

ADSORPTION OF MALACHITE GREEN ONTO STYRENE-METHACRYLATE BASED MOLECULARLY IMPRINTED POLYMER

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ABSTRACT

The adsorption of malachite green (MG) from aqueous medium by non-imprinted and molecularly imprinted styrene/methacrylate polymers was studied. The synthesized materials were characterized by powder X-ray diffraction, Fourier transform infra-red spectroscopy, scanning electron microscopy, and energy dispersive X-ray spectroscopy. The effects of initial dye concentration, contact time and temperature on the adsorption capacity for malachite green were investigated and found to be about 200 g kg⁻¹ for the imprinted polymer and 44 g kg⁻¹ for the non-imprinted polymer. The X-ray diffraction peaks at $2\theta = 18^\circ, 30^\circ$ and 42° indicate the crystalline nature of the polymers. Uptake of malachite green increased with rise in contact time and concentration, for both polymers, while decrease in uptake was observed with rise in temperature. The kinetics of the adsorption of the dye on the imprinted polymer followed the pseudo-second order ($R^2 = 0.97$), while that of the non-imprinted polymer followed the pseudo-first order ($R^2 = 0.87$). Equilibrium study showed that the Freundlich isotherm better describes the adsorption of the dye on both polymers, indicating a multilayer adsorption. The values of ΔG° indicate the spontaneity and non-spontaneity of the dye removal by the imprinted and non-imprinted polymers respectively. The negative ΔH° and ΔS° for the imprinted polymer signify that the process is exothermic and occurred with decrease in the degree of randomness. Thus, the high quantity of MG adsorbed onto the imprinted polymer indicates the high potential of the use of the imprinting technology in the removal of toxic waste from water.

Keywords: Styrene-methacrylate, Imprinted polymer, Malachite green, Adsorption, Equilibrium

INTRODUCTION

Environmental pollution by synthetic dyes is an important issue in many countries especially when dumping is more economical than recycling (Vergis *et al.*, 2018) due to insufficient legal regulations or controls. The estimated production of synthetic dyes is 7×10^5 to 1×10^6 tons per year worldwide. They are used in dyeing of textiles, paper, pulp, plastics, color photographs, foods, cosmetics and other industrial products (Ali and Gupta 2006; Rajeshkannan 2011; Khan *et al.*, 2011; He *et al.*, 2012; Ali *et al.*, 2016). In the textile industries, approximately 50 % of dyes is lost during the dyeing process and about 10 to 15 % is discarded into environment as effluents (Yang *et al.*, 2009) posing serious adverse effects on aquatic and human lives. Some dye compounds may even be carcinogenic or mutagenic (Umbuzeiro *et al.*, 2005; Novotny *et al.*, 2006; Mathur and Bhatnagar 2007; Tsuboy *et al.*, 2007). Depending on the type of dyeing process and dyes used, the

concentrations in textile effluents may vary from 10 mg/L to as high as 7000 mg/L (Koprivanac *et al.*, 1993; Ghaly *et al.*, 2014).

Basic dyes of high color intensity are mostly of the triphenylmethane class, an example being malachite green (MG). MG is water-soluble and is widely used as dye for paper, nylon and leather (He *et al.*, 2012).

Methods that have been developed for cost-effective dye removal include chemical oxidation, irradiation, coagulation-flocculation and precipitation, adsorption, combination of anaerobic and aerobic processes, membrane technologies, and ion exchange processes (Weber and Adams 1995; Wang *et al.*, 2008; Parvin 2015; Zewail and Yousef 2015). Adsorption has been reported to be promising due to its efficiency, low cost and reusability of the sorbents (Ali *et al.*, 2016; Khan *et al.*, 2014a; Khan *et al.*, 2014b; Khan *et al.*, 2015; Khan and Nazir 2015; Khan *et al.*,

2018; Rahman 2016). However, as promising as these adsorbents are, many suffer from the limitations of non-selectivity and attrition. These can be overcome by the use of molecularly imprinted polymer (MIPs) (Awokoya *et al.*, 2013). Adsorption on MIPs has been reported to be highly efficient, selective and robust. MIPs are reusable and are physically and chemically stable (Marty and Mauzac 2005; Awokoya *et al.*, 2013). Other important advantages include long shelf life, low cost of production, applicability in harsh environment, and easy preparation (Zeng *et al.*, 2012; Sharma *et al.*, 2012).

Although MIPs have been reported since the 70s (Takagishi and Klotz 1972), MIP for dyes are comparatively recent and were initially reported in 2005 (Puoci *et al.*, 2005). Amongst reported works, MIPs for dyes are mainly used as sorbents for solid phase extraction due to their high selectivity in complex samples (Zhu *et al.*, 2009).

Therefore, the main aim of this work was to explore the use of styrene-methacrylate based imprinting material in the removal of MG from aqueous medium.

MG is an appropriate template on account of its π - π interaction points with styrene to maintain stable functional monomer-template complexation. In addition, the attractive interactions between aromatic π systems are one of the principal noncovalent forces governing supramolecular organization and recognition processes.

MATERIALS AND METHODS

Materials

Styrene, ethyleneglycol dimethacrylate (EGDMA), MG, azobisisobutyronitrile (AIBN), methanol (MeOH), and acetic acid were supplied by Sigma-Aldrich, Steinheim, Germany, and used as obtained. All chemicals used were of analytical grade.

Preparation styrene-methacrylate based molecularly imprinted polymer

Briefly, 0.822 mmol (300 mg) MG was dissolved with 8.0 mL distilled water in a 100 mL standard flask, followed by the addition of 87.4 mmol (10

mL) styrene. Afterwards, 238.4 mmol (45 mL) EGDMA and 0.12 mmol (30 mg) AIBN were added to the flask. The mixture was stirred until all the solids were dissolved. The flask was then placed on a heating module and polymerization was carried out at 70 °C for 35 min. After polymerization, the flask was broken and the resulting hard green solid polymer was wiped free of the flask fragments and the monolith was ground with a mortar and pestle. As a control, a non-imprinted polymer (NIP) was also prepared, following the same procedure except that MG was omitted.

Template removal

The template was removed from the MIP as previously described (Awokoya *et al.* 2013) with minor modification. The MIP was exhaustively washed by magnetic stirring for 4 h with a mixture of MeOH and acetic acid (90:10, v/v) at room temperature. The mixture was centrifuged and the photometric absorbance at 617 nm of the supernatant liquid was determined with a UV-Vis spectrophotometer (UV-1800 Shimadzu, Kyoto, Japan). The washing process was repeated and continued until the absorbance of the filtrate at 617 nm was nil. Afterward, the MIP was washed for at least five times with MeOH to remove the acetic acid and facilitate drying.

Characterization of MIP

The functional groups of the polymers were characterized by Fourier transform infrared spectrophotometer (330 Nicolet Avatar FT-IR spectrometer, Shimadzu, Kyoto, Japan) in the range of 400 – 4000 cm^{-1} . Images of the polymers were taken by scanning electron microscopy (SEM) (FEGSEM 6100 Zeiss ultra plus, Oberkochen, Germany), coupled with energy dispersive X-ray spectroscopy (EDS). The crystalline structures in the polymers were studied with powder X-ray diffraction (XRD) (Bruker D2, Phaser DOC-M88-EXX, 155 V4-07, 2010, Karlsruhe, Germany) using Cu tube with 1.5418 (Å) radiation. Data were recorded at a scan rate of 4°/min over a 2 θ range of 10° – 90°.

Adsorption of MG onto MIP

Concentration dependence study

The adsorption of MG onto the polymers was

performed in 100 mL plastic containers with lids in a thermostatic water bath at 27 °C with speed controllable shaker (GFL, Burgwedel, Germany), 200 rpm. Amounts of 50 mg each of leached MIP were added to 20 mL of MG solutions with initial concentrations of 10, 50, 100, 200, 400 and 500 mg/L. After shaking for 6 h, the MIP was separated by centrifugation at 6000 rpm for 10 min, and the residual concentration of MG in the supernatant was determined photometrically at 617 nm. The experiment was repeated using NIP in place of MIP. Each experiment was carried out in triplicate. The quantity of MG adsorbed, q_e (g kg^{-1}), was calculated according to equation 1:

$$q_e = \frac{(C_o - C_e)V}{m} \quad (1)$$

where C_o (g L^{-1}) is the initial concentration of MG, C_e (g L^{-1}) is the concentration of MG in the solution after 6 h; m (kg) is the mass of MIP/NIP; and V (L) is the solution volume. The experimental data were fitted into the Langmuir (1918) and Freundlich (1906) isotherm models.

Time dependence study

Aliquots of 50 mg adsorbent were added to 20 mL of an aqueous solution 100 mg L^{-1} MG solution of MG and agitated for 6 h (0 – 360 min). The adsorbent was separated by centrifugation at 6000 rpm for 10 min and the MG concentration in the supernatant was determined photometrically at 617 nm. Data obtained were fitted to the pseudo-first order (Lagergren 1898; Ghorai *et al.* 2014) and pseudo-second order (Ho and McKay 1999) kinetic models.

Thermodynamic study

The thermodynamic behavior of the adsorption process was evaluated by performing the adsorption study at four different temperatures (30, 40, 50, 60 °C). The study involved the use of 50 mg adsorbent dose and the initial MG concentration of 100 mg L^{-1} . The mixture was agitated for 6 h.

Selectivity study

The selectivity of MIP-MG cavities was performed using two different dyes, commonly used in the industry. The dyes used in this study

were methyl violet (MV) and methylene blue (MB). 50 mg of MIP was mixed with 20 mL of MV and MB solutions with initial concentration of 500 mg L^{-1} at room temperature. The recognition coefficient (α) of each dye to the polymer was compared to the rebinding of MG. This coefficient was used to evaluate the selectivity (Yang *et al.* 2005), and was calculated according to

$$\alpha = \frac{[\hat{S}]_{(imprinted)}}{[S]_{(non-imprinted)}} \quad (2)$$

Where $[S]_{(imprinted)}$ represents the quantity of dye adsorbed onto the MIP (g kg^{-1}) and $[S]_{(non-imprinted)}$ is the quantity of dye adsorbed onto the NIP (g kg^{-1}).

RESULTS AND DISCUSSION

Structural analysis of the MIP and NIP

Fourier Transform Infrared (FT-IR) Analyses

FTIR spectroscopy is a useful tool for monitoring changes in chemical environments resulting from the addition or removal of functional groups in imprinted polymers (Cormack and Elorza 2004). The FT-IR spectra of leached (LMIP), unleached (UMIP) and control NIP materials within the range of 4000 to 450 cm^{-1} are shown in Fig. 1. LMIP, UMIP, and NIP spectra are similar because the materials have similar components, such as template, monomer, initiator and cross linker. Spectra with similar behavior have been reported by Abdallah *et al.*, 2017). Analyses of these spectra (1a, b and c) reveal the existence a typical OH bands of H_2O at 3549, 3535, 3441, 3437 cm^{-1} and CH vibrations at 2985, 2955, 1456, 1454, 1321, 759, 758 cm^{-1} . In addition, the peaks at 2360 and 2359 cm^{-1} confirm the presence of $\text{C}\equiv\text{N}$ bonds of AIBN. The stretching band of $\text{C}=\text{O}$ at 1724 cm^{-1} affirms the structural characteristic of EGDMA (Zhang *et al.* 2017). All the spectra have a very strong and sharp peak at 1637 cm^{-1} , which may be attributed to the existence of a large number of olefinic carbon-carbons ($\text{C}=\text{C}$) bonds of MG, styrene and EGDMA (Wang *et al.* 2009; Khasanah *et al.* 2010). The presence of the above characteristic peaks suggests that polymerization process actually occurred.

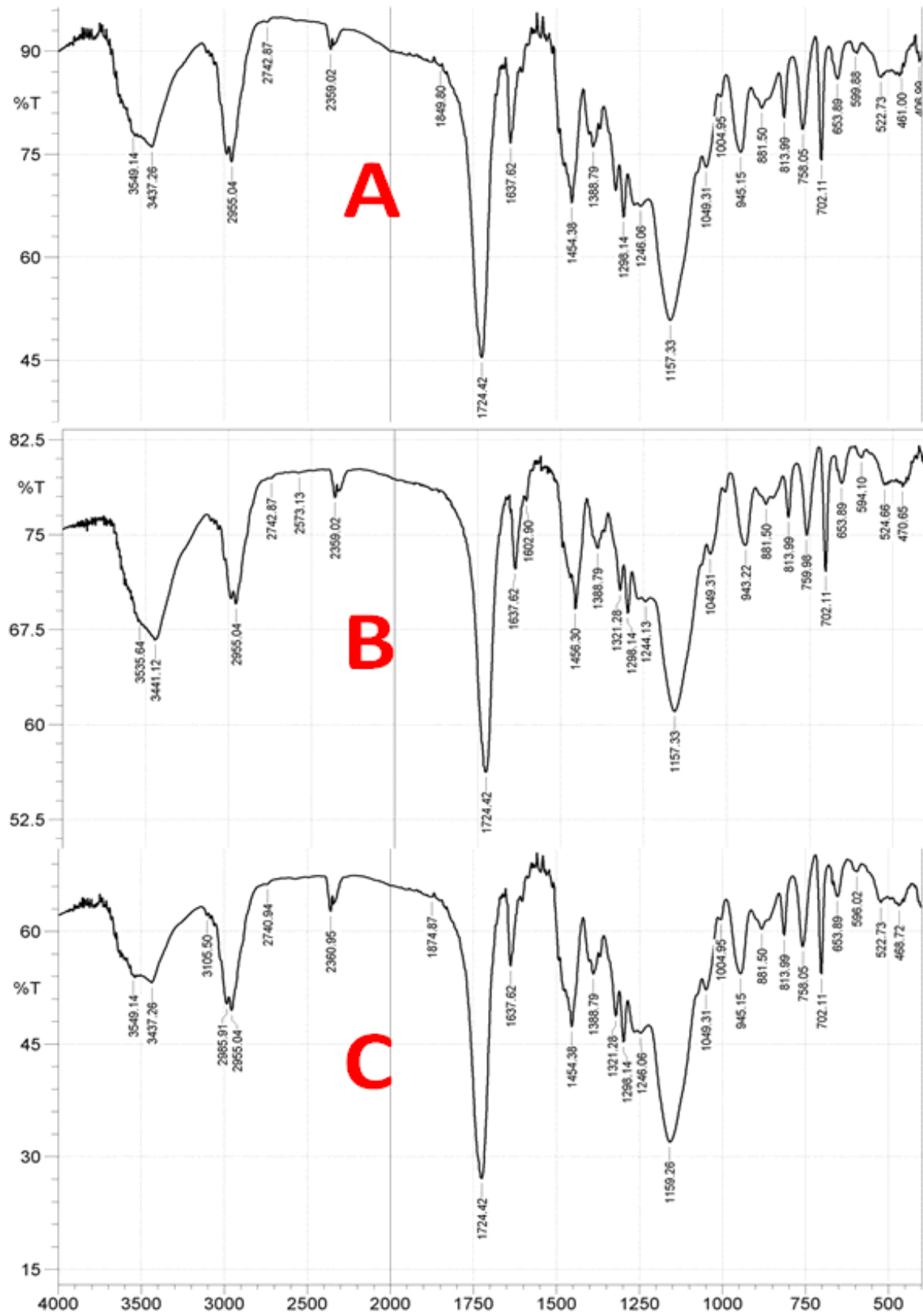


Fig. 1: FT-IR spectra of polymer particles: (A) leached MIP (B) unleached MIP (C) control NIP

SEM and EDS

Surface morphology properties play an important role in a number of applications where both natural and synthetic polymeric materials are utilized. The surface morphology of the LMIP, UMIP and NIP were investigated by SEM. The main goal was to evaluate the physical appearance and internal structure of the polymer particles. As shown in Fig. 2A, the surface morphology of the leached polymer was relatively smooth compared to its unleached and non-imprinted counterparts (Figs. 2B and 2C). This phenomenon could be principally attributed to the removal of template

molecule from the polymer matrix, as reported by Ji *et al.* (2008). The EDS spectra for all the polymers are shown in Figs. 2 (a, b and c). The EDS spectrum of UMIP (Fig. 2b) showed the presence Cl atom, suggesting that the polymer network was formed with MG template molecule embedded in the inner matrix of the polymer. However, no trace of Cl atom was detected in the spectra of LMIP and NIP (Figs. 2a and 2c). The absence of Cl atom from the LMIP indicates a successful removal of MG from the polymer, hence the similarity between the two polymers.

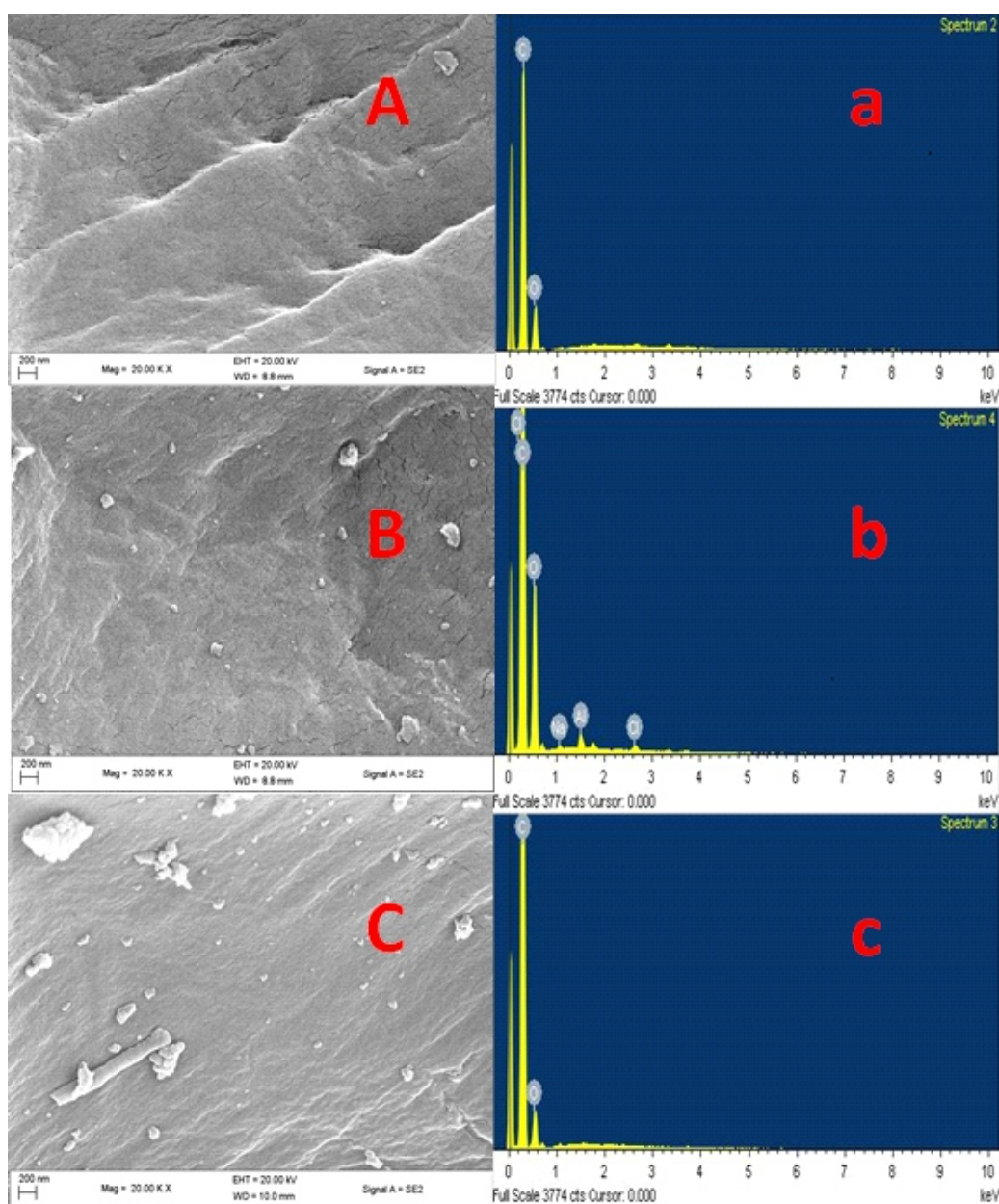


Fig. 2: Scanning electron micrographs and energy dispersive spectra of the polymers. A and a: LMIP, B and b: UMIP, C and c: NIP.

X-ray Diffraction

XRD analysis (Chauhan and Chauhan 2017) was performed to check if the removal and non-inclusion of the template disrupted the crystalline orientation of the polymer materials. The XRD patterns of the LMIP, UMIP and NIP are shown in Fig. 3. The distinct three characteristic diffraction peaks around $2\theta = 18^\circ$, 30° and 42° were observed for all the polymers. The diffraction peak positions were unaltered after

removal of the template (LMIP), which indicate that the crystalline structure of the unleached MIP was substantially maintained. This is basically consistent with the work by Qi *et al.* (2016). Moreover, the additional diffraction peak with $2\theta = 10^\circ$ observed in the unleached MIP was assigned to MG, which is in agreement with the FT-IR spectra and thus is a confirmation that the MG template was successfully imprinted.

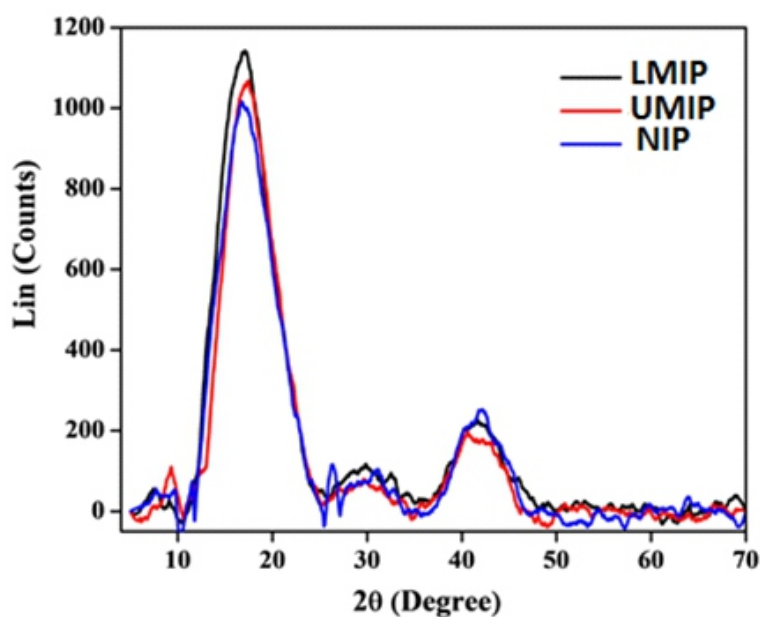


Fig. 3: X-ray diffraction patterns of leached MIP, unleached MIP and NIP.

Quantitative assessment

Effect of contact time

Figure 4 shows the time dependent adsorption of MG onto MIP and NIP at 27°C . The results showed a steady rise in MG uptake by the MIP, with increase in contact time from 0 to 240 min, followed by a moderate rise in uptake up to 360 min. Equilibrium MG uptake was, however, not reached after the maximum time of 360 min considered. At the initial stage, especially within the first 60 min, uptake of the dye was rapid, possibly due to the exposure of most of the

binding sites on the MIP. Similar results have been reported in literature for adsorption of crystal violet onto alkali-modified rice husk by Chakraborty *et al.* (2011). Broadly speaking, dye adsorption consists of two phases: a very swift initial sorption, followed by a long period of much slower uptake (Sun *et al.* 2008). Under the same conditions, the MIP exhibited much higher recognition than the control NIP, indicating that binding sites complementary to the template were not present in the latter.

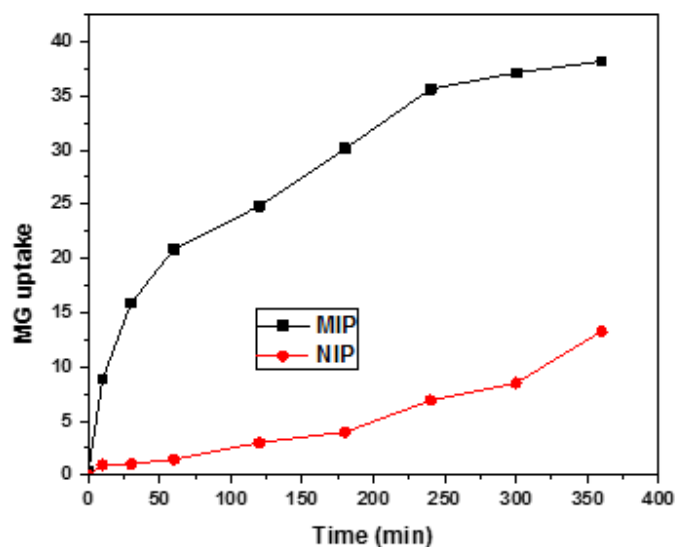


Fig. 4: Uptake of MG dye at different contact time

Effect of initial adsorbate concentration

The effect of the initial MG concentration on the dye adsorption capacity was investigated in the range ($10 - 500 \text{ mg L}^{-1}$) at room temperature. The initial adsorbate concentration factor depends on the instantaneous affinity between the dye concentration and the accessible binding sites on an adsorbent surface (Umoren *et al.* 2013). When the initial adsorbate concentrations were increased, uptake of MG by the MIP and NIP increased (Figure 5). This may be due to the increase in the driving force of the concentration activity (Chiou and Li 2002). The amount of MG adsorbed by both the MIP and NIP increased slightly when the adsorbate concentration was

increased from 10 to 50 mg L^{-1} . Afterwards, when the MG concentration was greater than 50 mg/L , the quantity adsorbed increased significantly for the MIP, while NIP has relatively lower quantity adsorbed. Maximum adsorption capacity for MIP was about 4.47 times that of the NIP. The maximum adsorption capacities for MIP and NIP were 197 g kg^{-1} and 44 g kg^{-1} respectively. This indicates that the MIP has excellent specific surface active sites for MG molecule. In comparison with other adsorbents, such as rice straw (Gong *et al.* 2006), the synthesized MIP showed very high efficiency in the removal of MG from aqueous medium.

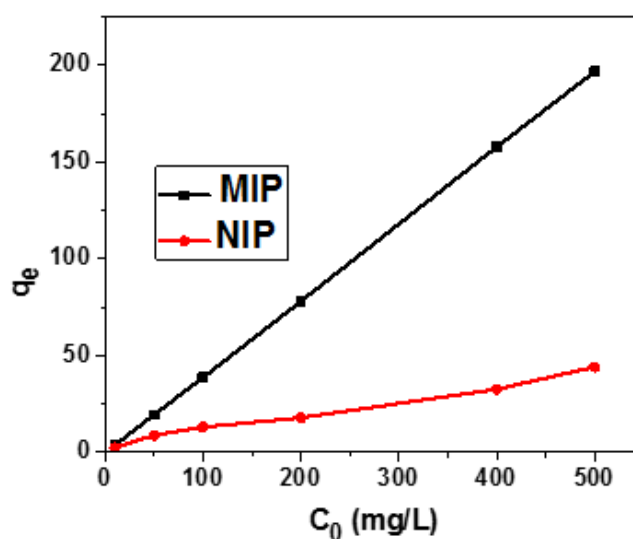


Fig. 5: Effect of initial adsorbate concentration on MG uptake by MIP/NIP

Effect of temperature and thermodynamic study

The adsorption process is usually not operated at high temperature because of increase in operational cost (Sag and Kutsal 2000). The extents of MG molecule adsorption on the MIP and NIP at four different temperatures (30 °C, 40 °C, 50 °C and 60 °C) are shown in Figure 6b. Results indicate that when the temperature increased from 30 °C to 60 °C, the amount of MG adsorbed onto MIP decreased from 38 g kg⁻¹ to 37 g kg⁻¹ while that of the NIP decreased from 2.9 g kg⁻¹ to 1.8 g kg⁻¹. This suggests that higher temperature did not favor the adsorption process. The decrease in adsorption with increasing temperature, suggests weak adsorption interaction between MIP surface and the dye molecule, which supports physisorption process (Sag and Kutsal 2000; Vijayaraghavan and Yun 2006). Furthermore, other plausible reason for the reduction in the dye uptake by the MIP at higher temperature might be due to the fact that bonds in the cavities of the MIP were weakened and broken which facilitated weak adsorption interaction. Increase in temperature may also cause cavity expansion which may leads to leaching of MG adsorbed on the MIP (Uwah *et al.* 2013).

The thermodynamics of the adsorption process was determined by evaluating the thermodynamic parameters such as free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°). The values of ΔS° and ΔH° for the

adsorption process were determined from the intercept and slope of the plot of $\ln K_c$ versus $1/T$ (Figure 6a), using the van't Hoff equation. The negative ΔG° values obtained for MIP at all temperatures (-7.8, -7.5, -7.3 and -6.9 kJ mol⁻¹) indicate the feasibility as well as spontaneous nature of the adsorption of MG onto the polymers. On the other hand, ΔG° values for the removal of MG by NIP (7.6, 5.5, 3.3 and 1.2 kJ mol⁻¹) show non-spontaneity of the process. The negative values of ΔG° for the MIP decreased with increase in temperature, suggesting a steady decrease in the spontaneity of the process with rise in temperature. Bulut and Tez (2007) also reported a similar behavior for the removal of heavy metals from aqueous solution by sawdust. The ΔG° values for the MIP are between -20 kJ/mol and 0 kJ/mol, indicating physical adsorption as the dominating mechanism in the adsorption process. The negative ΔH° (-15.9 kJ mol⁻¹) and positive ΔS° (0.03 kJ mol⁻¹) values obtained for the MIP imply that the adsorption process was exothermic and occurred with decreased randomness at the solid/solution interface during the adsorption process (Nithya *et al.* 2017). The positive ΔH° value (72.2 kJ mol⁻¹) obtained for the adsorption of MG onto NIP indicates that the adsorption process was endothermic, while the corresponding positive ΔS° value (0.2 kJ mol⁻¹) signify that the freedom of MG is not too confined in the NIP, confirming a physical adsorption (Horsfall and Spiff 2005).

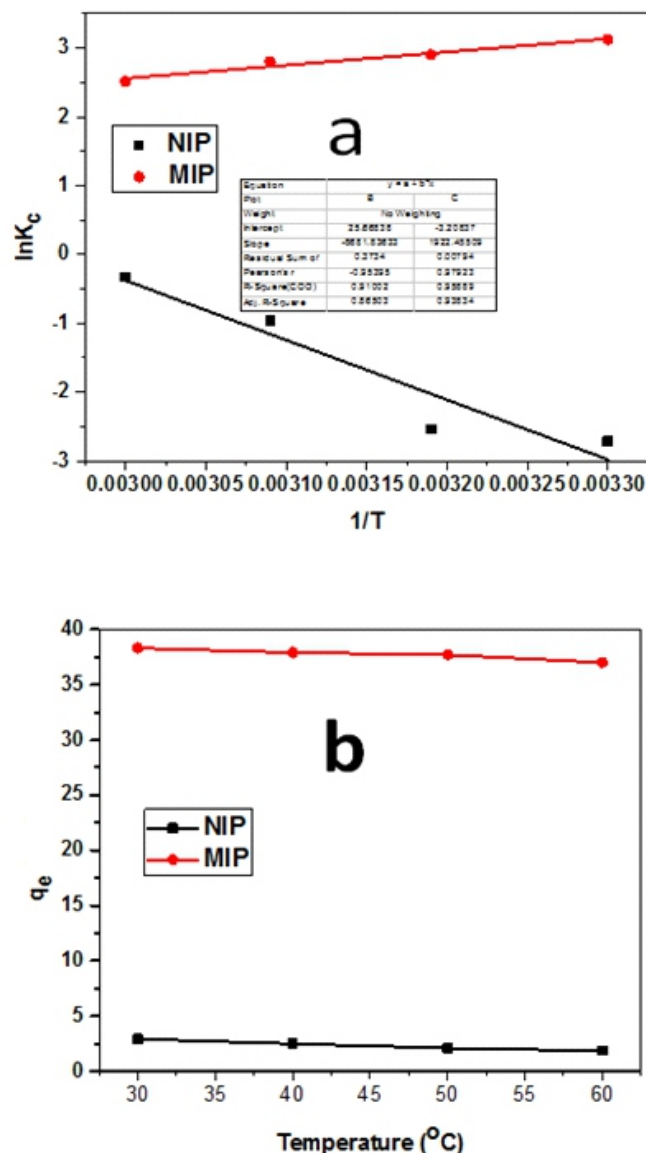


Fig. 6: Thermodynamic parameters plot (a) and effects of temperature (b) on adsorption of MG onto MIP and NIP.

Modeling of the sorption process

Kinetics of the adsorption process

Kinetics of adsorption is an essential characteristic in determining the effectiveness of any adsorption process. It describes solute uptake rate, which in turn governs the residence time of the reaction (Hema and Arivolis 2008). In evaluating the kinetics of the adsorption of MG onto MIP and NIP, the pseudo-first-order (Lagergren 1898) and the pseudo-second-order (Ho and McKay 1999) kinetic models were used to fit the experimental data (Figures and Table not shown). The values of the correlation coefficient (R^2), indicate that the pseudo-second order ($R^2 = 0.97$) was better than the pseudo-first order

model ($R^2 = 0.61$) in describing the adsorption of MG onto MIP. This assertion was also corroborated by the closeness of the calculated quantity of MG adsorbed ($q_{e(\text{calc})} = 42.5 \text{ g kg}^{-1}$) to the experimental value ($q_{e(\text{expt})} = 40.8 \text{ g kg}^{-1}$). It thus signifies that the adsorption rate was controlled by the concentration of MG in solution as well as the specific surface active sites on the MIP (Wang 2015). On the other hand, the R^2 value of 0.87 for the adsorption of MG by NIP shows that the kinetics of the process followed the pseudo-first order. This claim is also supported by the relatively large difference between the calculated q_e value ($q_{e(\text{calc})} = 25.7 \text{ g kg}^{-1}$) and experimental q_e value ($q_{e(\text{expt})} = 19.8 \text{ g kg}^{-1}$) determined for the removal of MG by

NIP.

Equilibrium modeling

The interaction mechanism between adsorbate and adsorbent at equilibrium time is explored by Freundlich and Langmuir models (Benhamou *et al.* 2009; Parvini 2014). Modeling the adsorption isotherm data is an essential way for predicting and measuring the adsorption performance, which is critical for optimization of the adsorption mechanism pathways, expression of the adsorbents capacities, and effective design of the adsorption systems (Thompson *et al.* 2001).

The parameters and correlation coefficients obtained from the equilibrium modeling plots of

both Langmuir and Freundlich are listed in Table 1. For both the MIP and NIP, the correlation coefficients of the Freundlich model were very close to unity (0.953 and 0.985) and larger than the Langmuir model (0.757 and 0.847), thereby indicating that the adsorption of MG onto MIP and NIP occurred via a multiple layer process. The Freundlich constant, K_f , obtained for the sorption of MG onto MIP was observed to be more than 5 fold that observed for NIP; indicating that the number of cavities with adequate geometry and good accessibility to the target analyte (MG) in MIP particles were higher than those in the NIP particles. This shows that the imprinting technology has made the polymer to be a better adsorbent for the target analyte.

Table 1: Parameters of Langmuir adsorption equation and Freundlich isothermal equation for adsorption experimental data.

Isotherm	Parameters	Values (MIP)	Values (NIP)
Langmuir	Q_m (g kg ⁻¹)	943.39	52.938
	K_a (mg/L)	0.397	0.006
	R^2	0.847	0.757
Freundlich	k_f	6.669	1.239
	n	0.607	1.758
	R^2	0.953	0.985

Selectivity analysis of MIP for MG

The specificity of the molecular recognition of different analytes by the MIP was evaluated by investigating the ability of the adsorbent to discriminate between two other analogue molecules, namely methyl violet (MV) and methylene blue (MB). Results showed that the MIP recognized and adsorbed MG better than MV and MB. The recognition coefficient for MG was 4.48, while the coefficients for MV and MB were 4.03 and 3.81, respectively. It is of interest to know that the adsorption of MG is relatively unaffected by other dyes with similar structures.

CONCLUSIONS

The ability of styrene-based imprinted polymer, synthesized by bulk polymerization, was found to

be affected by operational parameters such as contact time, temperature and initial adsorbate concentration. The introduction and eventual leaching of MG template favored the formation of specific active sites in the imprinted material in the form of cavities complementary to MG. Compared with the NIP, the MIP matrix showed cavities responsible for its higher adsorption capacity. High maximum adsorption capacity recorded for MIP is an indication of it being a good adsorbent in the removal of MG. Kinetic data indicate that the rate determining step in the adsorption process is chemisorption. Equilibrium data indicate multilayer adsorption. Thermodynamic parameters indicate that the adsorption process was exothermic and spontaneous. Thus, the styrene-based MIP showed a very great potential in the removal of

MG dye from aqueous medium, thereby suggesting the applicability of molecular imprinting technology in the removal pollutants from aqueous solution.

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