



Synthesis of Molecularly Imprinted Polymer Nanoparticles for Removal of Sudan III Dye

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Molecularly imprinted polymer (MIP) nanoparticles of Sudan III dye as template were synthesized by using non-covalent approach. The molecularly imprinted polymers were synthesized in a microemulsion contained Sudan III as a template, acrylic acid (AA) as a monomer, 1,4-butanediol dimethacrylate as a cross-linker and 2,2-azo-bis(isobutyronitrile) (AIBN) as an initiator. The synthesized beads were characterized by TEM and FTIR. The TEM results revealed the nanosize beads of polymers were produced. The efficiency of imprinted and non-imprinted polymers was evaluated by batch binding studies. The results showed that the MIP 3 (0.1: 6: 10, Sudan III: AA: 1,4-butanediol dimethacrylate) was best among all polymers with highest rebinding efficiency. The removal efficiency of selected MIP 3 in the spiked Sudan III dye river water sample was about 80%. This study was conducted to produce nanosized molecularly imprinted polymers by using microemulsion polymerization technique.

Keywords: Sudan III, Template, Molecular imprinting polymer, Emulsion polymerization.

INTRODUCTION

Sudan III dye belongs to lipophilic azo dyes, which are extensively used in the industrial and scientific applications. However, they are banned as food colorants in food due to the harmful effects towards mankind [1]. Sudan dyes have toxic effects in human organs due to their azoic structure. These compounds can produce aniline and its derivatives, which could attack the hepatocytes and could lead to the toxic hepatic disease. The nervous system could be destroyed by the long-term intake of aniline [2] and the development of liver carcinoma due to the splitting of the azo function into dangerous aromatics amines [3]. Unfortunately, they are still used in food stuffs due to its low cost and to enhance the product appearance. It will not only affect the transparency of water but also could be toxic on aquatic lives and eventually affect human health. Many studies have been conducted to determine the presence of Sudan dyes in different food matrices [4]. Several methods have been developed to detect and separate Sudan dyes in different food samples such as in hot chilli products [5], boiled

egg yolk [6], tomato sauces [7], sausages [4] and other food-stuffs. Gomez *et al.* [8] determined Sudan dyes in drinks containing Sunset yellow with adsorptive stripping voltammetry. Ji *et al.* [9] removed water-insoluble Sudan dyes by using *Shewanella oneidensis* MR-1. Sun *et al.* [10] synthesized magnetic carbon nanotubes (MCNTs), which were used as adsorbents for the removal of Sudan dyes from aqueous solution.

Molecularly imprinted polymer (MIP) has been considered as an attractive approach to develop artificial receptors obtained with memory of the shape, size and functional groups of the template molecules [7]. Generally, five components are needed to produce MIP such as template, crosslinker, monomer, porogen and the polymerization initiator. In the polymerization method, the functional monomer is copolymerized with the template molecule. The molecularly imprinted polymer (MIP) is formed after removal of the template. The size, shape and position of functional groups and the cavities of the molecular imprinted polymers are complementary to the template. Molecularly imprinted polymers (MIPs) provide good stability, simple preparation and specificity [7]. The MIPs have been applied

for the removal/extraction of various analytes such as dyes [11,12], fungicides [13-15], melamine [16,17], vanillic acid [18], gallic acid [19], cinnamic acid [20], piperine [21] and *p*-coumaric acid [22]. Piao & Chen [23] had developed a simple method based on magnetic molecularly imprinted polymers (MMIPs) to separate Sudan dyes from chilli powder samples. While Yan *et al.* [24] synthesized a new kind of aniline-naphthol molecularly imprinted microsphere (MIM) by aqueous suspension polymerization, which was applied as a selective sorbent of miniaturized matrix solid-phase dispersion combining with dispersive liquid-liquid microextraction (MSPD-DLLME) for the simultaneous determination of four Sudan dyes in egg yolk samples. Xu *et al.* [25] synthesized a novel surface molecularly imprinted polymer using sol-gel process for selective recognition of Sudan III dye in methanolic solution. However, there were lack of studies about removal of Sudan dyes in environmental water using MIPs synthesized by microemulsion polymerization method.

In this study, a self-assembling approach which uses non-covalent forces is used for the interaction of template with monomer. For example, van der Waals interaction, hydrogen bonding, ion or hydrophobic interaction and metal-coordination. The imprinting efficiency is very high in non-covalent imprinting technology. Many non-covalent methods for the preparation of MIP, such as bulk polymerization, suspension polymerization [26] and precipitation polymerization [27] were employed. In non-covalent molecular imprinting approach, the number of moles of functional monomer are used in excess to favour the complex formation between template and the functional monomer. The functionality of template with the functionality of monomer should be complementary to each other [28]. For example, one act as hydrogen bond donor while the other one as hydrogen bond acceptor ensuring maximum complex formation of template with the functional monomer and excellent imprinting effect. Acidic monomers have been more frequently used to form the ionic interactions with the templates than basic monomers [29]. The double bond in the monomer will be copolymerized with the crosslinker in the formation of MIP. The crosslinker is responsible to secure the monomers around the template, which is important to preserve the binding site structure or the cavity formed after the removal of template [30]. High ratios of crosslinkers were used in order to get porous structure of MIP with adequate mechanical stability [28] and to maintain the stability of the recognition sites after removal of the template. In this study, an interaction between Sudan III dye has been established with acrylic acid by using non-covalent approach. The most interesting part of this study is the use of microemulsion as a solvent medium for the polymerization reaction.

EXPERIMENTAL

The chemicals and solvents, *viz.* acrylic acid (AA), Sudan III (Merck Chemicals), 1,4-butanediol dimethacrylate (Merck Chemicals), *N*-cetyl-*N,N,N*-trimethylammonium (CTAB), azobisisobutyronitrile (AIBN), hexane, methanol, *n*-butanol, acetic acid and acetone (R&M Chemicals) were procured from the commercial grade and of highest purity.

Characterization techniques: The UV spectrophotometer, FTIR spectrometry (Model ThermoScientific Nicolet iS10), transmittance electron microscopy (TEM) (Erlangeng ES500W GATAN MODEL 782) were employed for the spectroscopic measurements.

Preparation of microemulsion: Microemulsion was prepared by dissolving 8 g CTAB into 10 mL distilled water followed by the addition of 160 mL hexane and 25 mL *n*-butanol.

Preparation of MIPs and NIP: Sudan III (0.1 mmol) as a template molecule was dissolved in a 250 mL conical flask containing 75 mL of microemulsion followed by the addition of 2 mmol of acrylic acid as functional monomers, 10 mmol of 1,4-butanediol dimethacrylate and 0.03 g AIBN as an initiator. The mixture was sonicated for 5 min and degassed with nitrogen for 15 min. Then, the flask was sealed and the contents were allowed to polymerize in a water bath at 60 °C for 4 h and 70 °C for 2 h. The obtained polymer was filtered by using filter paper. The other two MIPs were synthesized by changing the molar ratio of monomer (4 and 6 mmol for MIP2 and MIP3, respectively). For the non-imprinted polymer (NIP), the synthesis was carried out without the presence of template (Sudan III).

Washing process: The synthesized polymers were washed with mixture of methanol and acetic acid (8:2, v/v) in order to remove the template from the polymer matrix. The washing procedure was repeated until the template was not detected by UV-vis spectrophotometry. The polymer particles (MIPs) were dried at 60 °C in an oven until further use.

Characterization of molecular imprinted polymer: Fourier transform-infrared analysis was performed to identify the functional groups of MIPs and NIP. All samples were mixed and whetted with spectroscopy grade KBr prior to be placed in the sample cell and reflectance spectra were scanned over the range of 4000-400 cm⁻¹. The surface morphology of the MIPs and NIP were observed by using transmittance electron microscope (TEM). The imprinted polymer was examined with a magnification such as ×50,000.

Batch binding experiment: Batch binding experiment was conducted to select the best time for the rebinding of Sudan III with the MIPs and NIP. In this study, 10 ppm of Sudan III was prepared in the mixture of methanol and distilled water (7:3). Then, 0.5 g of MIP1, MIP2, MIP3 and NIP were weighed and put into four 150 mL conical flasks containing 10 ppm of Sudan III, respectively. Then, the conical flasks were agitated on shaker at 250 rpm and then samples were collected at different time intervals (0, 30, 60, 90, 120, 150, 180, 210, 240, 270 and 300 min). The absorbance of the collected sample was analyzed by using UV spectrophotometry. The percentage of Sudan III rebinding by MIPs and NIPs was plotted over time. The following formula was used to calculate the rebinding efficiency:

$$\text{Rebinding efficiency (\%)} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where C_i is the initial concentration of Sudan III in the solution and C_f is the final concentration Sudan III in the solution.

Adsorption isotherms: Using Langmuir and Freundlich equations, the adsorption isotherms were studied for a range of initial dye concentrations [31,32].

Langmuir isotherm: The Langmuir isotherm is a term that describes the adsorption of single molecule layers on the surface of an adsorbent [33]. The linearized Langmuir equation is given as:

$$\frac{C_e}{Q_e} = \frac{1}{kQ_m} + \frac{C_e}{Q_m} \quad (2)$$

where, Q_m = the maximum adsorption capacity of the adsorbent (mg/g), Q_e = equilibrium adsorption capacity of the adsorbent (mg/g), b = the adsorption equilibrium constant (L/mg) and C_e = equilibrium concentration of template (mg/L).

This isotherm's shape can also be represented in terms of the separation factor (R_L), which is as follows:

$$R_L = \frac{1}{1 + K_L C} \quad (3)$$

where K_L = Langmuir constant (L/mg) is related to the affinity of binding sites and the free energy of sorption. C_e is template concentration at equilibrium in solution (mg/L).

Freundlich isotherm: For a heterogeneous surface, the Freundlich isotherm is ideal. The Freundlich equation can be written as follows [34]:

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (4)$$

where C_e , Q_e are the concentration of template and amount of template adsorbed at equilibrium, respectively.

The Freundlich empirical parameters are K_f (mg/g) and n . The parameters K_f and $1/n$ are related to the system's sorption capacity and sorption intensity. The magnitude of the term ($1/n$) gives an indication of the favourability of the sorbent/adsorbate systems [35].

Kinetic models: Two kinetic models *viz.* pseudo-first and pseudo-second order models were applied in this work. Eqns. 5 and 6, respectively represents the two kinetic models.

$$\ln q_t = \ln B + K_f (\ln t) \quad (5)$$

$$\ln (q_{eq} - q_t) = \ln q_{eq} - K_1 t \quad (6)$$

Selectivity of MIP: For selectivity experiment, a certain mass of MIP and NIP was added to certain known concentration of template in the solution. After the system attains equilibrium, the free template concentration in solution was recorded and the quantity of template accumulate on the MIP surface was calculated. MIP and NIP (100 mg) containing in two different conical flasks were added with 20 mL of a mixed substrate solution (containing 15 ppm Sudan III and 15 ppm methylene blue solutions). The flasks were shaken at room temperature for 60 min (time for maximum adsorption of MIP). The resulting solution was centrifuged for 20 min and filtered to remove suspended MIP particles and then the concentration was determined by spectrophotometry.

The selectivity of MIP was determined by using eqn. 7:

$$k_{sel} = \frac{K_D(\text{Sudan III})}{K_D(\text{MB})} \quad (7)$$

where

$$K_D = \frac{(C_i - C_f)V}{MC_i} \quad (8)$$

where C_i = initial MR/MB concentration, C_f = final MR/MB concentration, V = volume of solution used and M = the mass of MIP/NIP used.

The imprinting factor can be calculated by using eqn. 9:

$$K = \frac{K_{sel}(\text{MIP})}{K_{sel}(\text{NIP})} \quad (9)$$

Application: The preparation was conducted the same as the batch binding experiment but only two polymers were used, MIP3 with the highest batch binding efficiency and the NIP. The river water sample was collected from Jetty at Kota Samarahan Sarawak, Malaysia. About 1000 mL of river water was collected in a glass bottle, filtered by using 0.45 μm filter paper and then stored in refrigerator. A spiked sample was prepared by mixing 7 mL of 100 ppm Sudan III (in methanol) with 63 mL of river water. The removal of Sudan III dye from spiked river water was carried out using the same procedure as followed in batch binding process. The samples collected were further analyzed under UV spectrophotometer. The NIP was also used in order to differentiate the efficiency of Sudan III imprinted polymer with the non-imprinted polymer.

RESULTS AND DISCUSSION

FTIR studies: Fourier transform-infrared analysis was performed to identify the functional groups of MIPs and NIP. The IR spectra of synthesized polymers is shown in Fig. 1. There are three chemical compounds involved in the chemical reaction in polymer synthesis such as template (Sudan III), monomer (acrylic acid) and cross-linker (1,4-butanediol dimethacrylate). The peaks contributed to these three compounds were expected to be present in the IR spectrum.

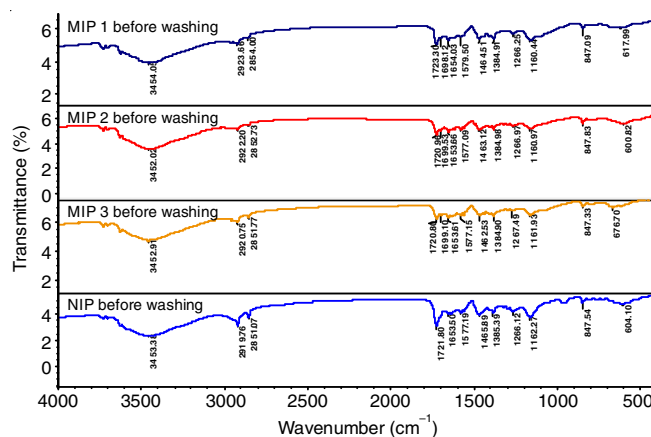


Fig. 1. FTIR analysis of MIP1, MIP2, MIP3 and NIP

A broad peak was observed at 3454.05, 3452.02, 3452.91 and 3453.38 cm^{-1} in IR spectra of MIP1, MIP2, MIP3 and NIP, respectively. This strong peak indicated the presence of intermolecular bonded -OH stretching. This peak may indicate the presence of carboxylic acid in acrylic acid monomer. While the peaks found at ~ 2960 and ~ 2850 cm^{-1} can be interpreted as the C-H vibration of alkyl group. The pair of peaks at 2922 and 2851 cm^{-1} corresponds to the asymmetrical and symmetrical stretching vibrations of CH_2 in an aliphatic hydrocarbon [36].

The absorption band at $\sim 1720\text{ cm}^{-1}$ is assigned to C=O bond stretching of either carboxylic acid in the monomer (acrylic acid) or ester group in the crosslinker (1,4-butanediol dimethacrylate). All the IR spectra of synthesized polymers showed this peak at 1723.30, 1720.96, 1720.80 and 1721.80 cm^{-1} for MIP1, MIP2, MIP3 and NIP, respectively. The peaks at the region 1300-1000 cm^{-1} correspond to the C-O-C stretch of ester group in 1,4-butanediol methacrylate. Two bands were observed at this region for all synthesized polymers at ~ 1260 and $\sim 1160\text{ cm}^{-1}$. This proved that the presence of crosslinker in the polymers. The significant peak at around 1699 cm^{-1} displayed the C=C stretch of aromatic ring of Sudan III dye. While in NIP, this peak does not exist, this shows that the presence of template in the polymer framework of the imprinted polymers (MIP1, MIP2 and MIP3).

TEM studies: The surface morphology of MIP was examined at magnification of $\times 50,000$ as shown in Fig. 2. The image revealed that the particles size of polymer particles was in nanosize (82 nm) and shape was spherical. This indicated that the uniform shape and size of polymers particles. Some particles are shown to be agglomerated, which may be because of the fact that the nanoparticles tend to agglomerate in the system after dispersion because of the high surface energy of the nanoparticles [37,38].

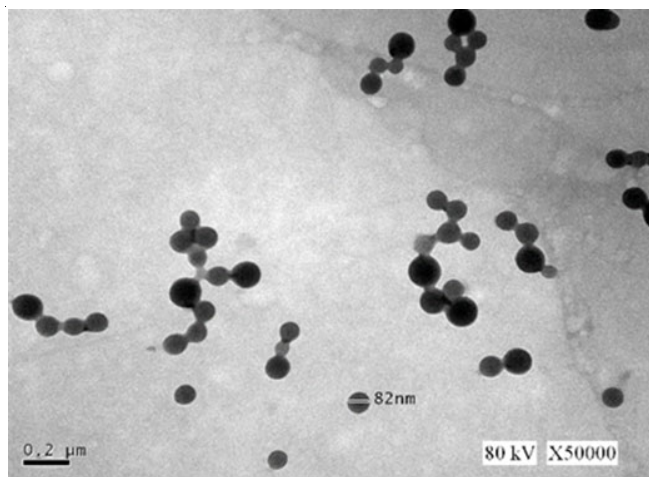


Fig. 2. TEM micrograph of MIP at 50,000x magnification

Batch binding experiment: The highest removal efficiency was achieved by MIP3 (83%), followed by MIP2 (72%), MIP1 (53%) and NIP (33%) (Fig. 3). This may be due to the different amount of monomer used in the MIPs synthesis. MIP 3 exhibit higher percent removal of Sudan III because of the higher amount of monomer used during the synthesis. The binding energies decreased by increasing the number of monomers used and the lower the value of the binding energy, the more stable the formation of the complex [37]. Thus, MIP3 with molar ratio of 0.1:6:10 provide good recognition properties compared to MIP1 (0.1:2:10) and MIP2 (0.1:4:10).

While in case of NIP the removal efficiency was very low as compared to all MIPs since, NIP does not have a specific binding sites of Sudan III resulting the poor selectivity towards the template molecule. Therefore, the MIPs showed good site

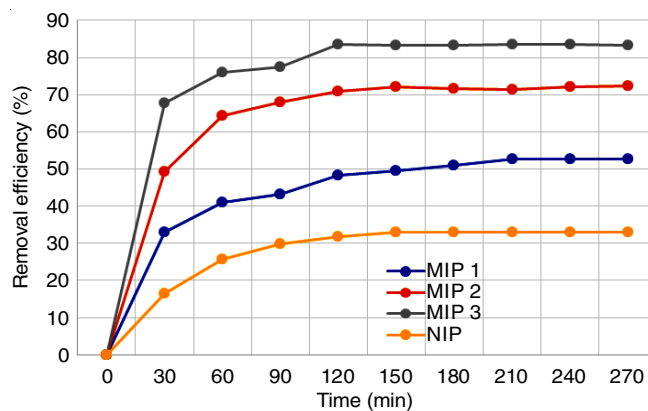


Fig. 3. Effect of contact time

accessibility for Sudan III molecule compared to NIP. The removal efficiency of MIPs and NIP increased as the time increased. The rapid binding capacity enhancement was seen in the first 30 min. Then, it increased slowly with the extension of time. The percent removal of Sudan III by MIP 1 reached a maximum binding capacity at 210 min with 52.69%, MIP 2 at 150 min with 72.06%, MIP 3 at 120 min with 83.54% while the NIP reached maximum removal efficiency at 150 min with 32.94%. This can be concluded that with the increase in time all the binding sites have been occupied by the template molecules and for every polymer there was a saturation point after that there was not any significant rebinding of template. This maximum is considered as the best time interval for the rebinding of template with polymer.

Adsorption studies: The linear regression analysis of adsorption isotherms was applied to determine the mechanism of adsorption and extent of adsorbate adsorb on the MIP surface. Langmuir and Freundlich adsorption isotherms were investigated for the exploration of mono and multi-layer adsorption of dyes by MIPs respectively. Freundlich adsorption isotherm (Fig. 4b) was found the best-fitted model with greater regression coefficient (R^2) value (0.952) showing that adsorption of Sudan III dye on the surface of MIPs was multi layered.

Linear adsorption generally occurs at a low solute concentration and low loading of the adsorbent [39]. The value of n of this model fell in the range of 1-10, indicating favourable sorption of Sudan III on MIP surface. The numerical value of $1/n < 1$ indicated that adsorption capacity of MIP3 was only slightly suppressed at lower equilibrium concentration. This isotherm did not predict any saturation of the MIP. Thus infinite surface coverage was predicted mathematically, indicating multilayer adsorption on the surface. The present study results indicated that the Freundlich model fit the experimental data well. In this study, Freundlich model was the best-fit isotherm for adsorption of Sudan III to MIP3. Freundlich isotherm model parameters K_f and n , calculated were 1.918 for adsorption capacity and 1.177 for intensity of the adsorption. The correlation coefficient of Freundlich isotherm (R^2) was 0.9821 (Fig. 4b) higher than Langmuir values (Fig. 4a) indicating that Freundlich isotherm is the best fitted isotherm for MIP3.

Kinetic models: The efficiency of the adsorption process of solutions media is determined by kinetic studies. Two kinetic

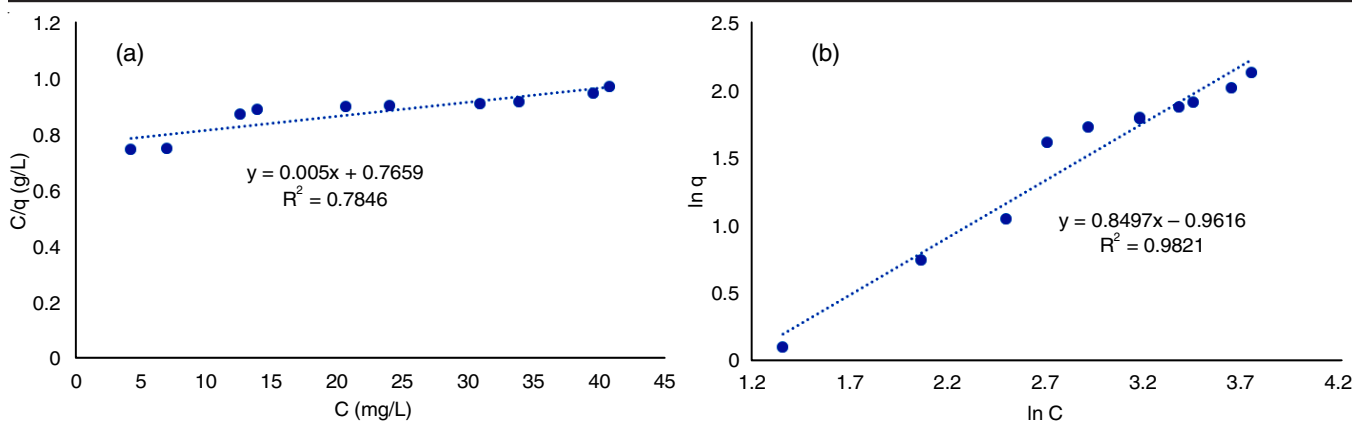


Fig. 4. (a) Langmuir isotherm and (b) Freundlich isotherm

models, pseudo-first-order and pseudo-second-order (Fig. 5), were examined in linearized forms to illustrate the sorption process of Sudan III on the surface of MIPs. Because of the high R^2 value (0.979), the pseudo-second-order kinetic model was found to be the best match, suggesting that the dye molecule and MIP are involved in the rate-determining stage of the adsorption process. The linearized pseudo-second order-kinetics model was the best fit because of the high R^2 value as reported for the removal of various dyes [40-44].

Selectivity: Sensing property of MIP3 for Sudan III was evaluated by employing the selectivity test. In this study, methylene blue was selected as possible interfering and competitive agent. The data was collected in the form of distribution ratios (K_D), selectivity coefficients (K_{sel}) and relative selectivity coefficients (k') as shown in Table-1, which revealed that distribution ratio of Sudan III is higher than the distribution ratios of its competitor methylene blue. Outstanding selectivity coefficient value indicates that the particular for methylene blue dye removal and the imprinting technique was very effective. The studies declared that functional groups of template located at the edges of molecules might have favourable interaction

with the active binding sites of MIP3 and was easily entrapped into the cavities rather than competitor [45]. The higher distribution ratio of Sudan III is also due to the fact that MIP3 can recognize and attach the template molecules by specific binding sites that have been preserved as a memory [28]. The template molecules can easily attach to the relatively matched cavities in size and shape, while an interferent can bind poorly due to nonspecific interactions [46].

Template	K_D (MIP) (mL g ⁻¹)	K_D (NIP) (mL g ⁻¹)	k_{sel}	k
Sudan III	95.00	15.60	2.12	3.21
Methylene blue	44.65	23.44	0.66	

Removal of Sudan III from river water: From the experimental investigation of removal of Sudan III from spiked river water sample, it was observed that MIP 3 exhibits a high percentage removal (80%) of Sudan III compared to the NIP (30%). But in case of distilled water, the removal efficiency was slightly higher as compared to in river water (Table-2),

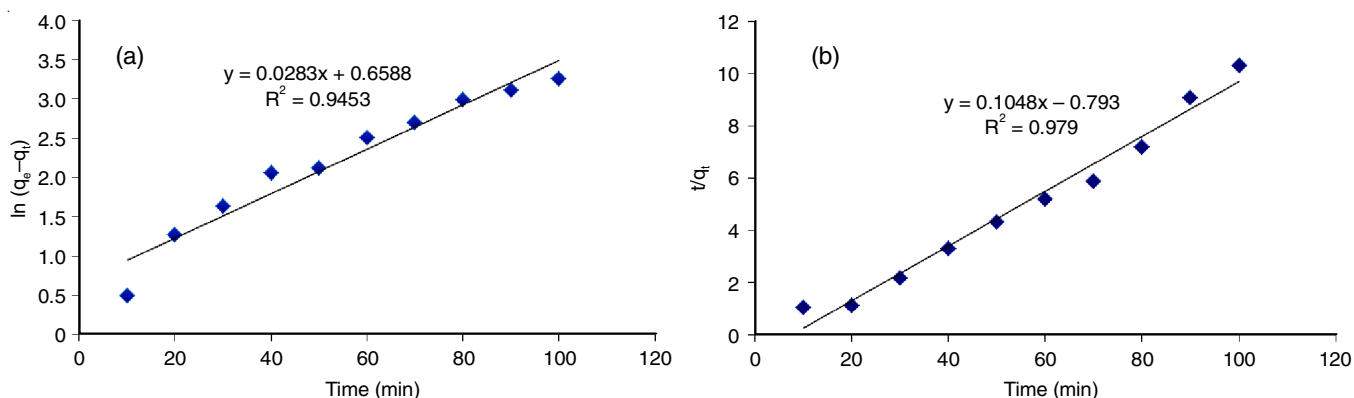


Fig. 5. (a) Pseudo-first-order and (b) pseudo-second-order kinetic model

Samples	Amount of Sudan III added (µg/mL) MIP	Amount of Sudan III found (µg/mL) MIP	Recovery (%)	RSD (%)	Amount of Sudan III found (µg/mL) NIP	Recovery (%)	RSD (%)
Distilled water	10	8.3	83	1.20	3.1	31	3.23
River water	10	8.0	80	1.89	3.0	30	3.33

which proved that MIP 3 have the specific recognition binding sites towards the Sudan III and showed good site accessibility for template molecule and imprinting ability than non-imprinted polymer. The molecular recognition mechanism is mainly based on intermolecular hydrogen binding between the template and the MIPs and the hydrogen bonding is the only possible contributor in the stabilization of the pre-polymerization complex [38].

Conclusion

In this study, Sudan III-imprinted acrylic acid-co-1,4-butanediol dimethacrylate polymers have been synthesized. The results of this study demonstrated the applications of MIP for removal of Sudan III in river water with the removal efficiency of 80%. This work will contribute to the development of new systems, based on imprinted polymer for the selective removal of various dyes from the polluted waters.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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