



## Synthesis and Characterization of a Molecularly Imprinted Polymer for Methylene Blue

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This study reports the preparation of a molecularly imprinted polymer for the removal of methylene blue dye from aqueous media. The methylene blue-molecularly imprinted polymer was prepared using bulk polymerization *via* radical polymerization containing methylene blue as a template, methacrylic acid, as a monomer, ethylene glycol dimethacrylate as a cross-linker, benzoyl peroxide as an initiator and tetrahydrofuran as a solvent (porogen) in ratios of 0.117 mmol, 0.930 mmol, 4.650 mmol, 10.000 mg and 30.000 mL, respectively. The polymer block obtained was ground and sieved using a 90  $\mu\text{m}$  sieve and the methylene blue template was removed from the methylene blue-molecularly imprinted polymer by extracting it with methanol/acetic acid/water (8:1:1) mixture. The non-molecularly imprinted polymer was synthesized as a reference. The methylene blue-molecularly imprinted polymer was characterized by using Fourier-transform infrared spectroscopy, scanning electron microscopy, a particle size analyzer and BET equation. The effect of different parameters such as pH, time and concentration of methylene blue, selectivity and reusability of the methylene blue-molecularly imprinted polymer were evaluated. Maximum sorption of methylene blue occurred at pH 5 in 30 s. The sorption followed a pseudo-second-order kinetic model. The adsorption isotherm of methylene blue followed the Freundlich isotherm model. The selectivity study had proved that the methylene blue-molecularly imprinted polymer was highly selective to the methylene blue analyte.

**Key Words:** Molecularly imprinted polymer, Methylene blue, Bulk polymerization, Reusability, Selectivity.

### INTRODUCTION

Many organic dyes are harmful to human beings and toxic to microorganisms. The removal of dyes from wastewater has received considerable attention over the past decades. Dyes include a broad spectrum of different chemical structures, primarily based on the substituted chemical structures and aromatic groups. Due to the complex chemical structure of these dyes, they are resistant to breakdown by chemical, physical and biological treatment<sup>1</sup>.

Aromatic compounds like dyes are the main pollutants of water and they may be found in trace quantities in these effluents. These substances, which are often encountered in the environment as a result of their numerous industrial applications, create serious water quality problems. Many compounds are known to be toxic or carcinogenic even at low concentrations<sup>2</sup>. It should be noted that the contamination of drinking water by dyes at even a concentration of 1 mg/L could impart significant colour, making it unfit for human consumption<sup>3</sup>.

Dyes are widely used in textile, paper, plastic, food and cosmetic industries. The wide use of dyes makes it easy to recognize the pollutant. There are many harmful impacts of dyes on the ecosystem. Depending on the dye concentration

and the exposure time, dyes can have chronic effects on an exposed organism. Dyes are inherently highly visible and may cause abnormal colouration of surface waters even with a minor release. The ability of the dye to absorb and reflect sunlight entering the water can have drastic effects on the growth of bacteria and their biological activity. The complicated and different molecular structures of dyes are difficult to treat and interfere with the waste treatment operations. Dyes can also consume dissolved oxygen from the stream and destroy aquatic life through chemical and biological changes<sup>4</sup>.

Many methods are available for the removal of methylene blue. Among these methods, absorption is by far the most versatile and widely used method because of its initial cost, simplicity of design, ease of operation and insensitivity to toxic substances. There are a number of agricultural waste and by-products that have been studied for removal of methylene blue. However, the qualifications of these products are limited, because the selectivity and specificity properties are very limited. Furthermore, the reusability of the products has not been reported. Many kinds of adsorbents such as activated carbon and silica<sup>5</sup>, natural polymeric materials and sewage sludge have been developed for various applications. However, their operating costs are high<sup>1</sup>. Catalyst  $\text{TiO}_2$  has proved to be an excellent

catalyst in the photodegradation of organic pollutants, due to its effective, photostable and reusable performance<sup>6,7</sup>. However, there are many limitations<sup>8</sup> such as the recollection and reuse of TiO<sub>2</sub>.

Molecularly imprinted polymers (MIPs) are cross-linked polymeric materials that exhibit high binding capacity and selectivity against a target molecule (template) present during the synthesis process. It has been used as a synthetic material that is able to rebind the target template analyte. Molecularly imprinted polymers are suitably used in solid-phase extraction, sensor and chromatographic analysis for its potential absorptive selectivity<sup>9</sup>. Molecularly imprinted polymers have high quality properties, they are, continuous, fast and accurate tools, more selective and sensitive, stable, easy to prepare, cheap, long storage endurance and reuse<sup>10</sup>.

The synthesized molecularly imprinted polymer is based on the non-covalent binding interaction between the template analyte and monomer. The binding interaction is supported with a cross-linker and initiator, which help to make a porous copolymer and morphology structure. The distinct cavities remain in the copolymer with the removal of the template analyte, which recognizes the site to the template molecule, with the same size, shape and functionality<sup>11</sup>. The bulk polymerization process is continued with grinding and sieving the methylene blue-molecularly imprinted polymer, from which a bead structure with irregular shape and size is obtained.

## EXPERIMENTAL

Methylene blue and methacrylic acid (MAA) were from Fluka, Ethylene glycol dimethacrylate acid (EGDMA) was from Sigma-Aldrich Chemicals and benzoyl peroxide (BPO) and tetrahydrofuran (THF) were obtained from R and M Chemicals. All other materials were of reagent grade and purchased from Merck (Germany). Distilled water was used throughout the experiment.

In this study, bulk polymerization was used for the preparation of methylene blue-molecularly imprinted polymer in tetrahydrofuran, as a porogenic solvent, using the methylene blue template, methacrylic acid, ethylene glycol dimethacrylate acid, benzoyl peroxide as a template, monomer, cross-linker and initiator, respectively. The non-molecularly imprinted polymer (non-molecularly imprinted polymer) was used as a reference. The continuous process was characterized using Fourier-transform infrared spectroscopy, scanning electron microscopy, a particle size analyzer and BET. In addition, the evaluation of the methylene blue-molecularly imprinted polymer was optimized by pH, kinetic study, sorption isotherm, selectivity and reusability studies.

**Preparation of methylene blue-molecularly imprinted polymer:** Bulk imprinted polymers were synthesized using a molar ratio of 5:1 (cross-linker/monomer). First, 0.117 mmol of methylene blue was dissolved in 0.930 mmol of methacrylic acid and 4.650 mmol of ethylene glycol dimethacrylate acid. This solution was then transferred to a beaker containing 10 mg of benzoyl peroxide and 30 mL of tetrahydrofuran. After thorough mixing, the mixture was sealed and purged with nitrogen gas for at least 10 min, before being placed in a water bath overnight. Once the polymerization was completed, the

resulting polymer was ground, crushed and sieved using a 90  $\mu\text{m}$  sieve before extraction. The extraction process was followed by removing the methylene blue template by washing with methanol/acetic acid/water (8:1:1) mixture until the template molecules were undetected. Non-imprinted polymers (non-molecularly imprinted polymer) as a reference were synthesized using the same procedure excluding the methylene blue template from the formulation.

### Characterization of the methylene blue-molecularly imprinted polymer

**IR study:** The FTIR spectrum of the methylene blue-molecularly imprinted polymer samples was obtained by using the FTIR Perkin-Elmer 1600 spectrophotometer in the range of 4000-400  $\text{cm}^{-1}$ . FTIR was carried out for the molecularly imprinted polymer and methacrylic acid monomers (as a reference). They were incubated using the silica gels for more than 24 h, at room temperature, to remove the water before analysis.

**Morphology analysis:** The morphology and surface structure of the methylene blue-molecularly imprinted polymer and non-molecularly imprinted polymer were obtained by means of a SEM, operated at an accelerating voltage of 15 kV. The samples suitable for SEM were prepared by dispersing the samples on a metallic sample holder and gluing them by using a double-sided tape. The samples were coated with a thin layer of gold, which was a type of conducting material, by using a BIO-RAS Sputter coater. Micrographs were recorded at various magnifications.

**Particle size analysis (PSA):** A Malvern particle size analyzer measured the sorbents particle size between 0.002-700  $\mu\text{m}$ . The samples were diluted in deionized water. They were sonicated for 10 min to keep the particles dispersed during measurement. The samples were put into a 1 cm quartz cell before analysis. The particle size distribution, determined from light diffraction, was measured either in terms of volume or weight distribution.

**Bruenauer, Emmet and Teller (BET):** In this study, BET analysis was conducted; to define the surface area and average pore diameter of the molecularly imprinted polymer and non-molecularly imprinted polymer powders. The analysis of the BET surface area measurements were obtained by performing nitrogen adsorption at liquid nitrogen temperature (77 K). Typically, at least a 0.5 g sample was used each time. The sample was previously degassed at 393 K, overnight. The specific surface area was calculated using the BET equation.

### Parameter studies

**Effect of pH on sorption of methylene blue by methylene blue-molecularly imprinted polymer:** To study the effect of pH, a 10 ppm dye solutions of methylene blue were prepared. The initial pH of the methylene blue solutions was adjusted to the range of 1-9, by adding dilute HCl and NaOH. Each 20 mL methylene blue solution was shaken with 0.0500 g methylene blue-molecularly imprinted polymer for 1 h. The experiment was carried out at room temperature. Methylene blue-molecularly imprinted polymer was filtered using a filter paper. The filtrate of the methylene blue solution was analyzed and the optimum pH for maximum sorption was determined.

### Effect of kinetics study on the sorption of methylene blue by methylene blue-molecularly imprinted polymer:

The kinetic experiments were performed using methylene blue solutions of different concentrations (50, 100 and 200 ppm). The kinetics on the sorption of methylene blue by methylene blue-molecularly imprinted polymer was studied from 1 to 30 min; 0.0500 g of methylene blue-molecularly imprinted polymer was added to 20 mL of each methylene blue solution. The solution was shaken and filtered before analysis. The filtrate was then analyzed using a UV-visible spectrophotometer.

**Effect of the sorption isotherm study on the sorption of the methylene blue by methylene blue-molecularly imprinted polymer:** The sorption isotherm was carried out by using different concentrations of methylene blue (10 ppm to 400 ppm) shaken with 0.05 g methylene blue-molecularly imprinted polymer in 20 mL of methylene blue solution at optimum pH and contact time. Then, the filtrate was analyzed using a UV-visible spectrophotometer.

**Selectivity study of the methylene blue-molecularly imprinted polymer:** Non-molecularly imprinted polymer 0.05 g was prepared using the same procedure, excluding the template molecules. The selectivity of the obtained particles was elucidated by the different rebinding capabilities of the methylene blue-molecularly imprinted polymer and non-molecularly imprinted polymer toward 20 mL of methylene blue solution shaken for 1 h. To study the selectivity of methylene blue-molecularly imprinted polymer, the binding of methylene blue and some other dye compounds such as methylene orange and fast green on the methylene blue-molecularly imprinted polymer of 0.05 g was mixed with 20 mL of each different dye and shaken for 1 h.

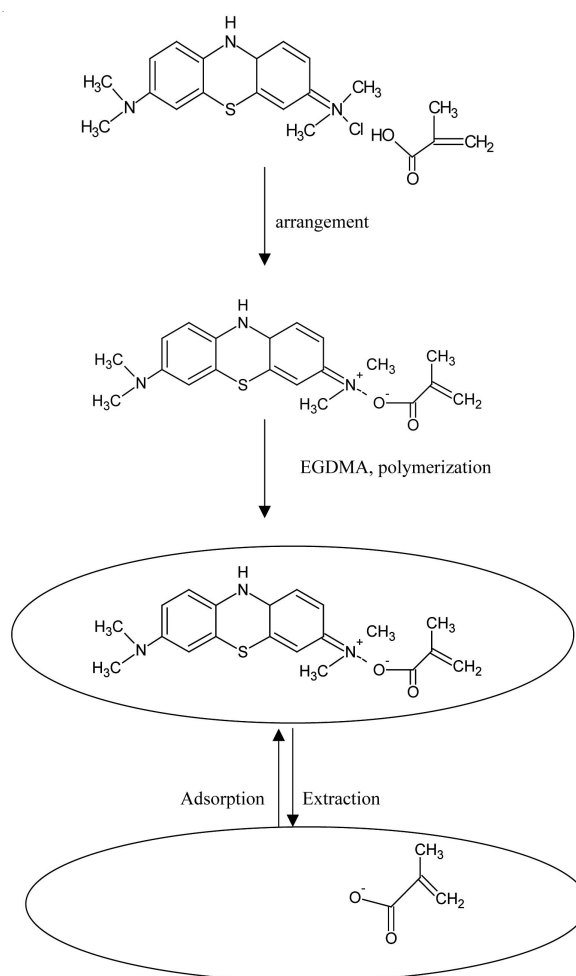
**Reusability study of methylene blue-molecularly imprinted polymer:** The reusability of the methylene blue-molecularly imprinted polymer was studied by using the same methylene blue-molecularly imprinted polymer after a regeneration process. Regenerated methylene blue-molecularly imprinted polymer of 0.0500 g was mixed with methylene blue solution and shaken for 1 h. The filtrate was then analyzed using UV-visible spectrophotometry.

## RESULTS AND DISCUSSION

**Preparation of methylene blue-molecularly imprinted polymer:** In this study, bulk polymerization was employed to synthesize methylene blue molecularly imprinted polymer in 30 mL of tetrahydrofuran using 0.117 mmol of methylene blue and a molar ratio of 5:1 (EGDMA/methacrylic acid), which are 0.930 mmol of methacrylic acid, 4.650 mmol of ethylene glycol dimethacrylate and 10 mg of benzoyl peroxide as the template, functional monomer, cross-linker and initiator, respectively. The ratio was based on methods proposed by Perez-Moral and Mayes<sup>12</sup>. This measure was also proposed by several researchers<sup>11,13,14</sup> for the synthesis of malachite green molecularly imprinted polymer, as well as, by Puoci *et al.*<sup>15</sup>, for the synthesis of Sudan I molecularly imprinted polymer. The total weight of the methylene blue-molecularly imprinted polymer product obtained was between 5.25-5.69 g. The

grinding and sieving process indicated that the bulk molecularly imprinted polymer obtained an irregular shape and size. This finding agreed with the previous studies<sup>12,16,17</sup>.

The carboxylic group in methacrylic acid can form an electrostatic interaction with the amino group in methylene blue (**Scheme-I**). The hydrogen is released from the OH group of methacrylic acid and the oxygen becomes charge negative. The ionic charge is obtained at the methylene blue molecule because the methylene blue solution is in an aqueous media. Therefore, the positive charge of the amino group in the methylene blue interacts with the negative charge of the carboxylic group. This interaction shows that the methylene blue-molecularly imprinted polymer is produced by the ionic interaction process. The extraction process leaves the specific and recognition sites for the methylene blue molecule and these vacant sites will occupy the same template analyte. Therefore, the specific and positioned interactions will contribute to the molecularly imprinted polymer's selective affinity. This finding also agrees with the research article of synthesizing the malachite green molecularly imprinted polymer by Yan *et al.*<sup>11</sup>. Methacrylic acid (carboxylic acid-based monomer) is often found to be suitable for ionic interaction binding<sup>18</sup>. Therefore, the methacrylic acid monomer was chosen for the synthesis of methylene blue-molecularly imprinted polymer.



**Scheme-I:** Schematic preparation of methylene blue-molecularly imprinted polymers

Fig. 1 shows the FTIR spectrum of methylene blue-molecularly imprinted polymer and the methacrylic acid monomer. methacrylic acid has been used as a reference to confirm the polymerization process. The FTIR spectrum for the methylene blue-molecularly imprinted polymer shows a broad adsorption at  $3450\text{ cm}^{-1}$ , which can be assigned to the ionic interactions that occur between the amino group in methylene blue and the carboxylic group in methacrylic acid. An adsorption at  $2990\text{ cm}^{-1}$  is usually ascribed to the  $\text{CH}_3$  group, whereas, the absorption at  $1728\text{ cm}^{-1}$ , is assigned to the  $\text{C}=\text{O}$  group. The adsorption at  $1636\text{ cm}^{-1}$  can be assigned to the  $\text{C}=\text{C}$  group, while  $1460\text{ cm}^{-1}$  is assigned to the  $\text{CH}_2$  group and  $1160\text{ cm}^{-1}$  is assigned to the  $\text{C}-\text{O}$  group. The  $\text{C}-\text{N}$  group is seen at  $1260\text{ cm}^{-1}$ , which indicates the amino group of methylene blue.

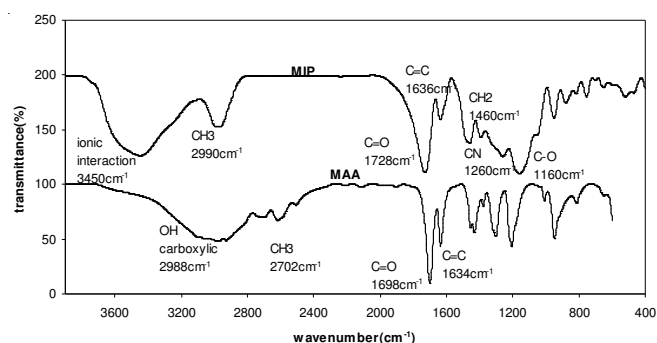
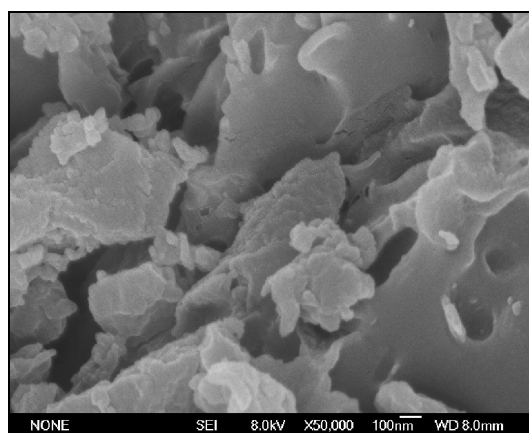


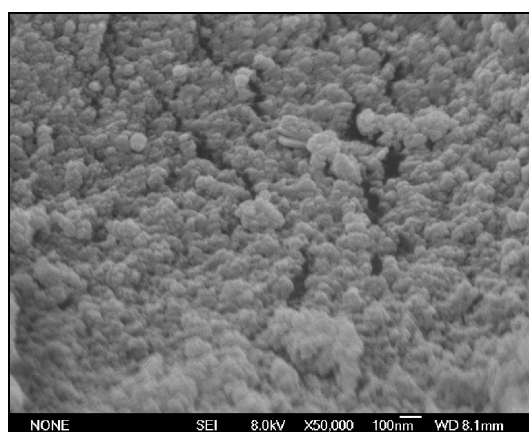
Fig. 1. FTIR spectrum for methylene blue-molecularly imprinted polymer and methacrylic acid

The FTIR spectrum of the methacrylic acid shows that the  $2988\text{ cm}^{-1}$  is assigned to the  $\text{O}-\text{H}$  group, which does not appear in the spectrum of the methylene blue-molecularly imprinted polymer. This  $\text{O}-\text{H}$  group is the characteristic of the  $\text{O}-\text{H}$  stretching of the carboxylic group. This is due to the  $\text{H}^+$  of the carboxylic group in the methacrylic acid that is removed during the polymerization process. Although the absorption at  $2702\text{ cm}^{-1}$  is assigned to the  $\text{CH}_3$  group,  $1698\text{ cm}^{-1}$  is assigned to the  $\text{C}=\text{O}$  group and  $1634\text{ cm}^{-1}$  is assigned to the  $\text{C}=\text{C}$  group. Theoretically, the  $\text{C}=\text{O}$  group should be in the range of  $1860-1600\text{ cm}^{-1}$ . However, the range of  $\text{C}=\text{O}$  in the FTIR spectrum of methylene blue-molecularly imprinted polymer and methacrylic acid so far, was apparently,  $1728$  and  $1698\text{ cm}^{-1}$ , respectively. This shifting occurred may be due to the ionic interaction, where the positive charge of the nitrogen atom from the methylene blue molecule was attached to the negative charge of the oxygen atom from the methacrylic acid molecule, which was attached to the  $\text{C}$  of the methacrylic acid monomer.

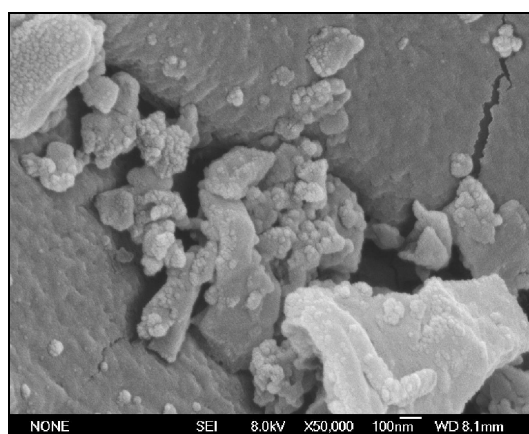
Fig. 2 shows the SEM micrographs with a magnification of  $50000\times$ . The polymeric particles (methylene blue-molecularly imprinted polymer before extraction and non-molecularly imprinted polymer) were obtained in irregular shape and sizes. They had rough surfaces due to the pores, with irregular shapes and sizes, which were formed during the polymerization process. However, the non-molecularly imprinted polymer particles had a more irregular shape and rough morphology. non-molecularly imprinted polymer had no specific binding sites created for the methylene blue analyte. The methylene blue-molecularly imprinted polymer, after extraction, showed particles with high porosity, with better-defined spherical



(a)



(b)



(c)

Fig. 2. SEM images of (a) methylene blue- molecularly imprinted polymer before extraction, (b) methylene blue- molecularly imprinted polymer after extraction and (c) non-molecularly imprinted polymer (x 50 000)

polymer microparticles. This study agreed with the previous studies<sup>12,19,20</sup>. The cavities in the methylene blue-molecularly imprinted polymer were probably caused by the structure of the target molecule (methylene blue)<sup>19</sup>.

Particle size analysis showed that the average particle size distributions for methylene blue-molecularly imprinted polymer before the extraction process, methylene blue-molecularly imprinted polymer after the extraction process and non-

molecularly imprinted polymer, were  $1358 \pm 156$ ,  $1051 \pm 238$  and  $1455.82 \pm 445$  nm, respectively (Figs. 3-5). Particle size of methylene blue-molecularly imprinted polymer after extraction was the smallest compared to methylene blue-molecularly imprinted polymer before extraction and non-molecularly imprinted polymer. This result showed that the methylene blue-molecularly imprinted polymer after extraction had more spacious surface adsorption compared to the others, which indicated that the methylene blue-molecularly imprinted polymer after extraction had vacancy sites and porosity surface (Fig. 3) for sorption methylene blue, but methylene blue-molecularly imprinted polymer before extraction and non-molecularly imprinted polymer did not have them.

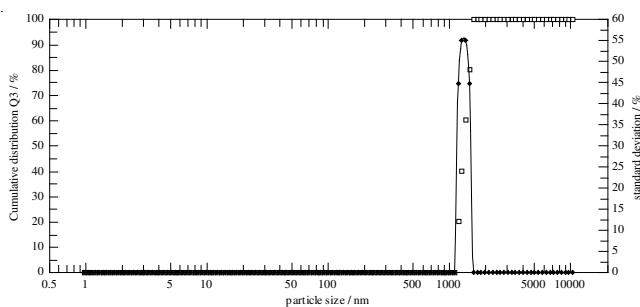


Fig. 3. Particle size analysis for methylene blue- molecularly imprinted polymer before extraction

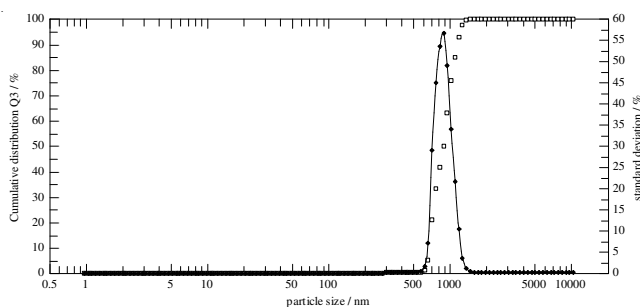


Fig. 4. Particle size analysis for methylene blue- molecularly imprinted polymer after extraction

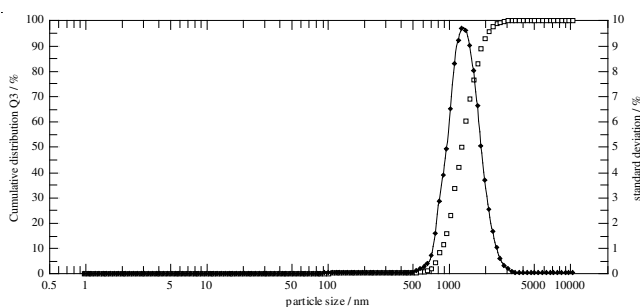


Fig. 5. Particle size analysis for non-molecularly imprinted polymer

Fig. 6 shows the nitrogen adsorption-desorption into methylene blue-molecularly imprinted polymer after extraction, to classify the isotherm of type IV. The type IV shows a hysteresis loop, which is commonly associated with the presence of mesoporosity. The shape is unique to each absorption system. Capillary condensation gives rise to a hysteresis loop and these isotherms also exhibit a limited uptake at high relative pressures. The peak shows that the adsorption increases rapidly at low relative pressure at  $P/P_0 = 0.4$ , with  $6 \text{ cm}^3/\text{g}$  at STP, until the

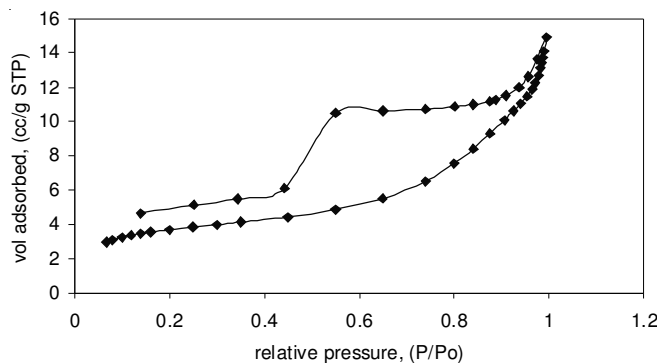


Fig. 6. The nitrogen adsorption and desorption of methylene blue-molecularly imprinted polymer after extraction

highest value at  $P/P_0 = 0.6$  at  $11 \text{ cm}^3/\text{g}$  at STP. The BET surface area characterization study is performed on the methylene blue-molecularly imprinted polymer particle (before and after extraction) and non-molecularly imprinted polymer, to know the effect of imprinting on the polymer surface area and pore diameter. The methylene blue-molecularly imprinted polymer after the extraction process exhibits a larger surface area ( $13.2 \text{ m}^2/\text{g}$ ) when compared to the methylene blue-molecularly imprinted polymer, before extraction. The BET surface area results indicate an enhancement in the surface area of methylene blue-molecularly imprinted polymer, due to imprinting. The pore diameter obtained for methylene blue-molecularly imprinted polymer after the extraction process is  $63 \text{ \AA}$ . However, the pore diameter for methylene blue-molecularly imprinted polymer before the extraction process and non-molecularly imprinted polymer cannot be determined. It is assumed that the particles do not have porosity and permeability structures, because methylene blue-molecularly imprinted polymer, before the extraction process, is occupied with methylene blue and non-molecularly imprinted polymer does not have recognition sites for the template analyte. However, the surface area and pore diameter enhancement due to imprinting is less in this study when compared to other reported values such as carbamepine-molecularly imprinted polymer and oxcabazepine-molecularly imprinted polymer<sup>21</sup>, copper-molecularly imprinted polymer<sup>22</sup> and chlorpromazine-molecularly imprinted polymer<sup>23</sup>. The use of a different template, porogenic solvent, cross-linker and other conditions, have probably played a role to enhance the surface area to a huge extent in the earlier study<sup>22</sup>.

The effect of pH on the sorption of methylene blue by the methylene blue-molecularly imprinted polymer pH of dye solution can significantly influence the sorption process<sup>24</sup>. The initial pH value of the solution has more influence<sup>7</sup> than the final pH. The binding capacities of methylene blue minimize at the initial pH of 1 and then increase and remain nearly constant over the initial pH ranges of 4-9 (Fig. 7). The binding capacity of the methylene blue is not significantly altered when the initial pH increases from 4 to 9 ( $4.29 \text{ mg/g}$ ). Therefore, pH 5 has been chosen for this study, on the basis of contact time and sorption concentration.

At a lower pH, the surface charge may get positively charged, thus making the ( $\text{H}^+$ ) ions compete effectively with the dye cations, causing a decrease in the amount of dye adsorbed<sup>25</sup>. At higher pH values, the methylene blue-molecularly imprinted

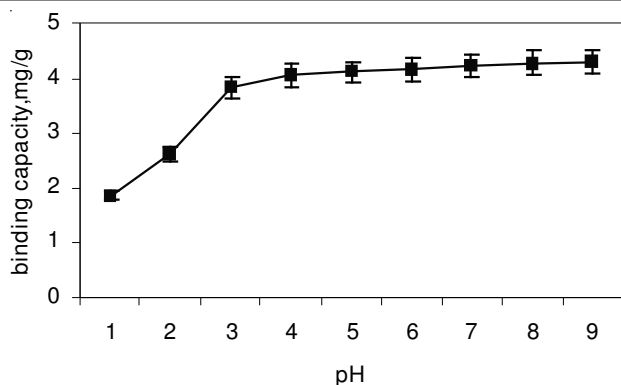


Fig. 7. Effect of pH on sorption of methylene blue- molecularly imprinted polymer toward methylene blue

polymer may get negatively charged, which enhances the electrostatic forces of attraction between the amino group for methylene blue and the carboxylic group for methacrylic acid. Similar results have also been reported for the sorption of methylene blue earlier<sup>1,7,24-27</sup>.

**Effect of kinetic study on sorption of methylene blue by methylene blue-molecularly imprinted polymer:** The binding capacity of methylene blue by methylene blue-molecularly imprinted polymer in various initial concentrations of methylene blue (50, 100, 200 ppm) at different contact times are shown in Fig. 8. In all the experiments, the temperature maintained is room temperature. The amount of methylene blue sorbed per unit mass of methylene blue-molecularly imprinted polymer increases with increasing dye concentration. The equilibrium sorption capacity is increased when the methylene blue concentration increases from 50 to 200 ppm. The results indicate that the curves have the same shape and show that the equilibrium states are attained in almost 1 min within the experimental concentration range. Similar trends and results have been observed for methylene blue sorption on giant duckweed<sup>7</sup>, sewage sludge and *Posidonia oceanica* fibers<sup>25</sup>. However, the sorption rapidness of the molecularly imprinted polymer is better than other sorbents, for example halloysite nanotubes<sup>1</sup> and Indian Roseweed sawdust<sup>3</sup>, with the maximum sorption occurring within 30 min and 5 min, 30 min and 60 min, respectively.

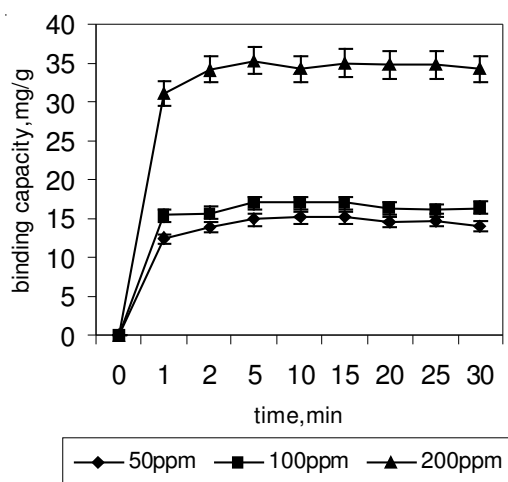


Fig. 8. Kinetic study of sorption of methylene blue by methylene blue-molecularly imprinted polymer

The sorption process at different concentrations is rapid in the initial stage (1 min), the fast uptake at the beginning may be attributed to the rapid attachment of the dye molecules to the surface of the sorbent<sup>28</sup> and this gradually decreases with the progress of adsorption until an equilibrium is reached. These changes in dye uptake may be due to the fact that initially, all sorbent sites are vacant and the solute concentration is high. After that period a very low increase in the dye uptake is observed, because there are few active sites on the surface sorbent<sup>24</sup>. During sorption of the dye, initially the dye molecules reach the boundary layer; then they have to diffuse into the sorbent surface; and finally, they have to diffuse into the porous structure of the sorbent<sup>26</sup>. Fig. 8 reveals that the curves are single, smooth and continuous, leading to saturation, suggesting the possible monolayer coverage of methylene blue on the methylene blue-molecularly imprinted polymer binding.

A linear plot of  $\log (q_e - q_t)$  against time allows one to obtain the rate constant (Fig. 9) and the linear regression of the sorption with the relation coefficient,  $R^2 = 0.1238$  (50 ppm),  $R^2 = 0.1229$  (100 ppm) and  $R^2 = 0.2406$  (200 ppm). The plots are not found to be linear with good correlation coefficients. Therefore, the sorption process is not suitable for the pseudo first order process. The rate constants, predicted equilibrium uptakes and the corresponding correlation coefficients for all concentrations tested have been calculated and summarized in Table-1. The correlation coefficients are found to be very low and the calculated  $q_e$  is not equal to the experimental  $q_e$  (Table-1), suggesting that the sorption of methylene blue on methylene blue-molecularly imprinted polymer is not likely to be a pseudo first order for the initial concentrations examined. The result also summarizes that the pseudo first order equation does not fit well with the whole range of contact time and is generally applicable over the initial stage of the sorption process<sup>24</sup>.

The slope of the plot  $(t/q_t)$  versus  $t$  gives the value of the  $q_e$  and from the intercept,  $k_2$  can be calculated. The calculated  $R^2$  for the pseudo second order kinetic model are shown in Fig. 10, which are 0.9994, 0.9983 and 0.9998 for 50, 100 and 200 ppm, respectively.

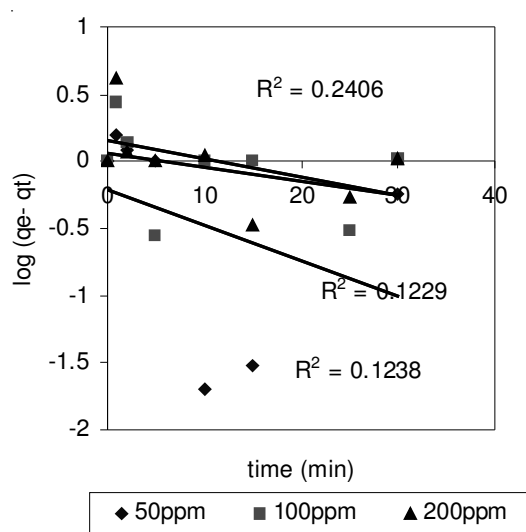


Fig. 9. Pseudo first order model for sorption of methylene blue by methylene blue-molecularly imprinted polymer

TABLE-1  
VALUES OF SORPTION AMOUNT AND SORPTION RATES OF METHYLENE BLUE SOLUTION ON THE  
METHYLENE BLUE-MOLECULARLY IMPRINTED POLYMER AT DIFFERENT CONCENTRATIONS

Concentration (ppm)	$q_e$ , exp. (mg/g)	Pseudo first order kinetic model			Pseudo second order kinetic model		
		$R^2$	$q_e$ , (mg/g)	$k$ (mg/g min <sup>-1</sup> )	$R^2$	$q_e$ , (mg/g)	$k$ (mg/g min <sup>-1</sup> )
50	16.99	0.1238	0.61	0.0608	0.9994	16.34	0.5945
100	15.17	0.1229	1.13	0.0233	0.9983	14.47	0.5366
200	35.32	0.2406	1.42	0.0311	0.9998	34.48	12.0162

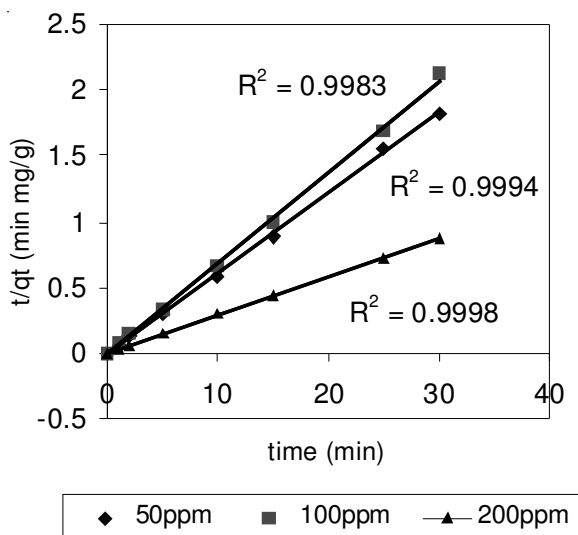


Fig. 10. Pseudo second order model for sorption of methylene blue by methylene blue-molecularly imprinted polymer

Table-1 presents the results of the rate constant studies for different initial dye concentrations by the pseudo first order and pseudo second order models. The experimental data (Table-1) show a good compliance with the pseudo second order equation and the correlation coefficient for the linear plots are near 0.99 for the experimental data.

This suggests that the pseudo second order sorption mechanism is predominant and the overall rate of the methylene blue sorption process appears to be controlled by the chemical process involving valency forces through sharing or exchange of electrons between the sorbent and the sorbate<sup>24</sup>. Similar kinetics were also observed for the removal of methylene blue from the aqueous solution, using raw *P. oceanica* (L.) fibers<sup>25</sup> and using an arganomineral sorbent<sup>29</sup>, by nitric-acid treated water-hyacinth<sup>6</sup>.

The sorption kinetics of methylene blue by methylene blue-molecularly imprinted polymer could quite successfully be fitted with a pseudo second order kinetics equation, suggesting a chemisorption process<sup>24,25</sup>, which is a process carried out in two stages, comprising of a fast initial phase and a second slower phase. In the first phase, the methylene blue molecules are sorbed on the external sites of the sorbent material in a fast process, which dominates the initial kinetics of sorption. In the second phase, the molecules of dye slowly diffuse into the pores of the material and are sorbed onto the internal sites<sup>26</sup>.

**Effect of the sorption isotherm study on the sorption of methylene blue by methylene blue-molecularly imprinted polymer:** The absorption isotherm indicates how the absorption molecules distribute between the liquid phase and the solid phase when the sorption process reaches an equilibrium state.

The amount of methylene blue absorbed has been plotted against the equilibrium concentration as shown in Fig. 11.

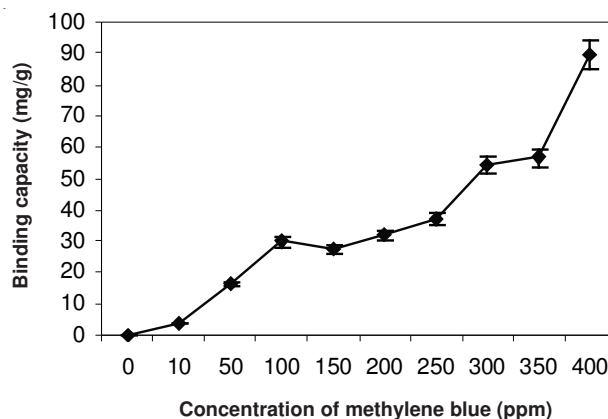


Fig. 11. Sorption isotherm study of methylene blue by methylene blue-molecularly imprinted polymer

The Langmuir isotherm suggests that every adsorption site is equivalent and the ability of a particle to bind is independent of whether or not the nearby sites are occupied and the adsorbent is a monolayer, saturated by adsorbate molecules on the homogeneous adsorbent surface. Once an adsorbate occupies a site, no further absorption can take place at that site. The energy of sorption is constant and there is no transmigration of the sorbate in the plane of the surface<sup>24</sup>.

The constants  $Q$  and  $b$  are Langmuir constants, which can be calculated from the intercept and the slopes of the plots  $C_e/q_e$  versus  $C_e$ .  $Q$  and  $b$  are the maximum number of absorption sites and the absorption affinity on the absorption sites, respectively.

The Freundlich model assumes that sorption takes place on heterogeneous surfaces and the absorption capacity depends on the concentration of the dyes at equilibrium. The isotherm is derived to model the multilayer absorption, where an infinite amount of adsorption can occur.

Langmuir and Freundlich are the most frequently employed models<sup>24</sup>. In this study, both models were used, to describe the relationship between the amount of dye adsorbed and its equilibrium concentrations. Fig. 12 shows the form of Langmuir sorption with the coefficient regression,  $R^2$  is 0.7134,  $b$  and  $q_0$  values were calculated to be 0.0139 and 59.1716 mg/g, respectively (Table-2). The plot was not linear with a good correlation coefficient, thus, the sorption process is not suited for the Langmuir isotherm.

Fig. 13 shows the plot of the Freundlich isotherm with the correlation coefficient,  $R^2 = 0.8523$ ,  $n$  and  $K_f$  values were calculated to be 1.7590 and 2.9168, respectively (Table-2). The sorption processed was likely to be modeled as the

TABLE-2  
LANGMUIR AND FREUNDLICH CONSTANTS FOR THE SORPTION OF METHYLENE BLUE DYE SOLUTIONS

Sorbent	Dye	Langmuir			Freundlich		
		Q (mg/g)	b (l/mg)	R <sup>2</sup>	K <sub>f</sub> (mg/g)	N (g/L)	R <sup>2</sup>
Molecularly imprinted polymer	Methylene blue	59.1716	0.0319	0.7134	2.9168	1.7590	0.8523

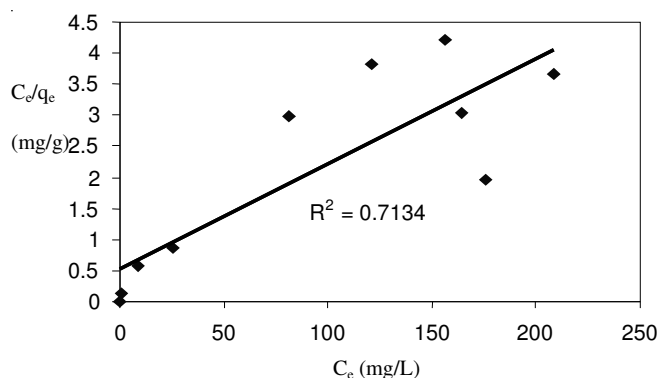


Fig. 12. Langmuir isotherm for sorption of methylene blue by methylene blue-molecularly imprinted polymer

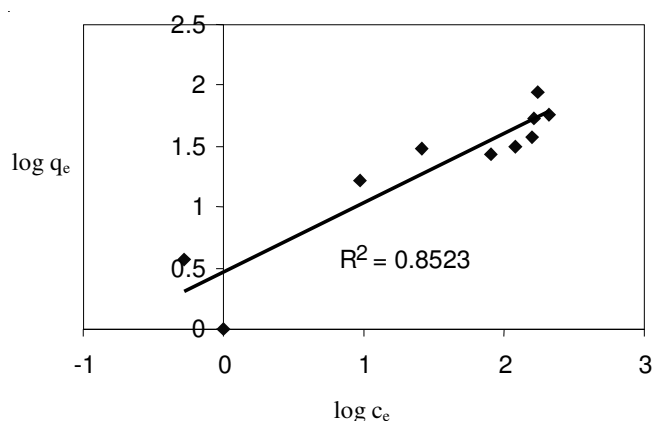


Fig. 13. Freundlich isotherm for sorption of methylene blue by methylene blue-molecularly imprinted polymer

Freundlich isotherm model, as the Freundlich model deals with physicochemical sorption on heterogeneous surfaces<sup>30</sup>. Umpleby II *et al.*<sup>31</sup> reported that the binding isotherm for molecularly imprinted polymer was normally observed with the Freundlich isotherm. They had synthesized molecularly imprinted polymer using non-covalent interactions, using templates such as ethyl adenine-9-acetate, cortisone, 9-ethyladenine and testosterone that applied to the Freundlich isotherm model.

**Selectivity study of the methylene blue-molecularly imprinted polymer:** The sorption binding capacities of the corresponding methylene blue-molecularly imprinted polymer particles, compared to the non-molecularly imprinted polymer particles, toward methylene blue, methylene orange and fast green are shown in Fig. 14. The binding capacity of methylene blue-molecularly imprinted polymer toward methylene blue, methylene orange and fast green is higher than non-molecularly imprinted polymer, indicating the higher specific binding of methylene blue-molecularly imprinted polymer. The results also indicate that methylene blue-molecularly imprinted polymer particles have higher binding capacities toward methylene blue compared to methylene orange or fast green. This is expected, as imprinting is expected to create the shape of selective cavities

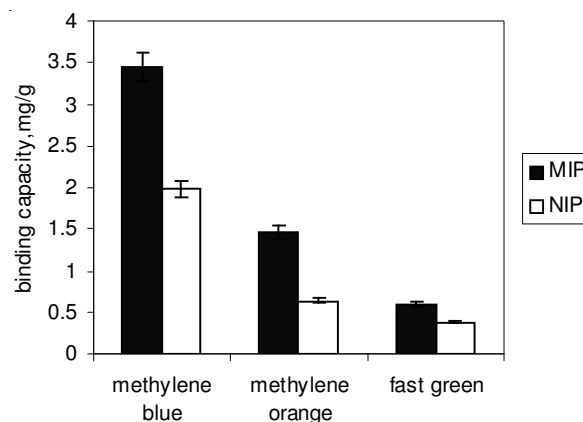


Fig. 14. Selectivity study of methylene blue-molecularly imprinted polymer

within the polymer structure<sup>20</sup>. The selectivity study of the molecularly imprinted polymer has also been reported by Yan *et al.*<sup>11</sup> and Sergeyeva *et al.*<sup>32</sup>. Each imprinted polymer has a higher affinity for the corresponding template molecules<sup>33</sup>.

**Reusability study of methylene blue-molecularly imprinted polymer:** In order to show the reusability of the methylene blue-molecularly imprinted polymer particles, the adsorption-desorption cycle was repeated five times using the same batch of methylene blue-molecularly imprinted polymer particles. The performance of the binding capacity after regeneration is shown in Fig. 15. The binding capacity did not vary much (between 3.8-4.0 mg/g) for each repeated usage. It proved that the molecularly imprinted polymer could be reused and it was also reported in the reusability of molecularly imprinted polymer-cholesterol by Yavuz *et al.*<sup>20</sup>. This result suggested that molecularly imprinted polymer particles were very stable and maintained their adsorption capacity at almost binding capacity constant value.

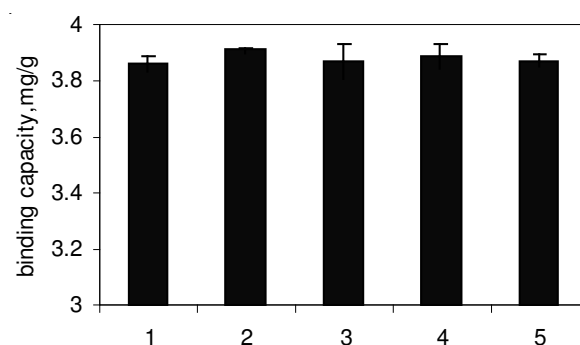


Fig. 14. Reusability of the methylene blue-molecularly imprinted polymer

## Conclusion

Removal of methylene blue using methylene blue-molecularly imprinted polymer was investigated in this study. The desired uniform methylene blue-molecularly imprinted polymer was synthesized with good yield by bulk polymerization.



The methylene blue-molecularly imprinted polymer exhibited good selectivity towards methylene blue. Maximum sorption of methylene blue occurred at pH 5 in 30 s. The sorption followed a pseudo-second-order kinetic model and the adsorption isotherm of methylene blue followed the Freundlich isotherm model. Methylene blue-molecularly imprinted polymer has proven to have a high potential as sorbent for removal of methylene blue in wastewater treatment.

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#### REFERENCES

- M. Zhao and P. Liu, *Micropor. Mesopor. Mater.*, **112**, 419 (2008).
- F. Delcyl, G. Crini, N. Morin, J. Vebrel, S. Bertini and G. Torri, *Dyes Pigments*, **53**, 79 (2002).
- V.K. Gary, M. Amita, R. Kumar and R. Gupta, *Dyes Pigments*, **63**, 243 (2004).
- E.N. El-Qada, S.J. Allen and G.M. Walker, *Chem. Eng. J.*, **124**, 103 (2006).
- J. Fan, A. Li, W. Yang, L. Yang and Q. Zhang, *Sep. Purif. Technol.*, **51**, 338 (2006).
- M.I. El-Khaiary, *J. Hazard. Mater.*, **147**, 28 (2007).
- P. Waranusantigul, P. Pokethitiyook, M. Kruatrakulue and E.S. Upatham, *Environ. Pollut.*, **125**, 385 (2003).
- Q. Li, H. Su, J. Li and T. Tan, *Process Biochem.*, **42**, 379 (2007).
- I. Sanchez-Barragan, K. Karim, J.M. Costa-Fernandez, S.A. Piletsky and A. Sanz-Medel, *Sens. Actuators B*, **123**, 798 (2007).
- R. Kielczynski and M. Bryjak, *Sep. Purif. Technol.*, **41**, 231 (2005).
- S. Yan, Z. Gao, Y. Fang, Y. Cheng, H. Zhou and H. Wang, *Dyes Pigments*, **74**, 572 (2007).
- N. Perez-Moral and A.G. Mayes, *Anal. Chim. Acta*, **504**, 15 (2004).
- L.Q. Su, S. Qiao and W.B. Zhang, *Chin. Chem. Lett.*, **18**, 229 (2007).
- Y. Li, T. Yang, X. Qi, Y. Qiao and A. Deng, *Anal. Chim. Acta*, **624**, 317 (2008).
- F. Pouci, C. Gareffa, F. Iellma, R. Muzzalupo, U.G. Sprizzirri and N. Picci, *Food Chem.*, **93**, 349 (2005).
- S.G. Hu, L. Li and X. He, *Anal. Chim. Acta*, **537**, 215 (2005).
- V. Pichon and F. Chapuis-Hugon, *Anal. Chim. Acta*, **622**, 48 (2008).
- A.G. Mayes and M.J. Whitcombe, *Adv. Drug Deliv. Rev.*, **57**, 1742 (2005).
- G.P. González, P.F. Hernando and J.S.D. Alegría, *Anal. Chim. Acta*, **557**, 179 (2006).
- H. Yavuz, V. Karakoç, D. Türkmen, R. Say and A. Denizli, *Biol. Macromol.*, **41**, 8 (2007).
- A. Beltran, R.M. Marcé, P.A.G. Cormack and F. Borrull, *J. Chromatogr. A*, **1216**, 2248 (2009).
- A. Baghel, M. Boopathi, B. Singh, P. Pandey, T.H. Mahato, P.K. Gutch and K. Sekhar, *Biosen. Bioelectron.*, **22**, 3326 (2007).
- S. Song, X. Shi, R. Li, Z. Lin, A. Wu and D. Zhang, *Process Biochem.*, **43**, 1209 (2008).
- B.H. Hameed, A.L. Ahmad and K.N.A. Latiff, *Dyes Pigments*, **75**, 143 (2007).
- M.C. Ncibi, B. Mahjoub and M. Seffen, *J. Hazard. Mater. B*, **139**, 280 (2007).
- O. Hamdaoui and M. Chica, *Acta Chim. Slov.*, **54**, 407 (2007).
- K.V. Kumar and A. Kumaran, *Biochem. Eng. J.*, **27**, 83 (2005).
- S.T. Ong, C.K. Lee and Z. Zainal, *Bioresour. Technol.*, **98**, 2792 (2007).
- P. Janoš and V. Šmidová, *J. Colloid Interf. Sci.*, **291**, 19 (2005).
- S.T. Ong, C.K. Lee and Z. Zainal, *Bioresour. Technol.*, **98**, 2792 (2007).
- R.J. Umpheby II, S.C. Baxter, M. Bode, J.K. Berch Jr, R.N. Shah and K.D. Shimizu, *Anal. Chim. Acta*, **435**, 35 (2001).
- T.A. Sergeyeva, O.O. Brovko, E.V. Piltka, S.A. Piletsky, L.A. Goncharova, L.V. Karabanova, L.M. Sergeyeva and A.V. El'skaya, *Anal. Chim. Acta*, **582**, 311 (2007).
- A. Kugimiya and H. Takei, *Anal. Chim. Acta*, **564**, 176 (2006).