 show the diffractograms for both MgFe₂O₄ at different temperatures (100, 300, 600 and 800°C) where Mg ferrite still existed as amorphous materials at 100°C. As the temperature increased to 300°C the material structure of Mg ferrite changed to semi-crystal with the appearance of some broaden peaks at certain 2θ (Bragg’s angle), and when the calcinations continued to 600°C and 800°C Mg ferrites existed in crystalline form with the existence of sharp peaks in characteristic patterns of Mg-ferrite respectively. The higher thermal effect gave larger movement to atoms to do self rearrangement forming their crystalline structure.

3.2 Adsorption CR by magnesium ferrite nanoparticle

3.2.1 Effect of pH.

The pH of the aqueous solution is an important parameter in controlling the adsorption process of Congo red. When pH is increased from 7 to 12, the colour removal increases slightly from 80% to 85% and then decreases slightly up to pH 13. There is significant decrease of 19% in colour removal, in the pH range of 13-14. The effect of solution pH on the uptake of CR is presented in Figure 3. As shown in the figure, the capacity of magnesium ferrite decreased from pH 12 to pH 14 and reached 22.90 mg/g maximum capacity adsorption at pH 12. condition for percentage uptake of CR using magnesium ferrite. The solution of pH 12 was then selected for other optimization experiment.
Figure 3. The effect of pH on the removal of Congo red solution using magnesium ferrite

3.2.2 Effect of Contact Time

The adsorption experiments to evaluate the contact time effect on percentage uptake of CR were brought within 5 minutes to 60 minutes. The experiments were conducted under the standard conditions; temperature of 298K, pH 12.0 and the concentration CR solution 100 ppm. As shown in Figure 4, percentage uptake of CR increased rapidly within 10 minutes and remained constant after 20 minutes indicating an equilibrium state. At the contact time of 20 minutes, the capacity adsorption of magnesium ferrite for CR 100 ppm is 21.8854 mg/g, respectively. A contact time at 20 minutes was then selected for other optimization experiment.

Figure 4: The effect of contact time on the removal of CR solution using magnesium ferrite
3.2.3 Effect of Initial Concentration
The adsorption study was completed with different concentration of CR at a fixed pH of 12, temperature of 298K, a contact time of 20 minutes using the same amount of magnesium ferrite 0.1 gram. The concentrations of CR were selected from 100 ppm, 200 ppm, 400 ppm, 600 ppm, 800 ppm and 1000 ppm. Figure 5 depicts the effect of different concentrations on percentage uptake of CR. It was found that dosage magnesium ferrite of 0.1 g, gained the capacity adsorption of 87,727 mg/g, for 700 ppm respective concentrations of CR. From the Figure 5, It can be concluded that the capacity adsorption of magnesium ferrite decreased with increment concentrations of CR.

![Figure 5](image)

Figure 5. The effect of concentration magnesium ferrite on the removal of CR

3.2.4 Adsorption Isotherm
Adsorption isotherm study is important to study in order to understand the interactions between adsorbent and adsorbate. The Langmuir model is based on assumption that uptake occurs on a homogenous surface by monolayer sorption without interaction between adsorbed molecules. It is expressed as:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0}$$

where, $q_e$ is the amount of Congo red adsorbed per unit mass of adsorbent (mg/g); $C_e$ is the equilibrium CR concentration (mg/L); and $Q_0$ and $b$ are the Langmuir constants representing the monolayer adsorption capacity (mg/g) and the energy of adsorption (L/mg), respectively. The plot of $C_e/q_e$ versus $C_e$ gives a straight line with a slope of $1/Q_0$ and an intercept of $1/Q_0 b$. The isotherm study percentage uptake of CR was generated in batch experiments using different initial concentrations range from 200 ppm to 1000 ppm at constant temperature of 298 K, a pH of 12.0 and 0.1 g dosage of MgFe$_2$O$_4$. The isotherm is presented in Figure 6 and from the Figure 6 it can be represented that equilibrium data fitted the Langmuir isotherm with high correlation coefficient ($R^2$) value of 0.9374. The calculated Langmuir isotherm constant for the maximum capacity adsorption silica gel $z$, $Q_0$ (mg/g) was 94.33 mg/g.
3.3 Kinetic Study

Pseudo-first order and pseudo-second order kinetic model were introduced to the experimental data in order to investigate the adsorption kinetics of CR onto magnesium ferrite adsorbent. Pseudo-first order was introduced by Lagergren[31] and the equation can be written as:

$$\log (q_e - q_t) = \frac{\log q_e - k_1 t}{2.303}$$

(3)

Pseudo-second order kinetics can be expressed as:

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

(4)

Where, $K_1$ is pseudo-first order rate constant (1/min), $K_2$ (g/CR min$^{-1}$) is pseudo-second order rate constant. $q_e$ (mg/g) is amount of solute absorbed on to at equilibrium, $q_t$ (mg/g is the amount of solute adsorbed at any time, t. Both $K_1$ and $K_2$ values can be calculated from the slopes of the plots log ($q_e$-$q_t$) against time and plot $t/q_t$ versus $t$, respectively.

Information about pseudo-first and pseudo-second order models are summarized in Table 1 which presents the comparison of adsorption kinetics data for both model with different initial CR concentrations. The correlation values for pseudo first order kinetic model obtained were relatively small whereas the experimental $q_e$ values did not fulfil the calculated values gained from the linear plots illustrated in Table 1. Therefore, adsorption CR onto magnesium ferrite adsorbent did not follow pseudo-first order model.

| C$_0$ CR (mg/g) | q$_e$, exp (mg/g) | First-order kinetic model | Second-order kinetic model |
|-----------------|-------------------|---------------------------|---------------------------|
|                 |                   | q$_e$, cal (mg/g) | $K_1$ | $R^2$ | q$_e$, cal (mg/g) | $K_2$ | $R^2$ |
| 40 ppm          | 53.33             | 6.15                  | 0.004 | 0.442 | 50.5               | 0.017  | 0.999 |
| 70 ppm          | 68.63             | 25                    | 0.011 | 0.694 | 66.22              | 0.001  | 0.994 |
| 100 ppm         | 47.73             | 16.1                  | 0.016 | 0.896 | 50.25              | 0.001  | 0.989 |

The correlation coefficient values for pseudo second order showed higher results as compared to the values of pseudo first order. The experimental and calculated $q_e$ are very close, indicating the
applicability of pseudo second order in order to describe the reaction of CR adsorbed onto magnesium ferrite adsorbent.

The kinetic study at 40 ppm concentration is presented in Figure 7. The equilibrium data fitted the second order kinetic model with high correlation coefficient (R²) value of 0.999. The calculated qe for the amounts of solute sorbed at equilibrium of CR, qe was 50.5 mg/g.

![Figure 7. Pseudo-second order kinetic at 40 ppm of CR concentration using magnesium ferrite](image)

3.4. Desorption studies
Desorption of the loaded Congo red were carried out at pH12.0. The elution of the Congo red from magnesium ferrite surface may be explained. Adsorption/desorption cycles, the elution efficiency was found to be 98.1 ± 1% for Congo red, respectively. Regeneration of the adsorbent was easily done using EDTA at pH 12.0 reaching efficiency of about 98%.

5. Conclusions
The present study shows that the crystal structure and morphology of the fabricated ferrites were influenced by the calcination temperatures. The FTIR spectra of magnesium ferrite showed the remarkable peak (400 cm⁻¹ – 600 cm⁻¹) both at the 600°C and 800°C, because the tetrahedral and octahedral structures were obviously formed after all volatile matters removed at both the temperatures of interest. The XRD spectra of magnesium ferrite showed the formation of pure magnesium ferrites at 600°C and 800°C in the crystalline structure compared to the semi-amorphous structure of the related ferrite at 300°C. The SEM micrograph of magnesium ferrite showed a flake-form structure which they were calcinated at 800°C. This study provides a meaningful correlation of the effects of calcination temperature on the crystalline structure of the ferrites of interest.

Also the present study shows that magnesium ferrite is suitable adsorbents for the removal of Congo red from aqueous solution. The removal of Congo red was shown to be dependent on pH, contact time, as well as initial concentration. The experimental data well fitted to Langmuir equation confirming the monolayer coverage of Congo red solution onto magnesium ferrite adsorbents. The reaction of Congo red adsorbed on magnesium ferrite was found closely to pseudo-second order model.

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