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# Decolorization of textile wastewater by dye-imprinted polymer

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**ABSTRACT**

Adsorption of dye molecules onto a sorbent can be an effective, low-cost method of decolorization of textile wastewater. Most of the techniques used for this aim were the high cost of production and the regeneration also makes them uneconomical. Molecular imprinting polymers are a new kind of materials which can be economical and effective adsorbents. In this study, a molecularly imprinted polymer (MIP) of textile dyes (Direct Red 23) was prepared for decolorization of textile wastewater and also used for leaching of this dye from the wastewater by adsorption of onto polymer. Acrylamide was used as a monomer and dimethyl sulfoxide was used as a porogen. The selective recognition ability of the MIP was studied by an equilibrium-adsorption batch method. The effective adsorption properties of the polymer were tested in synthetic dye wastewater. The high adsorption rate and the amount of imprinted dye that was removed from the polymer was nearly 65%. 80% of the dye was adsorbed by imprinted polymer in synthetic wastewater.

*Keywords:* Molecularly imprinted polymer; Textile dye; Wastewater; Decolorization; Recognition

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## 1. Introduction

Textile dyes are widely used in the world today. Direct dyes are one of the popular types of colorant owing to low cost, excellent color range, good lightness, and in addition to ease of application. The stable, recalcitrant, colorant, and even potentially carcinogenic and toxic structure of these dyes can cause serious environmental, esthetic, and health problems. Because many industries like the textile industry produces wastewater containing these dyes with a strong color. Textile dyes are very difficult to degrade and may cause many toxicity problems while receiving from the waters. Many studies exist for the decolarization of textile dye wastewater [1–7]. Nowadays, there is a growing interest in developing low-cost and effective adsorbents.

For reasons of their recognition properties, stability, reproducibility, low cost, and manufacturing potential, molecularly imprinted polymers (MIPs) are regarded as promising candidates for wastewater treatments. Molecular imprinting can generally be defined as a process during the course of which polymeric matrices with specific binding sites are generated by template-induced prearrangement of complementary interactive functional groups. In this process; the functional monomer forms a complex via covalent or non-covalent interactions with

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template and, by adding cross-linker and initiator polymerization was started. After polymerization, their functional groups are held by the highly cross-linking polymeric structure. After removing the template molecule from the polymer matrix, a polymer with binding sites complementary in size and shape of the imprint molecule is created [8–12].

The goal of this study is to prepare dye-imprinted polymer to research the molecular recognition characteristics, so that to get valuable results for contamination of dyes in wastewater. It is also important and valuable to recognize dye molecules and their removal from wastewater for the protection of the environment. In this study, textile dye, Direct Red 23 (Fig. 1) used as a template in imprinted polymer was prepared by the thermal bulk polymerization method. Acrylamide (ACM) was as a monomer and dimethyl sulfoxide (DMSO) was used as a porogen. The template was removed by methanol: conc. HCl washings. The main aim of this study was to remove Direct Red 23 dye nearby several and similar structural organic compounds. The dye-imprinted polymer can also be used as a solid-phase adsorbent for Direct Red 23 dye to detect whether it was present in wastewater.

## 2. Materials and methods

### 2.1. Chemicals

ACM, ethylene glycol dimethacrylate (EGDMA), methanol (MeOH), and DMSO were obtained from Sigma Chem. Co. (St. Louis, MO, USA). Azobisisobutyronitrile (AIBN) was purchased from Wako Pure Chem. Ind. (Osaka, Japan). All other chemicals and reagents were of the highest available purity and used as purchased. Direct Red was obtained from Huntsman (Basel, Switzerland).

### 2.2. Synthesis of Direct Red-imprinted polymers

The MIP synthesis was based on non-covalent interactions between template and functional monomer. Direct Red 23 (dye) imprinted polymer was synthesized according to thermal bulk polymerization procedure. Briefly; appropriate amount of dye (10 mg) was mixed with monomer ACM (80 mg) (1:8) and cross-linker EGDMA (1 ml) was dissolved in 5 ml of DMSO until a homogenous solution was obtained. Appropriate amount of initiator AIBN (10 mg) was dissolved in this solution and it was purged with nitrogen for 10 min. The polymerization was carried out at 50˚C for 20 h. Control polymer without dye molecule was prepared (non-imprinted polymer (NIP)) under identical conditions. The dye molecule was extracted by washing the dye-imprinted polymer with 3 × runs of methanol: conc. HCl (9.5:0.5) and 2 × runs with methanol, incubating in each solution for 3 × 6 h and 2 × 3 h. After each washing step, the polymers were centrifuged at 5,000 rpm for 15 min. NIP polymer was also washed with the same procedure. At the end of washing process, all polymers were dried in vacuum at 40˚C for 12 h and then ground into particles of 50 μm diameter or smaller. The amount of dye molecules extracted from MIP was assayed by spectrophotometrically. To calculate the concentration of the dye from each experiment, a calibration curve of dye was (1–100 μg/ml) prepared. The absorbance was measured using a Perkin Elmer UV–vis Spectrophotometer yielding a maximum absorption rate of 510 nm.

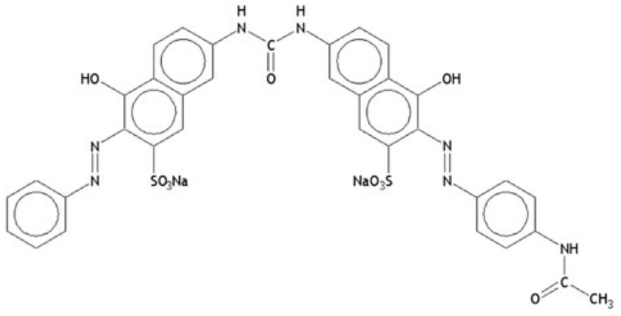

Fig. 1. Direct Red 23.

#### 2.2.1. Characterization of the Direct Red 23-imprinted polymer

The spectroscopic characterization of the polymer was done with FTIR. FTIR is a technique that has a capability of determining the modifications of template–monomer interaction during the imprinting process. The complexation between a functional monomer and template generally via hydrogen bonding and the formation of this bond can be identified using FTIR by the changing the stretching frequency. To identify the complexity of the template and monomer effectively, the FTIR analysis of dye imprinted, and NIP was carried out at room temperature. KBr tablet method was applied.

### 2.3. Adsorption experiments

Adsorption experiments such as binding isotherms, effects of pH, and adsorption kinetics were performed to evaluate the recognition properties of MIPs. The binding efficiency of polymers towards dye was assayed in the batch rebinding experiments. Briefly, 20 mg of the each washed polymers was placed in an Eppendorf tube which includes a known concentration of dye (5–50 μg/ml) in 1 ml of water and mechanically shaken at room temperature for 4 h. After that, the polymers were centrifuged and the concentration of the remaining substrate in the solution was determined spectrophotometrically (at 510 NM). The NIP was used as a control to determine the non-specific binding. The amount of dyes ($Q$) bound to the polymers was calculated by subtracting the amount of free substrate from the initial concentration. The amount of Direct Red 23 that bound to the polymer was defined according to the Eq. (1):

$$Q = \frac{[(C_0 - C_t)V]}{W} \tag{1}$$

where $W$ (g) is the weight of the polymers, $V$ (L) is the volume of solution, $C_0$ (μmol/L) and $C_t$ (μmol/L) are the initial concentration of the dye and the concentration of dye at the supernatant at the time, respectively.

To evaluate binding sites of dye-imprinted polymer Scatchard plot analysis were determined in a batch mode. Ten milligrams of imprinted and non-imprinted polymers with different concentrations of dye (10–200 μmol) were shaken for 4 h. After reaching adsorption equilibrium the tubes centrifuged and the supernatant was analyzed spectrophotometrically.

The equilibrium adsorbed amount $Q_e$ (μmol/g) was calculated by the following equation:

$$Q_e = \frac{[(C_0 - C_e)V]}{W} \tag{2}$$

where $W$ (g) is the weight of polymers, $V$ (L) is the volume of the solution, $C_0$ (μmol/L) and $C_e$ (μmol/L) are the initial concentration and the equilibrium concentration of dye, respectively. These experiments were repeated for three times both for imprinted and non-imprinted polymers.

The binding parameter of dye-imprinted polymer was estimated by Scatchard analysis with the data of static binding experiment. The Scatchard equation is:

$$\frac{Q_e}{C_e} = \frac{(Q_{max} - Q_e)}{K_d} \tag{3}$$

where $K_d$ (μmol/mL) is the equilibrium dissociation constant, $C_e$ (μmol/mL) is the equilibrium concentration of dye, $Q_{max}$ (μmol/g) and $Q_e$ (μmol/g) are the apparent maximum adsorbed amount and the equilibrium adsorbed amount of dye, respectively.

pH plays a major role in binding to the polymer at the solution. It is important because of the degree of ionization of the dye in solution can be changed. The reactive groups on the dye such as sulfonate or aryl groups can ionize at different pHs so that the rebinding of dye can change according the pH of the solution. The influence of pH on rebinding of dye to polymer was investigated by applying the proposed procedure. According to the procedure, the rebinding medium and the solution that dye was solved was changed to 100 mM sodium acetate (pH 4–5), phosphate (pH 6–8), and tris-HCl (pH 9–10). Hundred milligrams of dye removed polymer was mixed with buffers and dye and shaken for 4 h. The polymers were centrifuged at 5,000 rpm for 15 min and supernatant was recorded spectrophotometrically.

### *2.4. Preparation of synthetic textile wastewater and treatment with textile dyes-imprinted polymers*

The synthetic dye wastewater was prepared by mimicking operating conditions of the dyeing process composition prepared as mentioned by Muda et al. [13].

About 3 mg/mL Direct Red 23 was mixed with synthetic wastewater. The Direct Red 23-contended synthetic wastewater was applied to 1,000 mg of Direct Red 23-imprinted polymer (the dye-removed polymer) and NIP and then shaken at constant speed (400 rpm) for 4 h (different hours were studied and the most adsorption of dye was found at 4 h), then centrifuged. The supernatant of polymer was assayed spectrophotometrically. The spectral analysis of textile wastewater was also done.

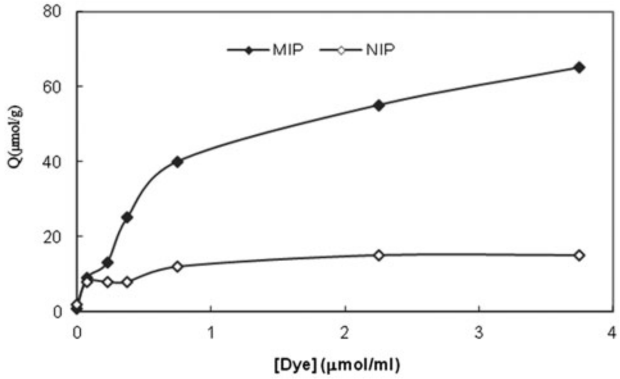

Fig. 2. Batch rebinding experiments of MIP (♦) and NIP (◊).

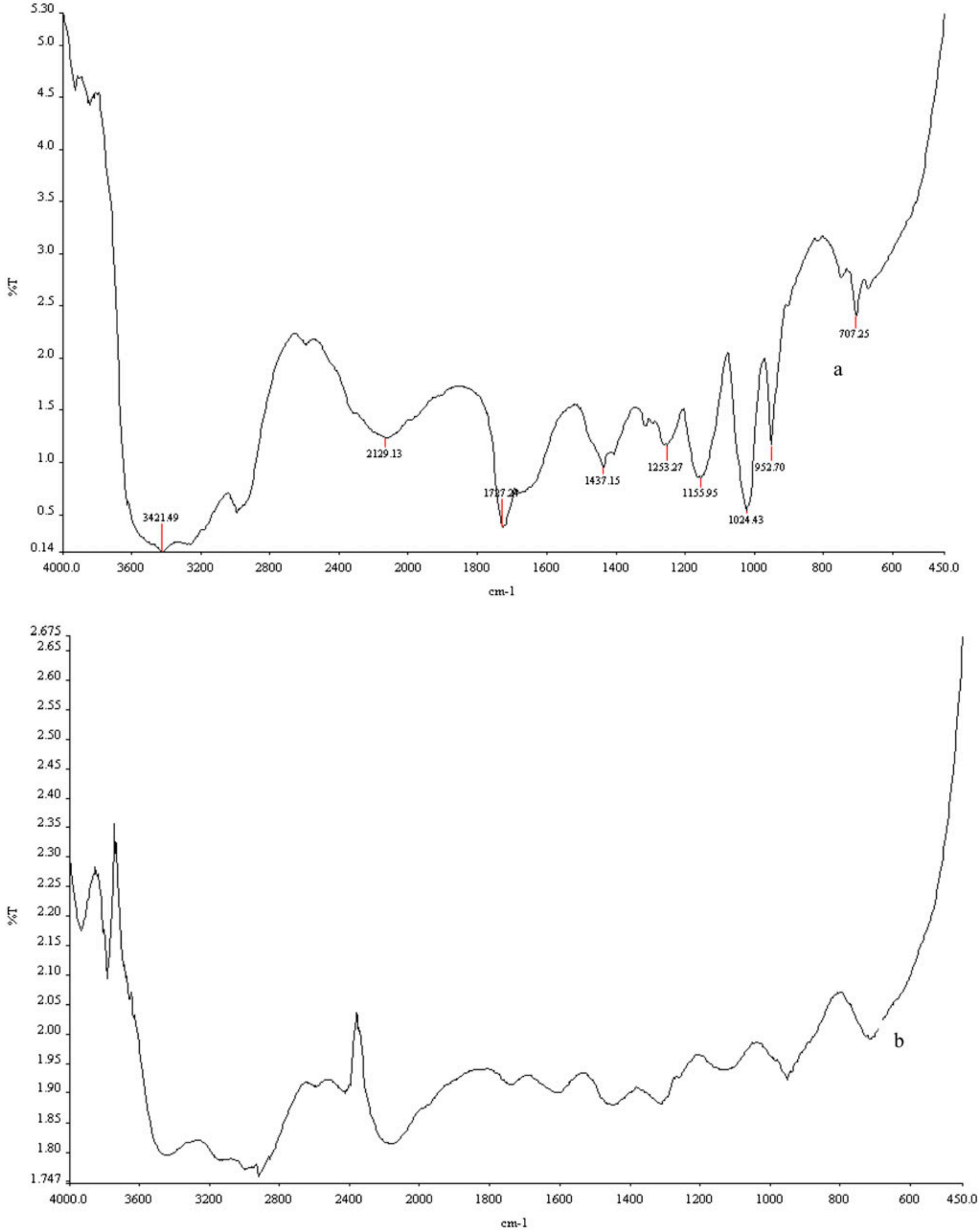

Fig. 3. FTIR results of control (a) and Direct Red 23-imprinted polymer (b).

## 3. Results and discussion

### 3.1. Polymer preparation

Depending on the chemical nature of the interactions between the template molecule and the functional groups (monomer), molecular imprinting technology may be categorized into covalent and the non-covalent approach. MIPs created by non-covalent imprinting are usually characterized by a comparatively small fraction of highly selective binding sites and majority of binding sites providing a wide range of binding affinities. This approach is much more flexible in terms of preparation because of the absence of complicated synthetic chemistry as well as the broad selection of functional monomers and possible target molecules available, it is thus being more commonly used. In addition, imprinted polymers prepared by the non-covalent imprinting show much faster rebinding kinetics. The polymers specify and affinity is directly related to the strength of the complex formed between template and monomers. In the non-covalent imprinting method, monomer–template has a dynamic association equilibrium and in order to facilitate formation of the template–monomer complex extra amount of monomer is commonly used. In this work, the molar ratio of template to monomer was chosen to be 1:8. The large chemical structure and many functional groups of dye effected the chosen molar ratio.

The chemical structure of the dye affected the removal efficiency of dye from polymers and also polymer morphology. Different conditions for extraction of dye from the polymer was studied; MeOH:AcA (4:1); MeOH:AcA (4:2); MeOH:NaOH (1 M) (4:1). The best result was evaluated by washing MeOH:conc. HCl (9.5:0.5). The amount of extracting dyes from MIP was nearly 65%. The amount of dye extracted from the polymer depends on dye structure, the amount of non-covalent bonds between the polymer and dye, and the interaction between polymer, dye, and the solvent (Fig. 2).

The MIPs traditionally demonstrate their best performance in hydrophobic organic solvents, but clinical and environmental analyses require MIPs that can work in aqueous solution. In our study, we studied rebinding in water and methanol. The dissolution problem of dye in methanol decreased the binding of the dye, as methanol is known as a polar protic solvent. In this solvent, the anions at dye will be salivating to H– bonding, inhibiting their ability to function as nucleophile. Because of this reason that depends on nature of methanol, the binding of dye decreased. The binding in water was used to assess hydrophobic interactions. The adsorption of dye to the functional groups in cavity of Direct red 23-imprinted in water medium was nearly 80%. The effect of pH is studied to obtain the effect of its rebinding and effective recognition pH of the polymer. As known, the reactive groups of dye can be ionized and electrostatic effect also plays a role in rebinding process. The influence of the pH on the adsorption of dye was also studied at different pH and buffers (Na acetate, pH 4–5; Phosphate pH 6–8; Tris- HCl 9–10). As expected, because of the acidic character of the dye, the best rebinding was found in the buffers between pH 4–7. There was no remarkable rebinding amount found for other buffers. The amount of rebinding in buffers were less than water and it was the claim of interactions between dye and polymer were hydrophobic interactions.

Because of the insoluble nature of imprinted polymers, the characterization is difficult. FTIR is one of the analytical techniques that can be used in the chemical and morphological characterization. Also FTIR is a technique that has a capability of determining the modifications of template–monomer interaction during the imprinting process. The complexation between a functional monomer and template generally via hydrogen bonding and the formation of this bond can be identified using FTIR by the changing of stretching frequency. One of the other advantage of FTIR analysis for imprinted polymers was to analysis and undergo if the binding between polymer and template molecule was existed.

As can be seen in Fig. 3(a), the primary amine groups of polymer gave signal in 3,421 $\text{cm}^{-1}$ and in 1,727 $\text{cm}^{-1}$ ketone group of polymer has its characteristic signal. Aliphatic chain of polymer gave a signal near 3,000 $\text{cm}^{-1}$. The dye-imprinted polymer can be seen in Fig. 3(b). The signals of control polymer have slightly changed. Primary amine groups of polymer still gave signal in the same region. Moreover, the signal of a ketone group still exists in the same area. However, the signal intensity has changed due to the

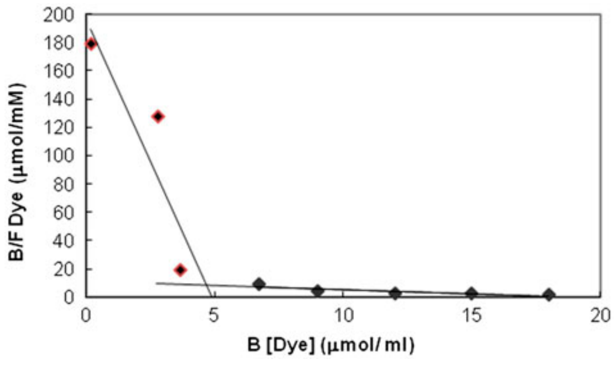

Fig. 4. Scatchard plot analysis of dye-imprinted polymer.

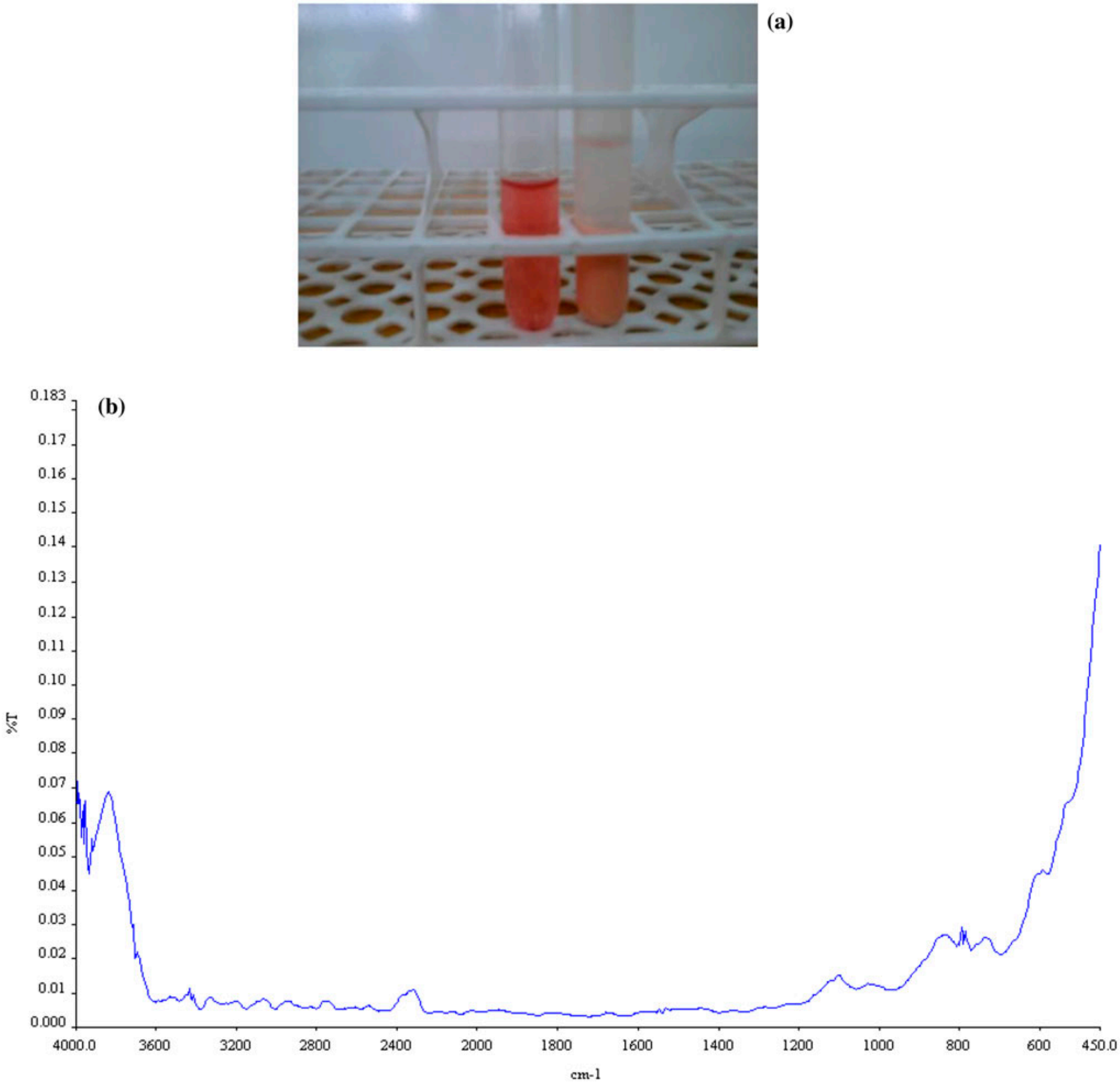

Fig. 5. (a) After synthetic dye wastewater treatment of dye-imprinted polymer and (b) FTIR of synthetic dye wastewater treatment of dye-imprinted polymer.

interaction of dye and polymer via hydrogen bonding. This evidence suggests that the imprinting of dye molecule has achieved success.

### 3.2. Scatchard analysis

The Scatchard analysis is an effortless and straightforward way to recognize multiple classes of binding sites and provides the most compact graphical presentation of binding data. The Scatchard plot is the easiest way to see multiple classes of binding sites. This is done by plotting the binding isotherm in a Scatchard format as bound/free template ratio (μmol/mM) vs. bound template (μmol). Each linear region of the binding isotherm is fitted with a straight line. As seen from the figure, there were two distinct linear sections that suggested two binding sites. One is of high selectivity with a high binding energy and the other is low affinity with a low binding energy. The $K_d$ and $Q_{max}$ values were calculated from the slopes and intercepts of the two straight lines of Scatchard plot. The $K_d$ and $Q_{max}$ values of dye polymer were $K_{d1}$ 0.02 $\mu$mol$^{-1}$ $Q_{max1}$ 4.915 $\mu$molg$^{-1}$ and $K_{d2}$ 1.77 $\mu$mol$^{-1}$ $Q_{max2}$ 19.48 $\mu$molg$^{-1}$ , respectively. It may be concluded that the binding site configuration in the MIP is heterogeneous with respect to the affinity for Direct red 23 and indicates that the binding sites could be classified into two distinct groups with different specific binding properties. It may be concluded that the binding site configuration of the MIPs is heterogeneous with respect to the affinity for dye and indicates that the binding sites could be classified into two distinct groups with different specific binding properties. The origin of molecular recognition in MIPs is generally attributed to both shape selectivity and pre-organization of functional groups, however, the contributions of these effects are difficult to compare. The shape selectivity also effected functional group pre-organization in our MIP [14–16] (Fig. 4).

### *3.3. Efficiency of dye-imprinted polymers for synthetic dye wastewater*

Initial environmental efforts with dyes dealt with color pollution, which has a strong psychological effect. The decolorization of textile waste water mainly depends on the type of dye and the structure of adsorbent used. Recently, the application of cationic polymeric materials for the removal of textile dyes is getting more concern. According to our results, after the treatment of synthetic dye waste water by dye-imprinted polymer, the decolorization of wastewater started in a very short time (Fig. 5(a)). The FTIR results also showed that the dye was adsorbed onto the polymer (Fig. 5(b)).

After treatment of Direct Red 23-imprinted polymer with wastewater that contains the target dye, the characteristics of polymer have changed. As can be seen in Fig. 5(b), amine groups and free hydroxyl groups gave a signal between 3,600 and 3,200 cm$^{-1}$, however their signals have overlapped. We can see the signs of the aromatic ring of dye in 3,100 cm$^{-1}$ and 1,600–1,500 cm$^{-1}$. Also, ketone groups of both dye and polymer overlapped and gave signal between 1,800 and 1,600 cm$^{-1}$. Signal change between control polymer, dye-imprinted polymer, and dye-treated polymer can be seen clearly from the figures.

## 4. Conclusions

In this study, MIP was prepared by bulk polymerization technique and characterized by adsorption experiments and spectral characteristics by FTIR. Our knowledge, as it was the first time, the Direct Red 23-imprinted polymers were prepared. The synthesis of low-cost and time-consuming adsorbent was very important for textile factories because they need large-scale adsorbent for repeated usage. The main advantages of this polymer were storage stability, reusability, and chemical stability of many chemicals, pH, and temperature. The development of new adsorbents having superior properties such as selectivity, specificity and the fast removing rate of dye from wastewater was very valuable.

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