Synthesis and characterization of MgO supported Fe–Co–Mn nanoparticles with exceptionally high adsorption capacity for Rhodamine B dye

Somayeh Rahdar\textsuperscript{a}, Abbas Rahdar\textsuperscript{b,*,} Muhammad Nadeem Zafar\textsuperscript{c,∗}, Syed Salman Shafqat\textsuperscript{d}, Shahin Ahmadi\textsuperscript{a}

\textsuperscript{a} Department of Environmental Health, Zabol University of Medical Sciences, Zabol, Iran
\textsuperscript{b} Department of Physics, University of Zabol, P.O. Box 98613-35856, Zabol, Iran
\textsuperscript{c} Department of Chemistry, University of Gujrat, Gujrat, 50700, Pakistan
\textsuperscript{d} Department of Chemistry, University of Education, Lahore, 54770, Pakistan

\textbf{A R T I C L E   I N F O}

Article history:
Received 11 April 2019
Accepted 25 June 2019
Available online 16 July 2019

Keywords:
MgO supported Fe–Co–Mn nanoparticle
Adsorption
Equilibrium
Kinetic
Rhodamine B
Thermodynamic

\textbf{A B S T R A C T}

In this work, MgO supported Fe–Co–Mn nanoparticles (MgO-FCM-NPs) are synthesized and utilized as adsorbent for the successful removal of Rhodamine B dye (RhB) from aqueous environments. In the first step, the synthesized MgO-FCM-NPs are identified using scanning electron microscopy (SEM), vibration sample magnetization (VSM), X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR) techniques. In the second step, the effects of different adsorption conditions such as solution pH (3–13), dye concentration (10–120 mg L\textsuperscript{-1}), adsorbent dosage (0.04–0.12 g L\textsuperscript{-1}), temperature (298–318 K) and contact time (20–100 min) are investigated. The pH 7 is found to be the optimized pH and the equilibrium is reached in 60 min for RhB adsorption onto MgO-FCM-NPs. The maximum adsorption capacity of RhB onto MgO-FCM-NPs is found to 1106 mg g\textsuperscript{-1} at pH 7, temperature 318 K and contact time 60 min using 120 mg L\textsuperscript{-1} RhB concentration. The adsorption data is fitted better to Langmuir isotherm model (R\textsuperscript{2} = 0.999) in comparison to Freundlich and Temkin equilibrium isotherm models. The n (Freundlich constant) values are in between 1–10, suggesting desirable adsorption of RhB onto MgO-FCM-NPs. Further the adsorption process of RhB onto MgO-FCM-NPs is followed pseudo-second-order kinetics (R\textsuperscript{2} = 0.9999). The negative values of Gibbs free energy (\Delta G\textsuperscript{°}) represents spontaneity of the process and the positive values of enthalpy (\Delta H\textsuperscript{°}) of RhB adsorption onto MgO-FCM-NPs indicates the endothermic nature. Finally, it is concluded that the MgO-FCM-NPs could be used for effective RhB removal from textile effluents.

© 2019 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
1. Introduction

Textile industries produce huge amounts of wastewater, which contains high concentrations of suspended solids, dyes, surfactants, and organic materials having high chemical oxygen demand (COD) and high pH [1-3]. There are over 100,000 different types of commercial dyes, which are annually produced by over 7 x 10^6 tons [4,5]. More than 1–15% of basic dyes enter into wastewater during the coloring process [1,3]. However, this low percentage claims a high carcinogenicity and toxicity. Rhodamine B dye (RhB) is a cationic artificial xanthine dye which is commonly used in industries particularly in textile, paper and food industries [6]. The exposition of humans and animals to RhB causes damages to the eyes, respiratory system and skin irritation. Medical studies have proven that the drinking water contaminated with RhB causes carcinogenic and neurotoxic effect, and additionally chronic poisoning [7,8]. Therefore, wastewaters contaminated with RhB should be treated before being discharged into the environment.

Currently there are various techniques in use to remove dyes from wastewater based on operability, effectiveness, availability, and insensitivity to toxic materials and costs. These include ion exchange, biological degradation, reverse osmosis, coagulation and flocculation, membrane filtration, electrochemistry, and chemical precipitation [3,9]. The resistant pollutants in wastewater of industries are often toxic to the living organisms, and thus, biological systems are not able to treat these wastewaters [10]. Based on these issues, the adsorption process is known as an efficient technique and also highly reported method to remove dyes, which is environmentally friendly at the same time [7,11-18]. The adsorption process shows a high efficiency in dye removal, which causes transference of synthetic dyes from wastewater to the solid phase, thus reducing their content in the output wastewater [19–21]. Different types of adsorbents have been employed to eliminate dyes from aqueous solutions [22-24].

The present study was aimed to synthesize MgO supported Fe–Co–Mn nanoparticles (MgO-FCM-NPs) and use them as adsorbent to remove RhB. The evaluation of MgO-FCM-NPs was performed using different techniques such as scanning electron microscopy (SEM), vibration sample magnetization (VSM), X-ray diffraction (XRD), and Fourier-transform infrared spectroscopy (FTIR). The main adsorption parameters such as pH, adsorption dose, temperature, initial RhB concentration and contact time were studied and optimized. Subsequently, the adsorption process were evaluated and reported by different equilibrium and thermodynamic parameters. Finally, the kinetics study of adsorption process was done using various kinetic models to test the experimental data validity.

2. Experimental

2.1. Materials and methods

Chemicals were used without further purification for this work. Mn(NO₃)₂·6H₂O (99%), Co (NO₃)₂·6H₂O (99%), Fe (NO₃)₃·6H₂O (99%) NaOH (98%), HCl (37%) were purchased from Merck. Rhodamine B, basic dye (RhB) with 95% purity and having M = 479.01 g mol⁻¹ was purchased from Sigma (Sigma–Aldrich, UK). The structure of RhB is presented in Fig. S1.

2.2. Synthesis of MgO-FCM-NPs

MgO-FCM-NPs were produced using previously described method with little modification [25]. Briefly, aqueous solutions of Mn(NO₃)₂·6H₂O (99%), Co(NO₃)₂·6H₂O (99%) and Fe(NO₃)₃·6H₂O (99%) were mixed together (with the same molar ratios). Then the 10 wt% of MgO was added to the aqueous solutions and the resulting solution was heated at 70 °C. After that the aqueous solution of Na₂CO₃ (99%) was added drop wise to the solution with constant stirring at the fixed temperature (70 °C) to achieve pH 9. The obtained suspension (after 2 h) was filtered and washed several times by deionize water to remove additive. The resulting precipitate was dried in an oven at 120 °C for 17 h and the synthesized MgO-FCM-NPs was calcined at 600 °C for 6 h.

2.3. Characterization of MgO-FCM-NPs

SEM (Mira 3-XMU apparatus proficient of 700,000 × magnifications) was used to study morphology of nanoparticles. Magnetic property of samples was studied using VSM (VSM, a Kavir Precise Magnetic instrument, Iran). XRD measurements were performed on a Bruker (Model D8 advance, Germany) diffractometer with Cu Ka radiation. FTIR (JASCO 640 plus machine, 4000–400 cm⁻¹) of MgO-FCM-NPs was done to determine functional groups at room temperature using KBr capsules. The nitrogen adsorption isotherm was measured using a Belsorp-mini-II (BEL Japan).

2.4. Preparation of RhB solutions

Stock solution of RhB with concentration of 1000 mg L⁻¹ was made by dissolving 0.5 g RhB per 500 mL of deionized water. Other solutions of the desired concentrations were prepared through continuous dilution of the stock solution. The concentration of RhB after adsorption was measured using UV–vis recording spectrophotometer (Shimadzu Model: CE-1021-UK) at λmax = 550 nm.

2.5. Adsorption experimental design

HCl and NaOH were used to adjust the RhB solutions pHs. The effect of pH was studied at pH 3, 5, 7, 9, 11 and 13 using 100 mg L⁻¹ RhB, 0.1 g L⁻¹ MgO-FCM-NPs and contact time of 40 min at 160 rpm. The effect of MgO-FCM-NPs dosage 0.04–0.12 g L⁻¹ on the RhB adsorption was studied using 200 mg L⁻¹ RhB at the contact time of 40 min and pH 7. Different RhB concentrations (10, 30, 60, 80 and 120 mg L⁻¹) were used to study the influence of initial RhB concentration at different contact time (20, 40, 60, 80 and 100 min) using 0.1 mg L⁻¹ MgO-FCM-NPs at pH 7. The effect of different temperatures (25, 35 and 45 °C) on the RhB was studied at pH 7, 0.1 mg L⁻¹ MgO-FCM-NPs and 60 min stirring. Isotherms were applied on adsorption experiments with different initial concentrations.
of RhB (10–120 mg L\(^{-1}\)) and kinetic tests were performed using various RhB concentrations.

The amount of adsorbed RhB at equilibrium \(q_e\) (mg g\(^{-1}\)) was calculated from the following Eq. 1:

\[
q_e = \frac{(C_o - C_f) V}{m}
\]

(1)

The removal percentage of RhB was calculated using Eq. 2:

\[
R, \% = \left(\frac{C_o - C_f}{C_o}\right) 100
\]

(2)

where \(C_o\) and \(C_f\) (mg L\(^{-1}\)) are the initial and final RhB concentrations, \(m\) (g) is the mass of MgO-FCM-NPs and \(V\) (L) is the volume of the RhB solution.

2.6. **Point of zero charge (pH\(_{\text{pzc}}\)) of MgO-FCM-NPs**

The determination of pH\(_{\text{pzc}}\) of MgO-FCM-NPs was accomplished by the salt addition method using 0.1 M KN\(_O_3\) solution \[26\]. The KN\(_O_3\) solutions of different pHs in the range of 2.0–10.0 were prepared. Then 0.04 g of MgO-FCM-NPs was added to each 20 mL of pH adjusted KN\(_O_3\) solution and agitated for 24 h at 180 rpm. After that the final pH of each solution was measured and the pH\(_{\text{pzc}}\) was estimated by plotting graph between initial pH and the pH difference (\(\Delta\)pH). The pH\(_{\text{pzc}}\) of MgO-FCM-NPs was found to be 5.

3. **Results and discussion**

3.1. **Characterization of MgO-FCM-NPs**

Morphology of MgO-FCM-NPs was characterized by SEM technique and SEM image of MgO-FCM-NPs is shown in Fig. 1A. The SEM image displays that the material consists of nearly spherical articles with changed sizes. The reported study indicates that unsupported Fe–Co–Mn sample has non-uniform texture, but the morphology was changed from non-uniform texture to sphere-like in the presence of supporting agent. The magnetic property of MgO-FCM-NPs was confirmed by VSM tool. Fig. 1B shows the VSM curve of the MgO-FCM-NPs calcined at 600 °C, which is measured at room temperature by VSM tool under the application of magnetic field (8000 Oe). As can be seen, the VSM curve of the nanoparticles indicates that the MgO-FCM-
NPs behave like super paramagnetic. The MgO-FCM-NPs were further examined by XRD technique (Fig. 1C). The Bragg peaks at 2θ values of 30.4° (2 2 0), 35.8° (3 1 1), 37.1° (2 2 2), 43.4° (4 0 0), 54.1° (4 2 2), 57.3° (5 1 1), 63.2° (4 4 0), 71.4° (6 2 0) and 74.1° (5 3 3) are corresponding to JCPDS: 22-1086. The relative intensities and positions of all the peaks suggest that the structure of the product supports the formation of cubic spinel phase.

The results related to characterization of FTIR of the MgO-FCM-NPs is shown in Fig. 1D. As seen in the Fig. 1D, IR of MgO-FCM-NPs after adsorption (red line) shows the absorption band at 657.73 cm⁻¹, which is related to M−O (M=Mn, Co, Fe) bond. The amine group (CH₃−N−CH₃) is dedicated to the absorption peak 1640.6 cm⁻¹. Absorption band at 2068.65 cm⁻¹ and broadband at 3459.14 cm⁻¹ is related to the =C−H aromatic group and the −COOH group of RhB (The interaction of RhB with cluster structure), respectively. In the IR spectrum, of MgO-FCM-NPs before adsorption, the peak at 1548.34 cm⁻¹ is assigned to the M−O bond, which was shifted to the right (657.73 cm⁻¹) in the IR spectrum of MgO-FCM-NPs after adsorption of RhB, which has electronnegative electron groups. An absorption peak at 1662.95 cm⁻¹ can be attributed to the structure of the −OH is due to the M−OH bond and weak band at 3472.80 cm⁻¹ was assigned to presence of H₂O in the structure. Further two extra peaks at 687.7 and 2068.6 are observed in the IR spectrum of RhB loaded MgO-FCM-NPs. The intensity of peak (1641.6) after adsorption is changed which confirms that the amine group plays a role in adsorption of RhB onto MgO-FCM-NPs [24].

The Brunauer–Emmett–Teller (BET) analysis for MgO-FCM-NPs is presented in Fig. S2. The specific BET surface area is estimated to be 59.33 m² g⁻¹. The average pore volume and diameter estimated using the Barrett–Joyner–Halenda (BJH) method are 0.311 cm³ g⁻¹ and 57.34 nm, respectively.

3.2. Effect of initial pH

pH has a considerable effect on dye removal from aqueous solutions, as it affects the superficial charge of the adsorbent, degree of dye ionization, separation of applied groups on the active site of the adsorbent, and molecular structure of the dye [10,27]. The maximum removal of RhB about 93.85% is obtained at pH 7.0. With the increase of pH from 7.0 to 9.0, the extent of removal has diminished from 93.85 to 92.57%. Further rise of pH from 9.0 to 13.0 led to further decrease in the removal of RhB (Fig. 2A). The maximum adsorption capacity of MgO-FCM-NPs is 1877.14 mg g⁻¹ at pH 7 using 100 mg L⁻¹ RhB. For that reason, all further experiments are approved out at pH 7.0.

It seems that changes in the pH caused formation of different ionic species on different surfaces of the adsorbent and
at neutral pH, RhB ions enter the structure of the pores of the MgO-FCM-NPs. According to the pHpzc obtained for MgO-FCM-NPs, which is equivalent to 5, the pH less than pHpzc causes dominance of positive charge on the adsorbent surface. On the other hand, at low pH of the dye solution, H⁺ ions dominate the adsorbent site, whereby the adsorbent surface becomes more positive and the repulsive force between the cationic RhB and the MgO-FCM-NPs surface grows, culminating in diminished removal [28]. However, at higher pH, zwitterions are formed causing accumulation of RhB in aqueous solutions, creating a larger molecular form, which is unable to permeate into the MgO-FCM-NPs structure [29]. Nevertheless, further elevation of pH above the pHpzc makes the MgO-FCM-NPs surface negative, causing enhanced attractive force between MgO-FCM-NPs surface and cationic RhB [28].

3.3. Effect of adsorbent dosage

The adsorbent dose is another important and highly influential parameter affecting the adsorption process and adsorption capacity. Therefore, the effect of the adsorbent dose within the range of 0.04–0.12 g L⁻¹ is studied and it is observed that the adsorption efficiency is increased from 98.50 to 98.79% when adsorbent dose is increased from 0.04 to 0.12 g L⁻¹ (Fig. 2B). The adsorption capacity decreases from 2462.5 to 823.273 mg g⁻¹ with the increase in adsorbent dosage from 0.04 to 0.12 g L⁻¹.

The increased dye removal percentage can be qualified to the enhanced adsorption surface and increased quantity of available sites for its adsorption. As previously mentioned by researchers [11], with elevation of adsorbent dose to more than 0.1 g L⁻¹, RhB removal level diminished. The reduction of adsorption capacity with elevation of the adsorbent dose of MgO-FCM-NPs can be attributed to the concentration of RhB, volume and saturation of adsorption sites by the interaction of particles such as accumulation across the entire surface and increase in the path length diffusion [30]. Furthermore, due to the gap in the concentration developed between the dye concentration on the adsorbent surface and solution, the adsorption capacity falls [31].

3.4. Effect of contact time and initial dye concentration

The significance of the initial dye concentration of RhB (10–120 mg L⁻¹) on adsorption of RhB onto MgO-FCM-NPs is observed at optimized conditions (adsorbent dosage = 0.1 g L⁻¹, pH = 7) at different contact times. It is detected that with the change in the initial RhB concentration the percentage removal changes from 95 to 92.20% with the change in the initial RhB concentration (Fig. 3A) as inversely proportional, while the actual quantity of RhB sorbed per unit mass of MgO-FCM-NPs increases from 95 to 1106.42 mg g⁻¹ at 60 min, 25 °C (Fig. 3B).

The available sites on the adsorbent become confined when the percentage removal decreased at higher concentration. However, with the increase in RhB concentration the adsorption capacity also increased, that may be due to higher adsorption rate and application of all accessible adsorption sites at higher concentrations [32]. The Fig. 3A shows that at 20–100 min the RhB acceptance was rapid. The percent removal increases from 93.57 to 95% when time increased from 20 to 60 min and attaining equilibrium in 60 min, which became slower during 60–100 min. This is anticipated because at the initial step there is a large number of sites is available for the adsorption of RhB while after passing time the remaining surface sites are difficult to occupy because of repulsion between RhB molecules of the solid and mass phases [11,32].

3.5. Effect of temperature

The temperature of the solution is one of the important and major factors that affect the adsorption system. It may also affect the adsorbent suitability when the removal efficiency of various pollutants from aqueous solution is temperature dependent and may also disturb the suitability of adsorbent [33]. Effluents of the different dyes are created at relatively high temperatures [34]. Therefore, to conclude the temperature effect, the adsorption process is studied at different temperature as 25, 35 and 45 °C. As it is shown in Fig. 4B, the adsorption capacity changes linearly with the change in temperature. The maximum adsorption capacity increases from 87.28 to 94 mg g⁻¹ with the increase in temperature from 25 to 45 °C. The percentage of adsorption became higher with temperature (Fig. 4A), which shows that the adsorption method of RhB onto MgO-FCM-NPs is endothermic.

Enhanced MgO-FCM-NPs adsorption capacity at higher temperatures can be recognized to increased movement and permeation of the dye substance in the adsorbent porous structure to overcome the activation energy obstacle [35,36].

3.6. Analysis of adsorption thermodynamic

The thermodynamics parameters are studied from temperature 25 to 45 °C. They reflect the possibility and spontaneity of processes, endothermicity or exothermicity of the actions as well as changes in the entropy during the adsorption [37]. Thermodynamic parameters such as the Gibbs free energy
In Fig. 3.7. of entropy change where adsorption and adsorption (dose = 0.1 g L\(^{-1}\), 10 mg L\(^{-1}\) RhB, temp = 25 ± 2 °C and pH = 7).

\[
\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \tag{3}
\]
\[
\Delta G = -RT \ln K_e \tag{4}
\]
\[
K_e = \frac{C_o}{C_e} \tag{5}
\]
\[
\ln K_e = \frac{\Delta S^\circ}{R} + \frac{\Delta H^\circ}{RT} \tag{6}
\]

where \(T\) is absolute temperature in Kelvin, \(R\) is the general gas constant, \(C_o\) is the initial concentration of dye, \(K\) is the distribution coefficient for the adsorption and \(C_e\) is the concentration of dye which is adsorbed at equilibrium (mg L\(^{-1}\)). The values of \(\Delta H^\circ\) and \(\Delta S^\circ\) are obtained from the slope and intercept of the plot between \(\ln K_e\) and \(1/T\) (van’t Hoff plot).

The results presented in the Table 1 suggest that enthalpy change of the RhB adsorption onto MgO-FCM-NPs is positive and thus the process is endothermic, which is a reason for the strong interaction between the MgO-FCM-NPs and RhB. Further, with rise in temperature causes enhanced maximum adsorption capacity of the adsorbt. The positive value of entropy change represents enhanced entropy on the solid-solution interface during the adsorption and development of some structural changes in the MgO-FCM-NPs and RhB, and thus irreversibility of the adsorption [38,39]. The negative values of the Gibbs free energy represent spontaneity of the reaction [40]. Elevation in \(\Delta G^\circ\) with temperature enhances the extent of adsorption and at higher temperatures, the dye becomes hydrated faster and its adsorption increases [41].

### 3.7 Adsortion isotherms

In order to show the interactive behavior between sorbate and sorbent the equilibrium sorption isotherm is fundamental and important. The isotherm records are estimated by putting them into Freundlich, Langmuir and Temkin isotherm models to check out the appropriate model that could be used for design consideration [11,33]. Langmuir isotherm equation is used to get the maximum monolayer adsorption capacity of RhB adsorption onto MgO-FCM-NPs. While the Freundlich isotherm is used to investigate the multilayer sorption that obtain through heterogeneous distribution of active sites. Temkin isotherm shows a micro-porous adsorbent surfaces and the area heterogeneity might be qualified to the whole structure as well as sorbate-adsorbent interaction. The all three isotherms are represented by the following equations [42–44]:

\[
\text{Langmuir} \quad \frac{1}{q_e} = \frac{1}{q_{lm}} + \frac{1}{K_L q_{lm} C_e} \tag{7}
\]
\[
\text{Freundlich} \quad \log q_e = \log K_f + \frac{1}{n} \log C_e \tag{8}
\]
\[
\text{Temkin} \quad q_e = B \ln K_T + B \ln C_e \tag{9}
\]

The main representative of Langmuir isotherm is a constant, which is called equilibrium parameter (\(R_L\)), which is represented by the following relation:

\[
R_L = \frac{1}{1 + BC_o} \tag{10}
\]

where \(C_o\) represents the RhB concentration, which is here 120 mg L\(^{-1}\) and \(R_L\) represents the type of isotherm. For desirable adsorption \(0 < R_L < 1\); for undesirable adsorption \(1 < R_L\), for linear adsorption \(R_L = 1\) and for the reversible adsorption \(R_L = 0\) [27].

The isotherm parameters and \(R^2\) values for Langmuir, Freundlich and Temkin models are calculated from slopes and intercepts by plotting \(1/C_e\) versus \(1/q_e\) (Fig. 5A), log \(C_e\) versus log \(q_e\) (Fig. 5B) and \(\ln C_e\) versus \(q_e\) (Fig. 5C), respectively. The \(R^2\) and isotherms constants obtained from RhB adsorption on MgO-FCM-NPs is presented in Table 2. The \(R^2\) value obtained from Langmuir model is higher compared to Freundlich and Temkin models. Further the theoretical adsorption capacity calculated from Langmuir model is in close agreement to experimental adsorption capacity. This equilibrium information indicates that the dye adsorption process follows Langmuir model so it is certain that at surface of MgO-FCM-NPs is monolayer coverage of RhB. Further \(R_L\) value ranges between 0 and 1 and \(n\) (Freundlich constant) value between 1–10, suggesting desirable adsorption of RhB onto MgO-FCM-NPs. From the Temkin isotherm model, the higher value of \(B\) demonstrates a strong interaction force between RhB and MgO-FCM-NPs.

#### 3.8 Comparison of Langmuir monolayer adsorption capacity with other adsorbents

An evaluation of RhB adsorption capacity onto MgO-FCM-NPs with other reported adsorbents is done and presented in Table 3. It is observed that the MgO-FCM-NPs has exceptionally higher adsorption capacity for RhB compared to other previously reported adsorbents. Thus MgO-FCM-NPs is an efficient and potential adsorbent to remove RhB from aqueous solution.
Table 1 – Thermodynamic factors for the adsorption of RhB onto MgO-FCM-NPs.

<table>
<thead>
<tr>
<th>( C_e ) (mgL(^{-1}))</th>
<th>( T ) (K)</th>
<th>( K_w ) (L g(^{-1}))</th>
<th>( \Delta G^\circ ) (kJ mol(^{-1}))</th>
<th>( \Delta H^\circ ) (kJ mol(^{-1}))</th>
<th>( \Delta S^\circ ) (J mol(^{-1})K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>298</td>
<td>130.1</td>
<td>–12.06</td>
<td>9.440</td>
<td>72.00</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>139.0</td>
<td>–12.64</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>165.1</td>
<td>–13.50</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 5 – Langmuir (A), Freundlich (B) and Temkin (C) models for adsorption of RhB by MgO-FCM-NPs.

3.9. Adsorption kinetics

Regarding the reactor system and its design, the changes in the rate and extent of changes occurring in the reactor should be specified. Thus, adsorption kinetics is studied for predicting adsorption rate, which is important for the proposal and modeling of the process as well as for determining the process of controlling adsorption mechanism [11,55].

In the first-order kinetic, it is expected that the rate of changes in the RhB uptake is directly related to the changes in the saturation concentration and the extent of adsorption uptake over time. The assumption in the second order kinetic model is that the adsorption process can be controlled by chemical adsorption. The pseudo first, pseudo second and modified Ritchie’s second-order model are represented in Eqs. 11–13 [56–60].

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

(11)

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

(12)

\[
\frac{1}{q_t} = \frac{1}{k_3 q_e} + \frac{1}{q_e} 
\]

(13)

Table 2 – Equilibrium parameters for Langmuir, Freundlich and Temkin models.

<table>
<thead>
<tr>
<th>Models</th>
<th>Parameters</th>
<th>Values</th>
<th>Definition of parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>( q_m )</td>
<td>2791</td>
<td>( K_l ): Langmuir constant of energy adsorption (L mg(^{-1}))</td>
</tr>
<tr>
<td></td>
<td>( K_l )</td>
<td>0.070</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( q_e )</td>
<td>0.999</td>
<td>( q_m ): Maximum adsorption capacity (mg g(^{-1}))</td>
</tr>
<tr>
<td>Freundlich</td>
<td>( K_r )</td>
<td>181.4</td>
<td>( K_r ): An indicator for adsorption capacity</td>
</tr>
<tr>
<td></td>
<td>( n )</td>
<td>1.197</td>
<td>1/n: Adsorption intensity</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.993</td>
<td></td>
</tr>
<tr>
<td>Temkin</td>
<td>( K_r )</td>
<td>0.998</td>
<td>( K_r ): Maximum binding energy (L g(^{-1}))</td>
</tr>
<tr>
<td></td>
<td>( B )</td>
<td>330.6</td>
<td>( B ): Constant of binding energy</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.925</td>
<td>heat (J mol(^{-1}))</td>
</tr>
</tbody>
</table>
Fig. 6 – Pseudo first order (A) and second order (B) kinetics models for adsorption of RhB by MgO-FCM-NPs.

Fig. 7 – Modified Ritchie’s-second-order model for adsorption of RhB by MgO-FCM-NPs.

where \( q_t \) (mg g\(^{-1}\)) is the adsorption of RhB on different time intervals, \( k_1 \) (min\(^{-1}\)) is the rate constant of first-order, \( k_2 \) is the rate constant of second-order and \( k_r \) is the rate constant of the modified Ritchie’s-second-order kinetic model. The values of \( q_e \) and \( k_1 \) for pseudo first order are estimated from the intercepts and slopes of plots between \( \log (q_e - q_t) \) versus \( t \) (Fig. 6A), \( q_e \) and \( k_2 \) for pseudo second order are estimated from slopes and intercepts of plots between \( t/q_t \) versus \( t \) (Fig. 6B) and \( q_e \) and \( k_r \) for modified Ritchie’s-second-order are calculated from intercepts and slopes of plots between \( 1/q_t \) versus \( 1/t \) (Fig. 7).

The values of \( R^2 \) and kinetic parameters are shown in Table 4. A comparatively high \( R^2 \) values and closeness between experimental \( q_e \) and the models expected \( q_e \) values specifies that the pseudo second order model effectively describe the adsorption process of RhB onto MgO-FCM-NPs.

In order to obtain more detailed information about adsorption mechanism and for describing rate influential step of

Table 4 – Kinetics parameters for pseudo first, pseudo second, modified Ritchie’s-second-order and intra-particle diffusion models.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>RhB (mg L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Pseudo first order</td>
<td></td>
</tr>
<tr>
<td>( q_e ) (mg g(^{-1}))</td>
<td>0.960</td>
</tr>
<tr>
<td>( k_1 ) (min(^{-1}))</td>
<td>3.925</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.9823</td>
</tr>
<tr>
<td>Pseudo second order</td>
<td></td>
</tr>
<tr>
<td>( q_e ) (mg g(^{-1}))</td>
<td>95.42</td>
</tr>
<tr>
<td>( k_2 ) (g mg(^{-1}) min(^{-1}))</td>
<td>0.0259</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.9999</td>
</tr>
<tr>
<td>Modified Ritchie’s-second-order</td>
<td></td>
</tr>
<tr>
<td>( q_e ) (mg g(^{-1}))</td>
<td>95.51</td>
</tr>
<tr>
<td>( k_r )</td>
<td>2.385</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.9982</td>
</tr>
<tr>
<td>Weber–Morris (intra-particle diffusion model)</td>
<td></td>
</tr>
<tr>
<td>( k_{ip} ) (mg g(^{-1}) min(^{-1/2}))</td>
<td>0.278</td>
</tr>
<tr>
<td>( C )</td>
<td>92.50</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.9234</td>
</tr>
</tbody>
</table>

Fig. 8 – Intra-particle diffusion model for adsorption of RhB by MgO-FCM-NPs.

RhB adsorption onto MgO-FCM-NPs, the intra-particle diffusion model is applied. The Eq. 14 represents this model [61].

\[
q_t = k_{ip} t^{1/2} + C \tag{14}
\]

where \( k_{ip} \) is the intra-particle diffusion rate constant (mg g\(^{-1}\) min\(^{-1/2}\)) and \( C \) is intercept. The values of \( k_{ip} \) and \( C \) are estimated from slop and intercept of plots between \( q_t \) versus \( t^{1/2} \) (Fig. 8) and are presented in Table 4. The plots between \( q_t \) and \( t^{1/2} \) show linear relationship, which means the adsorption process of RhB onto MgO-FCM-NPs is controlled by intra particle diffusion only [36,62].

3.10 Desorption study

The desorption study of RhB onto MgO-FCM-NPs is performed using mixture of acetic acid/ethanol (5% (v/v)) and the results are shown in Fig. S3. The adsorbent is regenerated and again re-used to adsorb RhB and the process is repeated three times. It is observed that the adsorption capacity is decreased after
second and third cycle and the MgO-FCM-NPs retains 61 and 53% adsorption capacity after second and third cycle. Thus, the MgO-FCM-NPs have the ability to regenerate and could be reused but it still needs further modification to improve its reusability for the dyes removal. Also in the next study we will use other combinations of solvents to increase the desorption of RhB from MgO-FCM-NPs.

4. Conclusions

In summary, the –Co–MgO-FCM-NPs are synthesized and characterized by means of SEM, VSM, XRD, and FTIR. Magnetic characterization of MgO-FCM-NPs by VSM tool indicates that NPs have super magnetic property. The efficacy of MgO-FCM-NPs as a nano-adsorbent is studied for the removal of RhB from aqueous solution. The maximum adsorption capacity of RhB onto MgO-FCM-NPs is found to 1106 mg·L⁻¹ using 120 mg·L⁻¹ RhB concentration which is the highest capacity for RhB reported so far. The best pH is found to be 7 where maximum adsorption of RhB is observed onto MgO-FCM-NPs. The equilibrium is reached in 60 min and maximum adsorption is observed in 100 min. The results indicate that adsorption of RhB on nanoparticle surface increases with temperature, which shows that the adsorption process of RhB on surface of MgO-FCM-NPs is endothermic, which further is confirmed by the values of ΔG° and ΔH°. The results show that the experimental data is best described by the pseudo-second kinetic order and Langmuir isotherm models. Hence, it can be concluded that the adsorption by MgO-FCM-NPs is a proficient and reliable method for Rhb removal from aqueous solutions.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgement

A. Rahdar would like to thank the University of Zabol, Zabol, Iran for financial support (UOZ-GR-9618-40) for this work. S. Rahdar and S. Ahmadi would like to thank the Zabol University of Medical Sciences, Zabol, Iran for financial support (Grant No. IR.ZBMU.REC-1398-018).

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jmrt.2019.06.041.

REFERENCES


[21] Asfaram A, Ghaedi M, Dashtian K, Ghezelbash GR. Preparation and characterization of Mn0.4Zn0.6Fe2O4 nanoparticles supported on dead cells of Yarrowia lipolytica as a novel and efficient adsorbent/biosorbent composite for the removal of azo food dyes: central composite design optimization study. ACS Sustain Chem Eng 2018;6:4549–63.


Alqadami AA, Naushad M, Alothman ZA, Ghfar AA. Novel metal-organic framework (MOF) based composite material for the sequestration of U(VI) and Th(IV) metal ions from aqueous environment. ACS Appl Mater Interfaces 2017;9:36026–37.

