Synthesis of Molecularly Imprinted Polymer on Magnetic Core-Shell Silica Nanoparticles for Recognition of Congo Red

Nooshin Nikzad Harsini 1, Mehdi Ansari 2, Maryam Kazemipour 1*

1 Department of Chemistry, Kerman Branch, Islamic Azad University, Kerman, IRAN
2 Department of Drug and Food Control, Faculty of Pharmacy, Kerman University of Medical Sciences, Kerman, IRAN

Received 20 August 2017 • Revised 14 November 2017 • Accepted 24 January 2018

ABSTRACT
The extraction of Congo red from aqueous media is reported by a synthesized magnetic molecularly imprinted polymer. This polymer was prepared by coating of synthesized molecularly imprinted polymer on pre-prepared amino-modified Fe3O4 nanoparticles (Fe3O4@NH2-SiO2) surface. Coating process was done through the chemical coprecipitation method by use of acrylamide as functional monomer, N, N’-methylenebisacrylamid as cross-linking agent, ammonium persulfate as initiator and N, N, N’, N’-tetramethylethylenediamine as co-initiator in the presence of Congo red. The polymer was characterized by Field emission scanning electron microscope, Fourier transform infrared spectrometer, vibrating sample magnetometer, X-ray diffraction, and re-binding experiments. In addition, more investigations were performed including isotherms, adsorption kinetics, competitive adsorption and reusability. The results proved the sensitivity of the prepared polymer toward magnetic field. Accordingly, it can be easily removed by an external magnet. It demonstrated effective recognition selectivity as well as ability to simultaneous separation and enrichment of Congo red.

Keywords: Fe3O4@NH2-SiO2 nanoparticles, magnetic molecularly imprinted polymers, Congo red

INTRODUCTION
Concern about environmental pollutions is raising dramatically as the rate of population growth increase. Considerable efforts have been dedicated to the elimination of various pollutants from environment [1]. Dyes are important and inseparable ingredients in diverse industries including textile, paints, carpet, cosmetics, pharmaceuticals, papers and printing [2]. They have dicey reputation because of their toxicity, carcinogenic and mutagenic effects on both human and aquatics [3]. The existence of trace concentrations of dyes (less than 1 ppm) is observable and unfavorable, and it is necessary to remove from sewage before entering the environment. In addition, “colored effluent” can affect photosynthetic processes of aquatic plants, reducing oxygen levels in water and in severe cases, resulting in the suffocation of aquatic flora and fauna” [4, 5]. Among dyes, Congo red (CR) as an anionic dye is attractive and widely being used. However, the water and waste waters contaminated with CR need to be refined well before draining off into environment to ensure the elimination of CR which is capable to metabolized to carcinogenic agents such as benzidine derivatives. Therefore, from the health and environmental point of view, the importance of CR removal from the wastewaters by cost-effective approaches has been highlighted [6]. Different physical and chemical methods have been applied in order to eliminate dyes from effluents featuring chemical precipitation [7], chemical oxidation [8], adsorption [9], microbial or enzymatic treatment [10], and photocatalysis [11], which among them some methods like adsorption on mineral composites [12], sorbents made by natural materials [13, 14], and simple dual molecularly imprinted polymers (MIPs) [15] attempted to remove or analyze CR. Although, none of these methods can completely remove dye molecules from aqueous solution. Nevertheless, the adsorption technique has been determined as more effective method in dyes elimination. In this method, the cost of the adsorbent and its regeneration is challenging. The MIPs benefit from considerable prominent characterizations such as high selectivity, easy, fast and cost-effective preparation and
physical and thermal stability [16]. Due to these properties MIPs have received wide interest from scientific
community, recently. Comparing new and traditional MIPs, the later have demerits including poor selectivity, low
mass transfer and binding capacity, and inefficient template removal [17-19]. In fact, the main drawbacks are related
to undesirable kinetics of the sorption/desorption process and mass transfer speed. To overcome these restrictions,
surface imprinted core-shell nanoparticles (NPs) have been introduced.

Separation based on magnetic field by nano and microparticles have attracted much attention because of
excellent superiorities such as suitable dispersion, fast and effective binding to target, reversible and controllable
flocculation. The procedure magnetic separation is directly applicable in samples containing either suspended
solids or biological particulates. This process is time saving and easier method, due to the elimination of
centrifugation, filtration, and membrane separation stages in sample pretreatment. In addition, this method of
separation is not only efficient and useful in laboratory but also in large scale operations. The surface of magnetic
NPs need to be modified before application. The MIPs which covered the magnetic NPs is used in convenient
separation and concentration of chemicals simply by use of an external magnetic field. Combination the merits of
magnetic NPs and molecular imprinting lead to valuable and potent analytical method high selectivity, flexibility
and simplicity [20]. Although there is a report regarding the use of magnetic particles for CR degradation [21], but
the main aim of this study was to incorporate the surface imprinting and nano techniques in the preparation of
uniform core-shell structure of Fe3O4@SiO2-NH2 MIPs for the extraction and removal of CR from aqueous solutions.
The effective factors on the maximum extraction is also investigated.

EXPERIMENTAL

Materials and Reagents

CR, N,N’ -methylenebisacrylamide (MBA), Ammonium persulfate (APS), Eosin (Eo), Malachite green (MG),
Methyl orange (MO) and Methyl red (MR) were purchased from Sigma-Aldrich Company (Germany). Glacial acetic
acid, Methanol, Acetonitrile, were purchased from Merck (Germany). 3-aminopropyl-triethoxysilane (APTES) was
obtained from Kayon Biological Technology Co. Ltd. (Shanghai, China). Iron (II) dichloride and iron (III) chloride
were obtained from Chemicals Co. Ltd. (Tianjin, China). Acrylamide (AAM) and N, N, N’, N’-
tetramethylmethylethylenediamine (TEMED) purchased from Merck (Germany).

Distilled water used was prepared from a Millipore Milli-Q purification system. (Millipore, Bedford, MA, USA).
A stock solution of 100 mg L\(^{-1}\) of CR was prepared in double distilled water and used for the preparation of other
concentration through consecutive dilutions.

Instruments

Morphology and the size of the synthesized polymer particles was attained by a Field emission scanning
electron microscopy (MIRA3/TESCAN Company, Czech Republic). Fourier transform infrared (FT-IR) spectra
were recorded on an FTIR spectrophotometer instrument (Bruker, Alpha, Germany). The vibrating sample
magnetometer (VSM) was carried out using a (Lake Shore Company, USA) instrument. X-ray diffraction (XRD)
study was conducted by D/max2400 (PANalytical X’Pert PRO).

Chromatographic Conditions

The chromatography analysis was carried out using an Agilent Technologies 1200 series liquid chromatography
system including a binary pump with two solvent lines, column oven, auto-sampler and photodiode array detector.
CR was separated on a XDB-C18 column (4.6mm×25cm, Agilent). The detector was set at a wavelength of 500nm.
The mobile phase which filtered before use was acetate buffer (10mM, pH 3) with acetonitrile in a 30:70 volumetric
ratio, and with a constant flow rate of 1ml min\(^{-1}\). All experiments were conducted at 40°C.

Preparation of Amino-modified Magnetic NPs

Synthesis of Fe3O4 NPs

In a three-neck flask containing 150 mL highly purified water, 0.2 g FeCl\(_2\)-4H\(_2\)O and 5.3 g FeCl\(_3\)-6H\(_2\)O were
added under nitrogen atmosphere while the mixture was heating and stirring. After the temperature reached 80
°C, 25 mL ammonium solution was added drop wise and stirred for 6 h. The product was collected by an external
magnetic field. Then, the collected product was added to a solution containing100 mL solution of sodium citrate
0.2 M using ultrasonic vibration for 5 min. Then, the product was separated by a magnet. The final black precipitate
product was separated by a magnet and washed with highly purified water until reaching neutral pH. Finally, it
was washed with ethanol, and dried in oven a 60 °C [22].
Synthesis of amino-modified Fe₃O₄ NPs (Fe₃O₄@SiO₂-NH₂)

In a typical procedure, 0.4 g Fe₃O₄ NPs were dispersed in 150 mL ethanol/H₂O with volume ratio of 1:1. While this mixture was stirring vigorously (300 rpm), droplet of 0.5 mL APTES was added. The pH value was controlled at 4.0 with glacial acetic acid. The reaction mixture was stirred at 60 ºC for 3 h, in a nitrogen purged atmosphere. The final black precipitate product was collected by a magnet and washed with highly purified water until reaching to pH of 7. Finally, the product of amino-modified Fe₃O₄ NPs was dried in oven [22].

Preparation of the core–shell MMIP and MNIP

0.1 g Fe₃O₄@SiO₂-NH₂, 1.6mmol AAm (monomer), 16mmol MBA (crosslinker), and 0.01mmol CR (template) were dissolved in 40mL of distilled water in a glass flask. In this method, the mixture of reagents was stirred for 2 h, and then 0.4 mL of ammonium persulfate solution 4% and 0.4 mL TEMED were added. The reaction mixture was purged with nitrogen. Then, the flask was immediately sealed and polymerization continued under stirring at 500rpm at room temperature for 24 h. The MMIP particles washed using methanol and acetic acid (9:1 v/v) for CR removal. Magnetic non-molecular imprinted polymer (MNIP) were prepared by the same method in the absence of CR. At final step, the obtained particles dried in an oven at 40°C.

Characterization

FTIR

The surface properties of the nanoparticles were investigated by transferring the dry samples onto the sample plate of the FTIR instrument. FTIR spectra were recorded in powder form in KBr discs in the range of 4000-400cm⁻¹.

FESEM

Surface morphologies of both MMIP and MNIP were analyzed by FESEM over a selected area, under high vacuum condition at 10 and 15kv. Spatial variations will be shown from 150kx-250kx magnification.

VSM

In order to study the superparamagnetic properties of the magnetized particles, the VSM was applied. Magnetic measurements were carried out with a using a 7410 VSM at room temperature.

XRD

Crystalline structure of MMIP was identified using XRD with the with cu kα source (λ=0.15406). Data collection was done using a scintillation counter between in the range of 10–80° with speed of 4°/min. The 2θ angels probed were from of 10–80°.

Binding experiments of MMIP and MNIP

50mg MMIP or MNIP was dispersed in 50 ml of a CR dye solution with certain concentration (25 mgL⁻¹) separately. Then the mixture was shaken in an ultrasonic (3min). The supernatants and polymers were separated by an external magnetic field. The concentration of CR in the supernatant solution was measured.

The adsorption capacity of MMIP or MNIP for CR was calculated using the following equation 1:

\[ Q = (C_0 - C_f)V/m \]  

where \( Q \) (mg g⁻¹) is the amount of CR adsorbed by the MMIP or MNIP, \( C_0 \) (mg mL⁻¹) is the initial concentration of CR, \( C \) (mg mL⁻¹) is the template molecule concentration of the supernatant solution after adsorption, \( V \) (mL) is the volume of the initial CR solution, \( m \) (g) is the weight of the MMIP or MNIP. The specific recognition properties of MMIP and MNIP respect to template were determined by imprinting factor (\( \alpha \)) equation 2, as follow:

\[ \alpha = Q_{MMIP}/Q_{MNIP} \]
The selectivity factor ($\beta$) is defined as equation 3:

$$\beta = \alpha_{\text{tem}} / \alpha_{\text{ana}}$$

(3)

Where $\alpha_{\text{tem}}$ is the imprinting factor toward the template molecule and $\alpha_{\text{ana}}$ is the imprinting factor toward the analogue [23].

**Effect of pH, concentration, time and amount of sorbent on removal of CR**

The pH of solution was varied in the range of 3-10 by 0.1 mol L$^{-1}$ NaOH or 0.1 mol L$^{-1}$ HCl solutions. The adsorption experiments were performed by adding 50 mg adsorbents with 50 mL of 25 mg L$^{-1}$ CR solution in ultrasonic for 3 min. The supernatant was separated by an external magnetic field and its remaining CR content was determined.

For optimizing the concentration effect, isothermal binding experiments were performed by addition of 50 mg MMIP or MNIP to 50 mL CR at various concentrations of 10, 15, 25, 35 and 45 mg L$^{-1}$. The supernatants and polymers were separated by an external magnetic field and the concentration of CR in the supernatants was estimated.

In the adsorbent amount experiments, the adsorption was carried out by using 10, 25, 50, and 75 mg of MMIP or MNIP in 50 mL CR 25mgL$^{-1}$ solution. The adsorption experiments were performed under shaking in ultrasonic bath for 3 min and CR concentration in separated supernatant solution was assessed.

In Kinetic experiments, 50 mg of MMIP and MNIP were added to solution of 50 mL CR (25mgL$^{-1}$). Then the mixture was shaken in an ultrasonic bath in different times of 10, 30, 60, 180, and 300 seconds. The supernatants and polymers were separated by an external magnetic field and CR concentration in separated supernatant solution was measured.

**Specific recognition of MMIP and MNIP**

In order to study the selectivity of MMIP and MNIP, other probable interfering dyes were introduced and the experiments were repeated under optimized conditions. For this purpose, MMIP or MNIP (0.05g) were added to a 50 mL of dyes such as MR, MG, EO and MO solutions (25mgL$^{-1}$). The supernatant and polymers were separated using an external magnetic field, and the amount of CR and other dyes were measured.

**Adsorption kinetic**

The effect of contact time (10, 30, 60, 180, and 300 seconds) on the removal efficiency of CR was investigated. According to the results, the adsorption kinetics CR conform to on pseudo-first order kinetic and pseudo-second-order kinetic model which can be expressed according to equation 4,5 as follow [24]:

$$
\ln \left( \frac{Q_e}{Q_t} \right) = k_1 t
$$

(4)

$$
\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}
$$

(5)

The correlation coefficient was the criterion for the applicability of each model.

**Isotherm study**

The imprinted magnetic nanoparticles were tested for the recognition ability toward the template CR. The adsorption isotherms of MMIP and MNIP were investigated at different concentration of CR in the range 10-45mgL$^{-1}$ [25], and the data were analyzed by Langmuir, Freundlich, DR, Temkin equations, respectively.

Further process on saturation binding data was performed with Langmuir equation in order to assess the binding properties of the MMIP and MNIP. The Langmuir equation is as follows equation 6:

$$
\frac{C_e}{Q_e} = \frac{C_e}{Q_{\text{max}}} + \frac{1}{(b Q_{\text{max}})}
$$

(6)

In which $C_e$ is the free analytical concentration at equilibrium of CR (mg mL$^{-1}$), $Q_e$ (mg g$^{-1}$) is the amount of CR bound to MMIP at equilibrium, $Q_{\text{max}}$ is the apparent maximum adsorption capacity (mg g$^{-1}$), and $b$ is the Langmuir adsorption equilibrium constant (mL mg$^{-1}$) [26]. The values of $b$ and $Q_{\text{max}}$ can be calculated from the slope and intercept of the linear plotted in $C_e/Q$ versus $C_e$.

Also, in this study, Freundlich isotherm equation was used to model the experimental binding data.
Freundlich model is described by the equation 7:

$$\log Q_e = \log \alpha + m \log C_e$$  (7)

where $Q_e$ (mg g$^{-1}$) is the amount of adsorbed analyte per unit of polymer mass, and $C_e$ (mg mL$^{-1}$) was the concentration of the analyte in solution. The constant $\alpha$ is a measure of the capacity and the average affinity. The parameter $m$ is the heterogeneity index, with values from 0 to 1, indicating homogeneity of the sites. In fact, $m$ becomes closer to 1 as heterogeneity decreases, a homogeneous system has $m=1$ [27].

In order to further analyze the isotherms of MMIP with a high degree of rectangularity, Dubinin–Radushkevich isotherm model is considered, and it is described as follows equation 8:

$$\ln Q_e = \ln Q_m - K_{DR} \varepsilon^2$$  (8)

where $\varepsilon$ can be correlated as equation 9:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e}\right)$$  (9)

where $R$ is the gas constant (8.314 Jmol$^{-1}$ k$^{-1}$) and $T$ is the absolute temperature. A plot of $\ln Q_e$ versus $\varepsilon^2$ enables the determination of the constants $Q_m$ and $E$ to be obtained. The constant $K_{DR}$ is related to free energy ($E$, kJmol) of adsorption per molecule of the adsorbate when it is transferred to the surface of the sorbent from the solution and can be calculated by equation 10 [28]:

$$E = \frac{1}{(2K_{DR})^{1/2}}$$  (10)

One of the most popular isotherms that is used to treat adsorption data is Temkin isotherm which is given as equation 11:

$$q_e = B_T \ln(A_T) + B_T \ln(C_e)$$  (11)

where $A_T$ represents the Temkin isotherm equilibrium binding constant (L g$^{-1}$ polymer), which corresponds to the maximum binding energy, and $B_T$ is the Temkin isotherm constant related to heat of adsorption (J mol$^{-1}$) [29].

**Optimization of desorption conditions**

Desorption of CR from MMIP was studied in batch experimental set-up. Typically, 50mg of MMIP was added to 50ml of 25mg L$^{-1}$ CR solution. In the next step MMIP containing CR was separated by filtration and washed with distilled water to remove free CR. The filtrate was dried at ambient temperature and was used in desorption studies.

After separating of polymer it was washed, dried and weighed. The effect of various parameters such as kind and amount of solvent, temperature, pH, and time on desorption of CR from MMIP (42 mg) were studied.

Effect of solvent type on desorption process was studied by addition of MMIP(42mg) with different solvents including water, 0.1 mol L$^{-1}$ NaOH, 0.1 mol L$^{-1}$ HCl, methanol, ethanol, methanol-water(20:80 v/v,50-50 v/v, and 80-20 v/v). Influence of pH on desorption in methanol-water (80:20 v/v) mixture was studied in the range of 3-12. Effect of temperature on desorption of CR from MMIP (42mg) was investigated from ambient temperature to 75°C. Effect of solvent volume on desorption process was assessed in the range of 3 to 10 ml. To investigate effect of time on the desorption process, experiments were performed in the range of 5 to 15 minutes.

**Reusability**

To estimate the reusability of MMIP, 0.05 g MMIP was added to 50ml CR 25mgL$^{-1}$ in ultrasonic bath for 3min. MMIP were separated by an external magnet. Recovered particles was eluted with 10ml of methanol-water (80:20 ml) for 15min at 45 C. The final well washed with distilled water and dried isolated polymer particles, were reused for adsorption of CR. The cycle of adsorption regeneration was repeated 5 times [30].

**RESULTS AND DISCUSSION**

**Preparation of MMIP and MNIP**

Fe$_3$O$_4$NPs were synthesized by a co-precipitation method. Then, the modification of Fe$_3$O$_4$ NPs was done APTES to make Fe$_3$O$_4$@SiO$_2$-NH$_2$. This modification causes the reduction in magnetic dipole attraction of the magnetite NPs which leads to improvement in dispersity of magnetite NPs. Moreover, the surface silica-NH$_2$ can be easily modified for bioconjugation purpose by various groups. Further, the surface amino groups of Fe$_3$O$_4$@SiO$_2$-NH$_2$ were reacted with the functional monomer (AAM). The MIPs shells were coated on the surface of Fe$_3$O$_4$@SiO$_2$-NH$_2$.
by the copolymerization of functional monomer (AAM), cross-linking agent (MBA), the initiator (APS) and co-initiator (TEMED) in the presence of template molecule (CR). Finally, after the templates were removed, the MMIP were obtained. Accordingly, it is expected that MMIP provide the recognition sites for CR with ease of removal from solution by an external magnetic field. Moreover, for comparison the MNIP were prepared in the absence of CR in a same procedure.

Characterization of MMIP and MNIP

The structure of Fe₃O₄, Fe₃O₄@SiO₂-NH₂, MMIP and MNIP were studied by FT-IR spectroscopy (Figure 1). Figure 1a shows the characteristic stretching peak of Fe-O around 579.92 cm⁻¹ presents in all samples. It indicates intact composition of Fe₃O₄ over the chemical modification and coating of polymer. However, as the modification shells increase, the strength of Fe–O stretching peak decrease implying the success in modification. After the surface modification of pure Fe₃O₄ by APTES, the peak position of Si–O–Si stretching vibration, N–H and O–H bonding vibrations related to 1065.61 cm⁻¹, 1615.54 cm⁻¹, 3384.91 cm⁻¹, respectively (Figure 1b). The presence of C=O stretching vibration at 1657.51 cm⁻¹ along with C–H stretching vibration of the methyl group at 2942.85cm⁻¹ Figures 1c and 1d, confirm that Fe₃O₄@SiO₂@NH₂ has been successfully coated by MIP or NIP. The same characteristic absorption peaks in both MMIP and MNIP prove almost the complete removal of templates. These results, not only confirm formation of MMIP and MNIP, but also the coating of MIP at the surface of Fe₃O₄@SiO₂-NH₂.

The sizes of Fe₃O₄, Fe₃O₄@SiO₂-NH₂, MMIP and MNIP were characterized using a FESEM (Figure 2). The diameter of Fe₃O₄ particles was 8-18nm. After modifying Fe₃O₄ by APTES, the diameter of the Fe₃O₄@SiO₂-NH₂ particles was 14-20nm, indicating to core–shell structure resulted from coupling of APTES on the Fe₃O₄ surface. In contrast with MNIP with smooth surface and inefficient adsorption sites, the uneven and porous surface of MMIP facilitate the adsorption of CR molecules.

XRD analysis was carried out to study the phase and the structure of Fe₃O₄, Fe₃O₄@SiO₂-NH₂, MMIP and MNIP. The XRD results for all samples are shown in Figure 3. In the 2θ range of 10–80°, characteristic peaks for Fe₃O₄ (2θ = 30.46°, 35.7°, 43.5°, 53.48°, 57.0°, and 63.2°) present for all samples. The peak position of corresponding 2θ value were indicated as 220, 311, 400, 422, 511 and 440, respectively. The presence of specific diffraction peaks in the XRD patterns indicate the highly crystalline structure of synthesized particles. No change is observed in the peak positions of samples after coating.

It demonstrates that coating process has not changed the crystalline structure change of the Fe₃O₄. The as-synthesized samples have different peak width is related to size differences.

The magnetic properties of the synthesized magnetic NPs were studied by VSM. The magnetic hysteresis loops of the Fe₃O₄, Fe₃O₄@SiO₂-NH₂, MMIP and MNIP at room temperature is depicted in Figure 4. There is no hysteresis phenomenon. The value of zero for the remanence and coercivity demonstrates the superparamagnetic property of samples. The values of saturation magnetization for Fe₃O₄, Fe₃O₄@SiO₂-NH₂, MMIP and MNIP were 52, 42, 26, 24 emu g⁻¹, respectively. As the core–shell structure thickness increases, the magnetization values decreases. Despite
the decline in saturation magnetization of MMIP, compared to the pure Fe₃O₄, it still retained strong magnetism and separated easily using an external magnetic field.

**Binding properties of MMIP and MNIP**

*Effect of pH*

The effect of pH on the removal of CR by MMIP and MNIP was investigated. The results showed that maximum removal difference of CR was obtained in solutions with pH 6.2 (unadjusted pH). The removal difference between MMIP and MNIP decreased in higher and lower pHSs in which CR predominantly exist in ionic form.
Effect of amount of adsorbent polymer

Results revealed that increment the amount of MMIP and MNIP up to 50mg, leads to the difference between removal of CR in MMIP and MNIP. Although, increasing more than 50 mg, decrease the removal difference between two species of adsorbent. It may be related to the increasing sites of adsorption on both of MMIP and MNIP and therefore increasing the chance of adsorption on nonspecific sites present in MNIP.

Effect of time

The effect of contact time on the amount of adsorbed dye indicated that a fast adsorption process occurs during 3 min which can be assumed as proper time in removal process.

The kinetic analysis, was carried out to study the mechanism of adsorption. Results have been summarized in Table 1. The analysis showed that the pseudo second order model will define the kinetic mechanism of the adsorption.

Adsorption specificity

Adsorption specificity results have been shown in Table 2. Results show that removal properties of MMIP and MNIP in term of SD is less than 1.2 which depicts a very good reproducibility. This means that if it is used for CR removal, it can be hoped that the results of the removal have acceptable repeatability. The results indicate adsorption of MR, EO, MO, MG, CR on the MMIP and MNIP. The results indicated a high selectivity of MMIP for EO.

---

**Table 1.** Adsorption rate constants for Pseudo-first and Pseudo-second model

<table>
<thead>
<tr>
<th>Initial Conc. C₀ (mg L⁻¹)</th>
<th>Pseudo-first-order model</th>
<th>Pseudo-second-order model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K₁ (h⁻¹)</td>
<td>qₑ (mg g⁻¹)</td>
</tr>
<tr>
<td>25</td>
<td>9.15×10⁻⁴</td>
<td>1.58</td>
</tr>
</tbody>
</table>

**Table 2.** Imprinting factor (α) and selectivity factor (β) of the polymers for various interfering dyes examined (Mean±SD, n=3)

<table>
<thead>
<tr>
<th>Dye</th>
<th>Q₉₅</th>
<th>Q₉₅</th>
<th>α</th>
<th>β</th>
</tr>
</thead>
<tbody>
<tr>
<td>CR</td>
<td>85.2 ± 0.3</td>
<td>35.3 ± 0.3</td>
<td>2.41</td>
<td>-</td>
</tr>
<tr>
<td>MG</td>
<td>65.5 ± 0.1</td>
<td>53.0 ± 0.4</td>
<td>1.24</td>
<td>1.94</td>
</tr>
<tr>
<td>MO</td>
<td>36.0 ± 0.2</td>
<td>5.3 ± 0.1</td>
<td>6.83</td>
<td>0.35</td>
</tr>
<tr>
<td>MR</td>
<td>68.5 ± 0.6</td>
<td>29.9 ± 1.2</td>
<td>2.29</td>
<td>0.95</td>
</tr>
<tr>
<td>EO</td>
<td>77.6 ± 0.2</td>
<td>5.8 ± 0.4</td>
<td>13.49</td>
<td>0.17</td>
</tr>
</tbody>
</table>

**Figure 4.** Magnetic properties of (a) Fe₃O₄, (b) Fe₃O₄@SiO₂-NH₂, (c) MMIP, (d) MNIP, e) The magnetic response of Fe₃O₄ to an external magnetic field.
Size, shape and electrical charge of the template molecule, the pore size and its distribution on the surface of MMIP, can affect the efficient adsorption process. Negative charge and molecular size are important parameters for CR adsorption process. The negative charge of CR molecule causes faster absorption and relatively large size of the CR decreases absorption. Results of two parameters determined the adsorption rate. Results revealed that MMIP also was selective for Eo, because of its smaller molecular size and negative charge. These two parameters have potentiated each other and result in to higher adsorption rate. The second reason for rapid adsorption of EO by MMIP is formation of hydrogen bonds between oxygen group of CR and EO, with N-H group of MMIP [14, 20, 28]. High adsorption capacity of MMIP toward EO may have some advantage and disadvantages. There may be present more than one dye in waste water, therefore the power of MMIP to remove all of them can be advantageous. But if the concentration of EO is high, it may prevent the removal of CR because of competitive adsorption. Therefore, the weak selectivity of MMIP toward CR in the presence of EO is conditional.

**Adsorption isotherms and kinetics**

To study the mechanism of CR removal by MMIP and MNIP, the adsorption isotherms were used. In order to evaluate the applicability of this method for adsorption study, a data comparison was done by considering the correlation coefficients, R² values. This study investigated the effect of adsorbent amount on CR adsorption by MMIP and MNIP, moreover, we studied the effects of various concentration on CR adsorption by MMIP and MNIP. The amount of CR adsorbed (mg) per unit weight (g) of adsorbent (MMIP or MNIP) is shown in the **Figure 5a**. Various isotherm models including Langmuir, Freundlich, DR and Temkin were used to fit the adsorption data. The adsorption isotherm experiments for MMIP and MNIP were carried out in the CR concentration range of 10-45 mg L⁻¹ and with 0.05 g of either MMIP or MNIP. Data were summarized in **Table 3** in which it can be seen that Langmuir model is best fitted and can be concluded that a monolayer CR molecules have been adsorbed on MMIP.

**Table 3.** Langmuir, Freundlich, DR, Temkin fitting parameters

<table>
<thead>
<tr>
<th>Adsorption isotherm</th>
<th>Constants</th>
<th>MMIP (0.05g)</th>
<th>MNIP (0.05g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>qₘ (mg g⁻¹)</td>
<td>35.3</td>
<td>18.0</td>
</tr>
<tr>
<td></td>
<td>b (ml mg⁻¹)</td>
<td>0.3</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.979</td>
<td>0.974</td>
</tr>
<tr>
<td>Freundlich</td>
<td>n</td>
<td>2.2</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>kₙ</td>
<td>8.7</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.848</td>
<td>0.978</td>
</tr>
<tr>
<td>DR</td>
<td>qₘ</td>
<td>34.5</td>
<td>14.6</td>
</tr>
<tr>
<td></td>
<td>Kₐ</td>
<td>-2.7</td>
<td>-7.4</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.955</td>
<td>0.964</td>
</tr>
<tr>
<td>Temkin</td>
<td>Aₑ (Lg⁻¹)</td>
<td>2.4</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>Bₑ (Jmol⁻¹)</td>
<td>8.1</td>
<td>4.4</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.907</td>
<td>0.978</td>
</tr>
</tbody>
</table>

**Figure 5.** Adsorption of CR on MMIP and MNIP at various CR concentrations

**Table 3** shows the isotherm parameters of regression equation.
Desorption experiments

**Effect of solvent, pH, temperature, volume, time**

Desorption process was performed by mixing the dried MMIP at different solvent and the maximum efficiency for adsorption percent was obtained in methanol: water at the ratio of 80:20. The results demonstrated in the Figure 6a. The effect of pH solution on desorption efficiency was studied in this solvent. Results are shown in Figure 6b. As it can be seen maximum desorption percent was achieved at pH 11.5.

Temperature effect on desorption have been studied and the results have been shown in Figure 6c. Results reveals that by increasing the temperature from 25°C to 75°C desorption percent increased and in the range of 45°C to 75°C the rate of increasing was less than 10%, therefore it can be concluded that for energy saving, temperature should be adjusted to around 45°C.

Results related to the effect of solvent volume on desorption have been depicted in Figure 6d. Results showed that by the volume of 10 mL, more than 90% of CR was desorbed. More volumes may increase desorption up to 100%, but the enrichment factor would be decreased significantly, therefore, 10 mL was selected as optimum solvent volume. Desorption studies at different times have been depicted in Figure 6e. It shows that near complete desorption obtained in 15 minutes.

(CR C<sub>0</sub>=25 mg L<sup>-1</sup>, V= 10 mL, Contact Time in ultrasonic bath = 3 min (a and b), 15 min (c, d, e), agitation speed = 300rpm (c, d, e), T=45ºC (d, e), pH 11.5 (d, e), n =3)

The determination of CR in water samples

It has been estimated that about 10–15% of these dyes are released as effluents during the dyeing processes [31]. CR usually applied at a concentration level of 0.01 to 0.05%, therefore it can be expected that the concentration in waste water effluents should be around 10 to 50 ppm. The prepared MMIP was applied to selective removal of CR in the tap water samples of Kerman city, containing CR concentration of 5, 15, 25 mg L<sup>-1</sup>. Results have been demonstrated in Figure 7.

The chromatograms of CR standard solution (25mgL<sup>-1</sup>) and spiked tap water samples at 25 mg L<sup>-1</sup> CR concentration which treated by MMIP and MNIP are shown in Figure 8. Desorption experiments of CR from loaded MMIP were performed by 10ml mixture of methanol: water (80:20v/v) solution and determined by HPLC. Results of recovery have been shown in Table 4.
As seen from the cyclic experiments (Table 5) the MMIP can be used at least 3 times for isolation and enrichment of CR in aqueous media.

Reusability

In this study, we successfully synthesized MMIP, using Fe₃O₄@SiO₂-NH₂ nanocomposite, CR and AAM as carrier material, template and functional monomer, respectively. The structure of uniform core-shell was obtained by surface imprinting and nano techniques. According to our results, the advantage of fast adsorption kinetics (180 second in ultrasonic), high adsorption capacity (Q=22.76 mg g⁻¹), acceptable selectivity (a = 2.41), and reusability of adsorbent for more than three times, have been achieved.
ACKNOWLEDGEMENTS

The authors would like to express their gratitude to Miss Roushan- Ahmadi at the research laboratory in the department of Chemistry, Islamic Azad University, Kerman branch. A word of thanks will also go to Mr. Mohammad Daneshpajhough at the faculty of pharmacy, Kerman University of Medical Sciences for his priceless technical support. Also, we thank Mr. Hamed Khorsandpour at west gas and oil Production Company for his kindness in preparing and interpreting of FTIR spectra. This research project was a part of PhD thesis approved in Kerman Branch, Islamic Azad University.

REFERENCES


http://www.eurasianjournals.com