



*Anal. Bioanal. Chem. Res., Vol. 4, No. 2, 269-283, December 2017.*

## A Novel Magnetic Nano-hybrid as a Sorbent for Solid-phase Extraction-spectrophotometric Determination of Methyl Violet 10B Dye

Naser Samadi<sup>a,\*</sup>, Hossein Abdolmohammad-Zadeh<sup>b</sup> and Marzieh Ahari Salmasi<sup>b</sup>

<sup>a</sup>Department of Chemistry Faculty of Science Urmia University, Urmia, Iran

<sup>b</sup>Department of Chemistry, Faculty of Sciences, Azarbaijan Shahid Madani University, Tabriz, Iran

(Received 9 February 2017, Accepted 12 June 2017)

In this research, the magnetite polystyrene maleic anhydride (MPSMA) was synthesized, and its structure and morphology were characterized by X-ray diffraction, Fourier transform infrared spectroscopy, and scanning electron microscopy techniques. The obtained nano-structured inorganic material was employed as a novel magnetic nanosorbent for separation and pre-concentration of Methyl violet (10B) dye from aqueous solutions, which can be spectrophotometrically monitored at  $\lambda = 585$  nm after pre-concentration by solid phase extraction (SPE). The effect of several parameters including pH of the sample solution, amount of the sorbent, extraction and desorption times, and elution conditions and sample volume were investigated and optimized. UV-Vis spectrophotometer was used for determination of MV (10B) concentration after desorption of the dye by nitric acid solution. Under the optimum experimental conditions, the limit of detection and the relative standard deviation were  $0.08 \mu\text{g l}^{-1}$  and 1.10%, respectively. The enrichment factor of 200 was achieved, and the calibration graph using the presented solid phase extraction system was linear in the range of  $0.3\text{-}1500 \mu\text{g l}^{-1}$  with a correlation coefficient of 0.9989. The method was successfully applied for pre-concentration of MV (10B) from several textile waste water effluents.

**Keywords:** Nano-hybrid, Magnetite, Polystyrene, Magnetic solid phase extraction, Methyl violet 10B

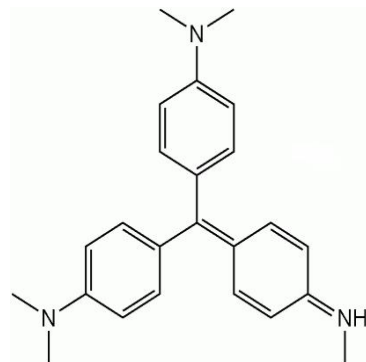
### INTRODUCTION

Synthetic dyes are extensively used in textile dyeing, paper, printing, color, photography, pharmaceuticals, cosmetics and other industries [1]. They add color and patterns to materials. Natural dyes extracted from vegetables, fruit and flowers have been used since 3500 BC to color fabrics and other materials [2]. These dyes were replaced by chemical dyes that through bonding with the fabric provide and retain a richer color throughout washing and exposure [2]. When used dyes and dye-based effluents are disposed into waterways without proper treatment, pollution of water would occur, causing serious threat to the environment [3-5]. Many of the dyes are extremely toxic. Among various dyes, methyl violet (10B), also known as basic violet 3, is a well-known cationic dye being used for

various purposes, such as biological stain, dermatological agent, veterinary medicine, an additive to poultry feed to inhibit propagation of mold, intestinal parasites and fungus, etc. It is also extensively used in coloring paper, temporary hair colorant, dyeing cottons, and wools [6]. It can cause some harmful effects, such as heartbeat increase, vomiting, shock, cyanosis, jaundice, quadriplegia and tissue necrosis in human [7]. The dye is responsible for moderate eye irritation, painful sensitization to light, and also permanent injury. Therefore, it is necessary to remove these dyes from wastewater prior to discharge into water bodies [7]. It can cause permanent injury to the cornea and conjunctiva because the product contains a cationic dye which causes toxicity to mammalian cells and in extreme cases it may lead to respiratory and kidney failure and permanent blindness. So, the water treatment is essential, particularly for wastewater of factories before pouring into the river. [8,9]. Up to now, different methods have been reported for

\*Corresponding author. E-mail: samadi76@yahoo.com

the determination of MV, such as high performance liquid chromatography [10,11] liquid-phase adsorption [12], spectrophotometry [13,14], chemical oxidation, [15] and electrochemical degradation [16]. Removal of dyes and pigments from aqueous solutions *via* adsorption processes is a simple method known to be relatively low-cost, and such effective technology has been adopted widely by water treatment plants [17]. Solid-phase micro-extraction (SPME) [18,19] including extraction and pre-concentration of analytes from aqueous samples or from headspace of the samples is also expensive, and most of the times reproducibility of the results is low. Various sample preparation techniques based on solid phase extraction (SPE) systems have been developed to isolate various types of analytes from different matrices. Despite whole advantages of SPE, it can still be tedious, time consuming, and relatively expensive [20]. Recently, a new mode of SPE called magnetic solid-phase extraction (MSPE) has been developed [21,22]. MSPE is based on the combination of magnetic inorganic material and non-magnetic adsorbent material. By taking advantages of the combined benefits of both materials, the MSPE technology exhibits excellent adsorption efficiency and rapid separation from the crude sample matrix by an external magnetic field [22]. Various MSPE materials have been successfully used for pre-concentration and extraction of dyes in trace amounts [23-26]. To improve the dispersibility and stability of adsorbents in aqueous solution, the surface of nanoparticles can be modified with a polymer [27]. A polymeric ligand is applied to selectively bind specific dyes into a mixture to isolate important dyes from wastewater and aqueous media [27-30]. The polymeric ligand is usually applied in an insoluble resin form to separate a specific dye from a liquid containing a mixture of dyes. Among the various types of polymers, MMSMA (modified magnetic styrene maleic anhydride) has attracted intense attention. These magnetic nanoparticles could be easily functionalized with desired molecules using silane agents. The silane group will be reacted with active hydroxyl and amine groups on the surface of particles and cause formation of functionalized magnetic nanoparticles. The SMA copolymer is biocompatible compound which has been used in drug delivery and controlled release systems [31]. It can be used in numerous applications, however its use in bio



**Fig. 1.** structure of Methyl violet (10B).

applications is proportional to its purity [32,33]. The SMA copolymer can be a suitable compound for environmental applications. So, any kind of the modified copolymers (SMA derivatives) can be used in the clean technology methods for the removal of toxic dyes. However, there has been no report concerning the synthesis of magnetic styrene maleic anhydride nano hybrids. This paper reports the preparation of CSMA coated  $\text{Fe}_3\text{O}_4$  nanoparticles for pre-concentration of Methyl violet (10B) from aqueous solutions. The effects of several parameters, including pH of the sample solution, amount of the sorbent, extraction and desorption times, elution conditions and sample volume are optimized. This method is applied to a numbers of industrial and natural samples. The concentration of MV in the stripped solutions was also monitored spectrophotometrically by measuring the absorbance of the desorbed dye by nitric acid at 585 nm. This paper describes a novel, simple and sensitive method for the determination of Methyl violet (10B) in water samples. The method is based on the extraction of MV mediated by sensitive magnetic nanosorbent (poly (styrene-alt-maleic acid)). The extracted dye is dissolved in nitric acid, and its absorbance is measured spectrophotometrically at 585 nm.

## EXPERIMENTAL

### Standard Solutions and Reagents

All chemicals were used of analytical-reagent grade and all solutions were prepared with highly purified deionized water from Artemia research center (Urmia, Iran). A stock standard solution of methyl violet ( $1000 \text{ mg l}^{-1}$ ) was

prepared by dissolving an appropriate amount of Methyl violet (10B) (obtained from Darmstadt, Germany) in deionized water in a 100 ml volumetric flask and diluting to mark with deionized water and stored in the dark. The working standard solutions were prepared daily by stepwise diluting the stock standard solution with deionized water. A phosphate buffer solution (0.1 M) was prepared by dissolving the appropriate amounts of sodium phosphate (Merck, Germany) in deionized water and adjusting to pH = 7 by adding diluted NaOH (Merck, Germany) solution. All reagents and solvents including methanol, ethanol, sulfuric acid, acetic acid, hydrochloric acid, H<sub>2</sub>O<sub>2</sub>, THF, SOCl<sub>2</sub>, 3-aminopropyltriethoxysilane (APTES), 1,3-diaminopropane (DAP), triethyl amine (TEA), styrene, maleic anhydride (MA), 3-aminobenzoic acid (ABA), benzoyl peroxide (BPO), ferric chloride (FeCl<sub>3</sub>·6H<sub>2</sub>O), ferrous chloride (FeCl<sub>2</sub>·7H<sub>2</sub>O), ammonia, and all salts used for the interference study were purchased from Merck. All plastics and glasswares used for trace analysis were kept in 15% (v/v) nitric acid at least overnight and rinsed three times with deionized water prior to use.

### Instrumentation

A single beam Agilent WPA (Biowave II) UV-Vis spectrophotometer equipped with a 1-cm quartz cell was used for determination of MV concentration in solutions. In order to structural study of the nanosorbent, powder X-ray diffraction (XRD) measurements were performed on a Bruker AXS model D8 Advance (Karlsruhe, Germany) instrument with Cu-K $\alpha$  radiation source (1.54 Å) between 2 and 70 $^{\circ}$  generated at 40 kV and 35 mA at room temperature. Samples for XRD were grounded into powder, and then pressed flat in the sample slot. In addition, FT-IR spectra (400-4000 cm<sup>-1</sup>) were recorded on a Bruker model Vector 22 (Ettlingen, Germany) Fourier transform infrared spectrometer using the KBr disk method with a ratio sample/KBr of 1:100 by mass. A scanning electron microscope (SEM, model LEO1430vp, Carl Zeiss, Germany) was additionally used to examine the morphological features of the sorbent. An ultrasonic bath (SONICA, Italy) was used to disperse the nanosorbent in sample solution vials. A shaker (Pars Azma Co., Iran) was used for controlled stirring the sample solution vials in adsorption and desorption steps. The pH values were

measured with a Metrohm digital pH-meter model 827 (Herisau, Switzerland) supplied with a glass-combined electrode. An electronic analytical balance, Mettler Toledo model PB303 (Greifensee, Switzerland), was used for weighting the solid materials.

### Synthesis of Modified Fe<sub>3</sub>O<sub>4</sub> Magnetic Nanoparticles

Magnetic Fe<sub>3</sub>O<sub>4</sub> NPs were prepared by chemical coprecipitation method [34]. The synthesized Fe<sub>3</sub>O<sub>4</sub> NPs (1 g) were dispersed in 200 ml of ethanol by sonication for 1 h. Then, the mixture was remained under the argon atmosphere for 30 min. Subsequently, 8 ml of APTES was added into the mixture under vigorous stirring and followed by sonication for 24 h at 50  $^{\circ}$ C. Finally, modified APTES-Fe<sub>3</sub>O<sub>4</sub> NPs were collected by applying a magnet, washed three times with ethanol, and dried in vacuum at 80  $^{\circ}$ C.

### Synthesis of Modified Styrene-maleic Anhydride (SMA) Copolymer

The SMA copolymer was prepared by free radical polymerization of maleic anhydride and styrene at 70  $^{\circ}$ C in the presence of benzoyl peroxide as initiator [35]. Briefly, styrene and maleic anhydride were dissolved in 50 ml of THF at 1:1 molar ratio in a 250 ml three-neck flask equipped with a magnetic stirrer, a condenser, and an inlet for inert gas. Then, BPO (0.05 mmol) was added and after stirring under argon atmosphere for 20 min, the mixture was heated at 70  $^{\circ}$ C and refluxed under these conditions for 7 h. After cooling down to room temperature, the SMA copolymer precipitation was completed by adding methanol into the mixture. Finally, the resultant white precipitate was separated by filtering and dried in vacuum at 80  $^{\circ}$ C.

For synthesis of the modified SMA copolymer, 1.25 g of the obtained SMA copolymer and 0.67 g ABA in ratio of 100:80 were poured in a three-neck flask equipped with condenser, magnetic stirring bar, inlet and outlet of argon gas, and ultrasonic irradiation probe. Then, 0.5 ml of TEA as catalyst and 50 ml of THF as solvent were added and the reaction mixture was refluxed for 1 h at 70  $^{\circ}$ C [35]. Next, after adding 2 ml of SOCl<sub>2</sub>, the reaction was continued at 65  $^{\circ}$ C for 24 h under argon atmosphere. Finally, the precipitation [poly (ABA-SMA)] was separated by filtration and dried in vacuum at 60  $^{\circ}$ C.

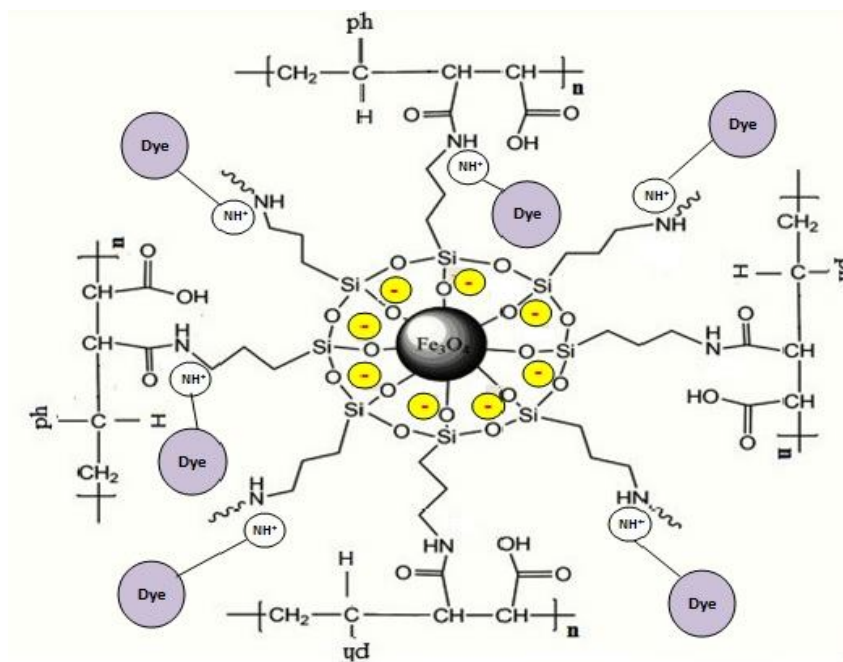


Fig. 2. Methyl violet (MV) adsorption by the synthesized sorbent.

### Synthesis of Magnetic Nano-composite

For synthesis of MNC, the modified APTES- $\text{Fe}_3\text{O}_4$  NPs were firstly sonicated in 30 ml of THF for 20 min. Then, the modified ABA-SMA copolymer in weight ratio of 0.5:1 (APTES- $\text{Fe}_3\text{O}_4$ :ABA-SMA) was added into the mixture, and the reaction mixture was sonicated for 24 h at 65 °C. After that, for further crosslinking, DAP in weight ratio of 1:1 (DAP: ABA-SMA) was added dropwise into the mixture under sonication for 1 h. Finally, the synthesized poly (ABA-SMA)@APTES- $\text{Fe}_3\text{O}_4$ MNC was collected by using a magnetic field, washed with THF to remove unreacted copolymers, washed several times with ethanol and dried in vacuum at 80 °C. Illustration of the procedure is shown in Fig. 2.

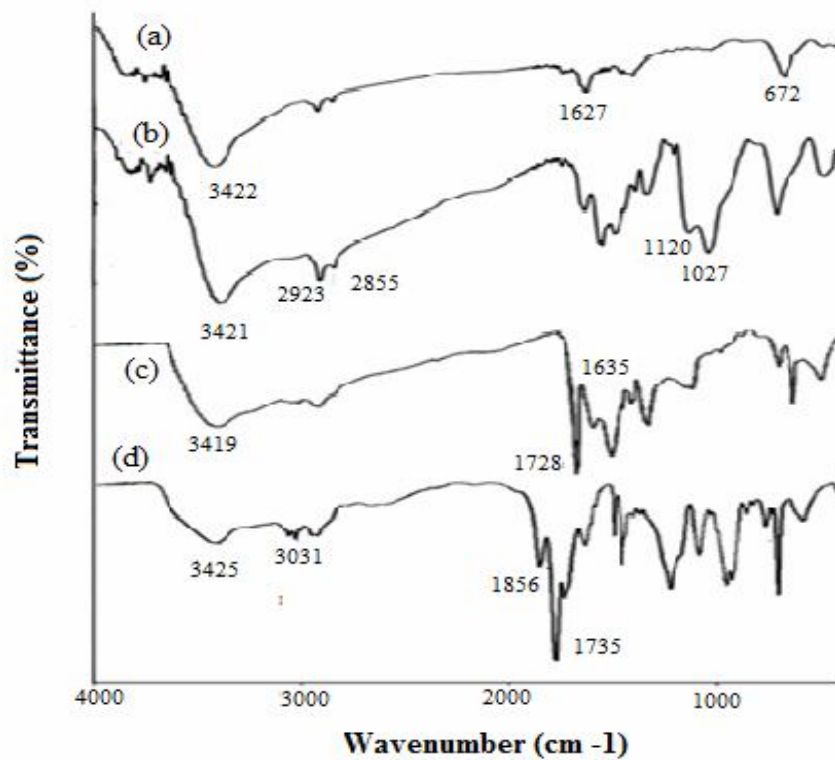
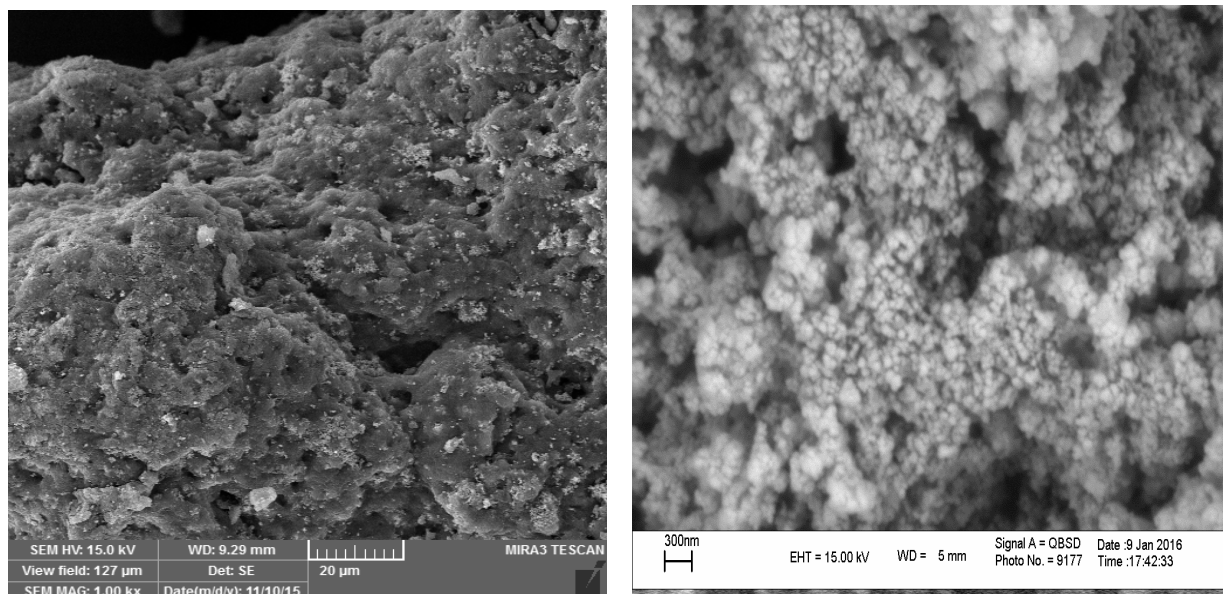
### General Procedure

Aliquots of 100 ml sample or standard solution containing MV (10B) in the range of 0.3-1500  $\mu\text{g l}^{-1}$  (pH 7, adjusted by 2 ml of 0.1 M phosphate buffer solution) was transferred into a 250 ml glassware beaker. Then, 50 mg of the synthesized magnetic nanosorbent was added to solution and the mixture was shaken for 5 min at room temperature. There upon, the magnetic nanosorbent was gathered at one

side of the beaker under a strong external magnetic field (Nd-Fe-B, 10,000 gauss) and the clear supernatant was directly decanted. To desorb the extracted analyte, 2 ml of 1 M  $\text{HNO}_3$  solution was added to the isolated nanosorbent. After shaking for 5 min, the nanosorbent particles were gathered again, with the aid of a magnet, the supernatant containing the concentrated dye was transferred into a small vial. Finally, the absorbance of MV (10B) as an analytical signal was measured by UV-Vis spectrophotometer at  $\lambda = 585$  nm. A blank solution was prepared using a similar procedure but without Methyl violet.

### Real Sample Preparation

Water samples including tap water, drinking water, river water and wastewater were chosen for the analysis. Each sample was collected from local sources; Drinking water from Urmia city, river water from Shahar chay and waste water collected from Khoy and Urmia textile wastewater factories. Then, on arrival to laboratory, water samples were filtered through Round filter paper (blue band, no. 300210) to remove suspended particulate matter, transferred into the PTFE container and stored in a refrigerator at 4 °C. Aliquots of 100 ml of each sample solution were analyzed within



**Fig. 3.** A) SEM image of SMA/Fe<sub>3</sub>O<sub>4</sub> nano-hybrid and B) FT-IR spectrum of a) Fe<sub>3</sub>O<sub>4</sub> b) APTES (3-aminopropyltriethoxysilane), C) APTES/SMA, d) SMA.

24 h of collection by following the general procedure.

## RESULTS AND DISCUSSIONS

### Characterization of (ABA-SMA/Fe<sub>3</sub>O<sub>4</sub> Nanohybrid)

Additionally, SEM or FESEM (field emission scanning electron microscopy) was employed to explore the morphology of the synthesized materials (Fig. 3A). The morphology of poly (ABA-SMA) reveals that the copolymer has amorphous nature and average diameter of the observed particles in FESEM image can be estimated under 100 nm with a reasonable monotony and grainy shape. FESEM image of poly (ABA-SMA)@APTES-Fe<sub>3</sub>O<sub>4</sub> magnetic nanohybrid demonstrates an aggregate that consists of MNH crystals of small pseudo-spherical particles with approximate sizes in the range of 10-50 nm which are stacking to make plate-like morphology.

Figure 3B shows the FT-IR spectra of (a) Fe<sub>3</sub>O<sub>4</sub> nanoparticles, (b) APTES-Fe<sub>3</sub>O<sub>4</sub> nanoparticles, (c) MSMA, and (d) poly (SMA). In (Fig. 3B (a, b)) the absorption bands at around 672 cm<sup>-1</sup> can be ascribed to the Fe-O stretching vibration of Fe<sub>3</sub>O<sub>4</sub>. In addition, O-H stretching vibration around 3422 cm<sup>-1</sup> and O-H deformed vibration at 1627 cm<sup>-1</sup> were observed in panels (a) and (b) of Fig. 1, suggesting that -OH groups coat on the surface of Fe<sub>3</sub>O<sub>4</sub> as reported. The presence of APTES on the surface of Fe<sub>3</sub>O<sub>4</sub> nanoparticles is also certified by the bands at 1120 and 1027 cm<sup>-1</sup> which are due to Si-O stretching vibrations. This reveals that the covalent bonds of Fe-O-Si are formed after modification of Fe<sub>3</sub>O<sub>4</sub> through silanization reaction with APTMS (b). The presentation of the broad band at 3421 cm<sup>-1</sup> is referred to the N-H stretching vibration which can be overlapped by the O-H stretching vibration band. The characteristic peaks of C-H stretching vibrations at 2856 and 2923 cm<sup>-1</sup> confirm the presence of an anchored propyl group. Comparison of the FT-IR spectrum of poly (MSMA) in Fig. (c) and (SMA) in Fig. (d) indicates that characteristic absorption bands of the anhydride linkage of poly (SMA) at 1735, 1784 and 1856 cm<sup>-1</sup> disappeared after reaction with the APTES-Fe<sub>3</sub>O<sub>4</sub>, and adsorption bands were observed for MSMA at 1728 cm<sup>-1</sup> related to the amide at 1635 and 3419 cm<sup>-1</sup> because of carboxylic groups.

Figure 4 shows XRD patterns of SMA and neat Fe<sub>3</sub>O<sub>4</sub> magnetic and SMA/Fe<sub>3</sub>O<sub>4</sub> nano-particles. The powder X-ray

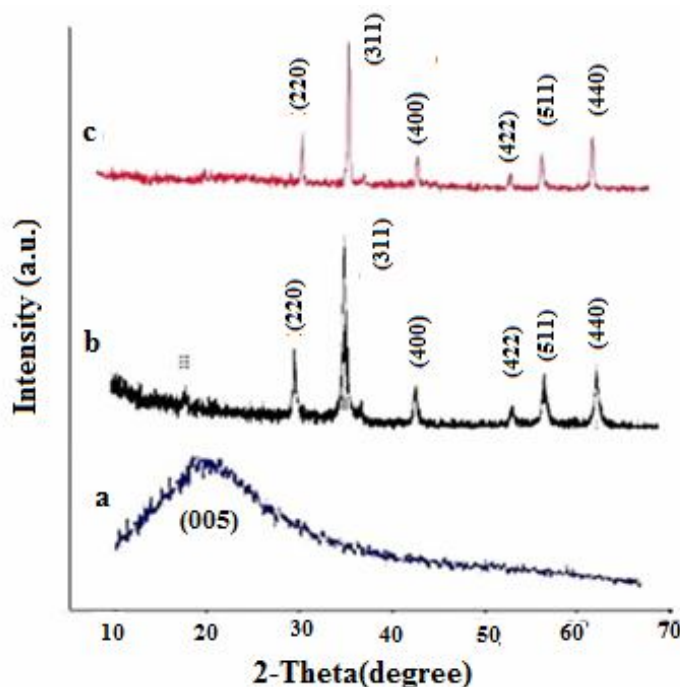
diffraction (XRD) is a very powerful technique for characterizing the structure of materials to study the crystal structure of poly (SMA) Fe<sub>3</sub>O<sub>4</sub> MNH (magnetic nanohybrid). The diffraction patterns showed that the copolymer is amorphous. The results show the approximate size of particles of the synthesized polymer in nano scale. So, ultrasonic waves have a significant role in the formation of particle size.

Indeed, there is only a broad diffraction hump at about  $2\theta = 20^\circ$  indicating the amorphous nature of the copolymer. As shown in (Fig. 4(a)) the diffraction peak at  $2\theta = 20^\circ$  is assigned to the (0 0 5) reflection of SMA. The XRD patterns of neat Fe<sub>3</sub>O<sub>4</sub> nanoparticles indicate their cubic spinel structures. The presence of sharp and intense peaks confirmed the formation of highly crystalline Fe<sub>3</sub>O<sub>4</sub> (Fig. 4(b)).

For the synthesized SMA/Fe<sub>3</sub>O<sub>4</sub> (Fig. 4(c)), the new diffraction peaks appeared at the Bragg angles of about 30.21, 35.51, 43.21, 53.61, 57.11 and 62.91 are respectively ascribed to the (220), (311), (400), (422), (511) and (440) figures of the cubic spinel crystal planes of Fe<sub>3</sub>O<sub>4</sub> (JCPDS No. 19-0629). So, the existence of Fe<sub>3</sub>O<sub>4</sub> NPs on SMA is confirmed, while the (0 0 5) reflection peak of layered SMA almost disappeared. It may be due to the fact that after covering with Fe<sub>3</sub>O<sub>4</sub> NPs, the SMA particles cannot aggregate anymore to form their shapes [37,38].

### Optimization of Magnetic Solid Phase Extraction Conditions

To evaluate the capability of the presented method for separation and pre-concentration of Methyl violet, the effect of several variables on the extraction efficiency including pH, amount of the sorbent, extraction and desorption times, sample volume and elution conditions were studied and optimized. In all cases, the recovery percentage, calculated from the amount of dye in the starting sample and the amount of dye eluted from the sorbent, was used as the analytical signal. Optimization was carried out using the one variable at a time method with a concentration of 1 ng ml<sup>-1</sup> of the Methyl violet (10B). In the impact parameters of optimization procedure, the limits marked on the figures were obtained from three experiments repeated under the same conditions (Table 1).



**Fig. 4.** XRD pattern of SMA and SMA/Fe<sub>3</sub>O<sub>4</sub> and /Fe<sub>3</sub>O<sub>4</sub> nanohybride, respectively.

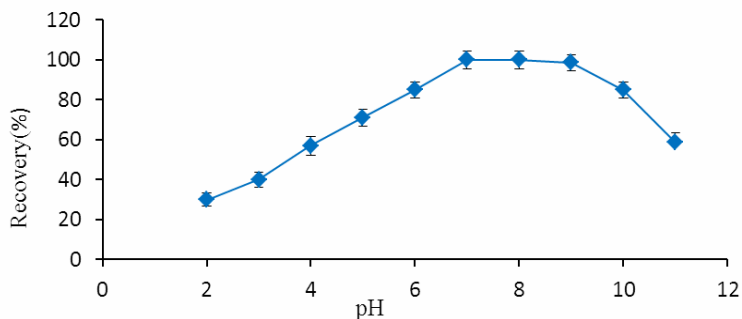
**Table 1.** Instrumental and Experimental Conditions for Dye Determination

Conditions	-	Unit
Wavelength	585	Nm
Micro-extraction conditions		Unite
Working pH	7	-
Methyl violet concentration	1	ppm
Buffer concentration	0.1	M
Shaking time	5	Min
Desorption time	5	Min

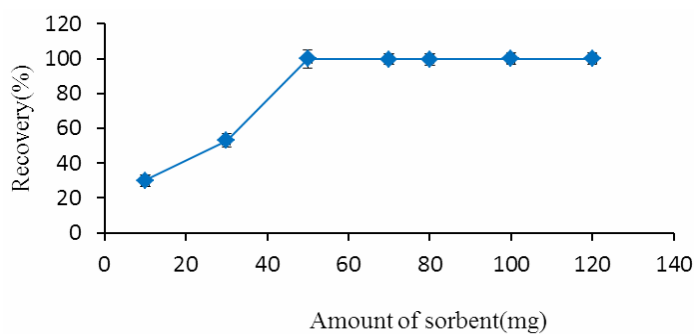
### Influences of pH

Since pH of the sample solution is an important factor in solid phase extraction studies, the influence of pH of the analyte solutions on the recoveries of Methyl violet was investigated in the pH range 3.0-9.0. In this approach, the pre-concentration method has been applied in different pH

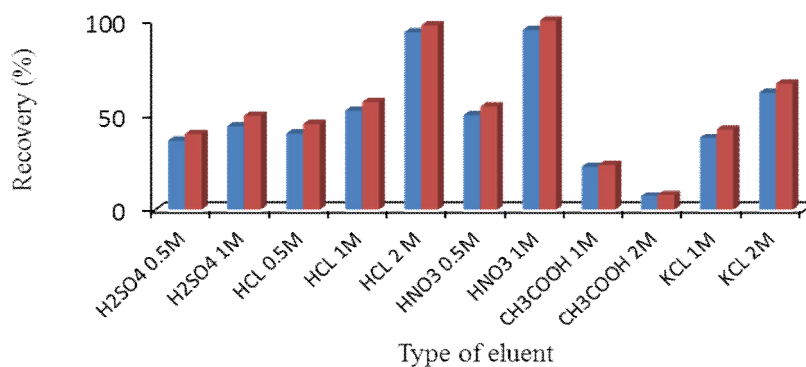
values and the recoveries were calculated. As the results showed, quantitative recovery (>99%) of dye was observed in pH of 7.0-9.0 (Fig. 5). For adsorption, the mechanism is different as the amine group should coordinate to Methyl violet. By increasing the pH, the coordination ability of amine groups will increase and the recovery will be



**Fig. 5.** Effect of pH on the extraction efficiency of methyl violet (10B). Utilized conditions: Methyl violet (10B), 1 mg l<sup>-1</sup>; poly (ABA-SMA)@APTES-Fe<sub>3</sub>O<sub>4</sub>MNC (magnetic nanosorbent), 100 mg; 3 ml of HNO<sub>3</sub> 1 M as eluent; centrifugation time, 20 min.



**Fig. 6.** Effect of the amount of nanosorbent on the extraction efficiency of methyl violet (10B). Utilized conditions: methyl violet (10B), 1 mg l<sup>-1</sup>; pH 7.0; 3 ml of HNO<sub>3</sub> 1 M as eluent; centrifugation time, 20 min.



**Fig. 7.** Effect of the eluent type and concentration on the recovery of 1 mg l<sup>-1</sup> methyl violet (10B) dye. Experimental conditions: pH 7, amount of sorbent 50 mg, sample volume 50 ml.



increased too (up to 99%). In high alkaline pHs, the recovery will be reduced, hence the studies were conducted at pH = 7 using phosphate buffer solutions

### Effect of the Amount of Poly(ABA-SMA) Fe<sub>3</sub>O<sub>4</sub> Nanosorbent

The amount of poly (ABA-SMA)@APTES-Fe<sub>3</sub>O<sub>4</sub> MNC nanosorbent used in this pre-concentration procedure is a critical factor for obtaining high recoveries of the analyte. Therefore, the extraction system was carefully studied in order to define the lowest amount of nanosorbent which is necessary for achieving the highest possible pre-concentration factor. The recovery is a function of the amount of nanosorbent, which was added to 50.0 ml sample. The effect of the amount of the sorbent was investigated in the range of 10-200 mg. It was observed that the extraction efficiency of the proposed system was remarkably affected by the amount of nanosorbent. Fig. 6 highlights that poly(ABA-SMA)@APTES-Fe<sub>3</sub>O<sub>4</sub> MNC magnetic nanosorbent quantitatively extracts the Methyl violet from aqueous sample with amount of 50 mg, using a single step extraction procedure. No significant changes were observed on the extraction efficiency for the higher amounts of nanosorbent. Therefore, in order to achieve a good enrichment factor, 50 mg nanosorbent was chosen as optimum amount. The obtained optimum amount of nanosorbent to achieve a good enrichment factor was 50 mg.

### Effect of Type and Concentration of Eluent

The nature of the eluent is very important and should optimally meet three criteria: efficiency, selectivity and compatibility. In addition, it may be desirable to recover the analytes in a small volume of solvent to ensure a significant enrichment factor. In this work, elution of the retained Methyl violet from poly(ABA-SMA)@APTES-Fe<sub>3</sub>O<sub>4</sub> MNC surface was examined using various reagent solutions, and the results are shown in (Figs. 7 and 8). As can be seen, the best recovery was achieved when 1 M of HNO<sub>3</sub> was used as an eluent. The effect of elution volume (0.5-4.0 ml) on the recovery was also investigated. The recovery of Methyl violet increased by increasing the volume of HCl up to 1.5 ml and remained constant afterward. So, to achieve the highest pre-concentration factor, 2 ml of the eluent was

chosen as the optimum value.

### Effect of Sorption/desorption Time

Due to the super paramagnetic property of the poly (ABA-SMA)@APTES-Fe<sub>3</sub>O<sub>4</sub> MNC, the sorbent could be separated rapidly from the sample solution using an external magnetic field instead of filtration or centrifugation. Therefore, the effect of adsorption/desorption time on the recovery of analyte was investigated as analysis time. Both of the adsorption and desorption times were varied in the range of 1-20 min. According to the obtained results, 5 min was sufficient for each step (Fig. 9).

### Effect of Sample Volume

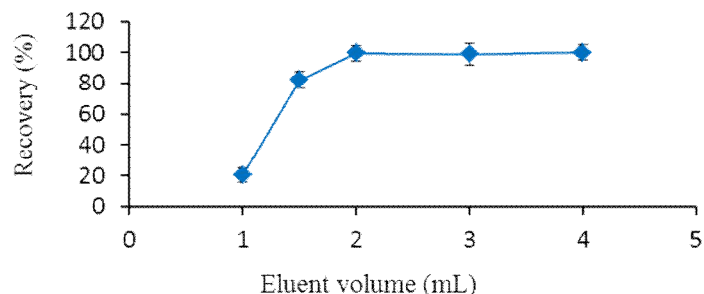
In order to obtain the best pre-concentration factor, the extraction system was studied to find the highest volume ratio between sample solution and nanosorbent. Thus, the effect of sample volume was examined in a range of 25-600 ml for 1 mg l<sup>-1</sup> of Methyl violet. After addition of constant amount of nanosorbent to the different volumes of aqueous samples, extraction procedure was performed for each solution. The data is shown in Fig. 10, all solutions were extracted under the optimum conditions by the proposed method. As shown in Fig. 10, quantitative recoveries of Methyl violet obtained up to 400 ml of sample solution. The quantitative recoveries of Methyl violets were obtained by 2 ml of eluent, so the pre-concentration factor obtained was 200.

### Maximum Sorption Capacity

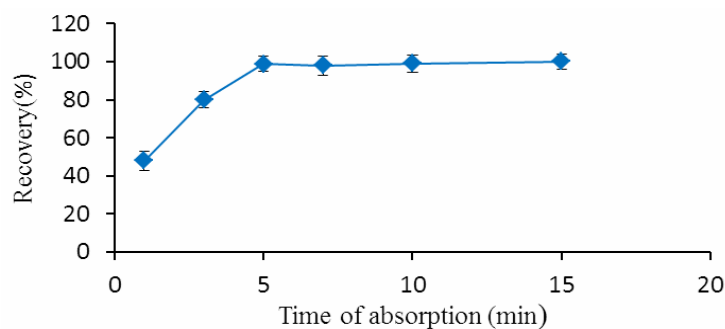
The adsorption capacity ( $q_e$ , mg g<sup>-1</sup>) of the nanosorbent for Methyl violet (10B) was calculated using the following equation:

$$q_e = \frac{V}{W}(C_0 - C_e) \quad (1)$$

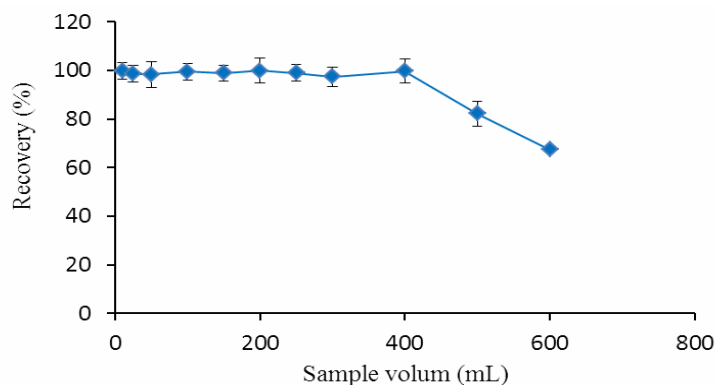
where, C<sub>0</sub> (mg l<sup>-1</sup>) and C<sub>e</sub> (mg l<sup>-1</sup>) are the initial and equilibrium concentrations of the analyte in aqueous solution, respectively, V (l) is the volume of sample solution, and W (g) is the mass of the used poly(ABA-SMA) Fe<sub>3</sub>O<sub>4</sub> magnetic nanohybrid. To determine the maximum sorption capacity, 100 mg of the nanosorbent was added to 200 ml of solution containing 100 mg of the



**Fig. 8.** Effect of the eluent volume on the extraction efficiency of methyl violet (10B). Utilized conditions: Methyl violet (10B),  $1 \text{ mg l}^{-1}$ ; poly(ABA-SMA)@APTES- $\text{Fe}_3\text{O}_4\text{MNC}$  (magnetic nanosorbent), 50 mg; (pH 7.0); centrifugation time, 20 min.



**Fig. 9.** Effect of the sorption time on the recovery of methyl violet (10B). Utilized conditions: Methyl violet (10B),  $1 \text{ mg l}^{-1}$ ; poly(ABA-SMA)@APTES- $\text{Fe}_3\text{O}_4\text{MNC}$  (magnetic nanosorbent), 50 mg; pH 7.0; eluent volume, 2 ml of  $\text{HNO}_3$  1 M.



**Fig. 10.** Evaluation of the extraction efficiency of methyl violet (10B) by using the different sample volumes and constant amount of poly(ABA-SMA)@APTES- $\text{Fe}_3\text{O}_4\text{MNC}$  as sorbent. Utilized conditions: Methyl violet (10B),  $1 \text{ mg l}^{-1}$ ; phosphate buffer (pH 7.0); MNC, 50 mg; eluent volume, 2 ml of  $\text{HNO}_3$  1 M; centrifugation time, 5 min.

**Table 2.** Tolerance Limits of Potentially Interfering Ions in the Determination of Methyl Violet (1 PPM)

Possible interfering ions	Interferent to analyte ratio
Li <sup>+</sup> , Na <sup>+</sup> , Cs <sup>+</sup> , Mg <sup>2+</sup> , CO <sub>3</sub> <sup>2-</sup> , Sr <sup>2+</sup> , Sn <sup>2+</sup> , K <sup>+</sup>	
Azo violet, Methyl orange, Congo red, Victoria blue, Alizarine	1000:1
Yellow, Congo red, Thymol blue, Acid orange 7, Ascorbic acid (AA), uric acid (UA), dopamine (DA)	
Ba <sup>2+</sup> , Ca <sup>2+</sup> , F <sup>-</sup> , PO <sub>4</sub> <sup>3-</sup> , CO <sub>3</sub> <sup>2-</sup> , Cl <sup>-</sup> , Br <sup>-</sup>	800:1
Fe <sup>2+</sup> , Cr <sup>2+</sup> , SO <sub>3</sub> <sup>2-</sup> , Cu <sup>2+</sup> , Zn <sup>2+</sup>	600:1
Pb <sup>2+</sup> , Co <sup>2+</sup> , Cd <sup>2+</sup> , Cr <sup>2+</sup> , NO <sub>3</sub> <sup>-</sup>	300:1
Malachite green	50:1

**Table 3.** Figures of Merit of the MSPE Method

Parameter	Analytical feature
%RSD (n = 5) <sup>a</sup>	1.10
Regression equation	y = 0.15860x - 0.001
Correlation coefficient (R <sup>2</sup> )	0.9989
Limit of detection (µg l <sup>-1</sup> )	0.08
Enrichment factor <sup>b</sup>	200
Linear range (µg l <sup>-1</sup> )	0.3-1500

<sup>a</sup>Relative standard deviation. <sup>b</sup>Calculated as the ratio between the volume of the initial aqueous solution and the final elution volume.

analyte and sonicated for 2 min. To reach equilibrium, the extraction process was continued for 60 min by stirring the solution on a mechanical stirrer at room temperature. Afterward, the nanosorbent was separated from the solution under magnetic field.

Then, the extracted dye were eluted from the nanosorbent with 2 ml of HNO<sub>3</sub> (1.0 M) solution. Finally, the concentration of the analyte was determined by UV-Vis absorption method, after appropriate dilution. As a result, maximum capacity of the nanosorbent for methyl violet

(10B) was found to be 167.3 mg g<sup>-1</sup>.

#### Regeneration and Reusability of the Sorbent

The reusability of this magnetic nanosorbent was investigated by subsequent sorption and elution cycles for dyes. The nanosorbent could be reused after regenerating with 2 ml of HNO<sub>3</sub> (1 M) and 10 ml deionized water, respectively. Moreover, based on the obtained results, there is no significant decrease in methyl violet recovery (less than 10%) after 100 adsorption-desorption cycles.

**Table 4.** Comparison of the Presented MSPE Method with other Pre-concentration Methods

Method	Linear range ( $\mu\text{g l}^{-1}$ )	LOD ( $\mu\text{g l}^{-1}$ )	EF <sup>a</sup>	RSD (%)	Ref.
RDSE-direct solid phase Spectrophotometry <sup>b</sup>	5-225	1.8	-	-	[20]
(IL-CIAME) <sup>c</sup>	3.6-200	1.16	152	2.30	[39]
CPE <sup>d</sup>	16-1000	4.8	-	-	[40]
HPLC-LITMS <sup>e</sup>	-	0.25-10	-	1.9-18.4	[41]
SPE <sup>f</sup>	1-20	0.5	-	5.5	[42]
SPE-FO-LADS <sup>g</sup>	4-200	1.3	200	1.3	[43]
SPE-Spectrophotometry <sup>h</sup>	120-8000	28	89-96	1.6-3.4	[43]
Spectrophotometry	0.3-1500	0.08	200	1.1	This work

<sup>a</sup>Enrichment factor. <sup>b</sup>Rotating disk sorptive extraction. <sup>c</sup>Cold-induced aggregation microextraction based on ionic liquid. <sup>d</sup>Cloud point extraction. <sup>e</sup>High-performance liquid chromatography-linear ion trap mass spectrometry. <sup>f</sup>Solid-phase extraction. <sup>g</sup>Nanoporous silica SBA-3 Fiber optic-linear array detection spectrophotometry. <sup>h</sup>Diatomite.

### Effect of Foreign Ions as Interfering Ions

In order to illustrate the selectivity of the extraction method for pre-concentration and determination of Methyl violet (10B) the effect of potential interfering ions and other dyes on the analytical signal was investigated. Different amounts of ions and other dyes in leather and textile like Azo violet, Crystal orange, Congo red, Victoria blue, Alizarine Yellow, Thymol blue, Acid orange 7, Ascorbic acid (AA), Uric acid (UA), Dopamine (DA) were added to the test solution containing Methyl violet (10B) and then operated as described previously. A dye was considered to interfere when its presence produced a variation of more than  $\pm 5\%$  in the analytical signal of the sample. The results

are given in Table 2. Some of cations and common anions and other dyes were found not to affect MV (10B) signal in the UV-Vis system. These results permit the application of the proposed system for interference-free determination of ultra-trace Methyl violet in water samples.

### Analytical Figures of Merit

Under the optimized experimental conditions, the analytical features of the presented method, such as the linear range of the calibration graph, the limit of detection (LOD) and limit of quantification (LOQ), the accuracy and the precision were examined. The calibration graph was linear in the range between 0.3 and 1500  $\mu\text{g l}^{-1}$  with the

**Table 5.** Determination of Methyl Violet in Water Samples (Results of Recoveries of Spiked Samples)

Sample	Added (ng ml <sup>-1</sup> )	Found (ng ml <sup>-1</sup> )	Recovery (%)
	0	N.D	-
Drinking water <sup>a</sup>	+100	100.54 ± 0.03	105.40
	+500	501.17 ± 0.02	102.34
	0	N.D	-
Mineral water <sup>b</sup>	+100	100.81 ± 0.18	108.11
	+500	500.56 ± 0.02	101.12
	0	N.D	-
River water <sup>b</sup>	+100	99.88 ± 0.02	98.82
	+500	499.87 ± 0.01	99.74
	0	10.2	-
West water <sup>d</sup>	+100	109.96 ± 0.13	98.87
	+500	509.93 ± 0.02	99.50
	0	N.D	-
West water <sup>f</sup>	+100	99.89 ± 0.03	98.89
	+500	499.88 ± 0.02	99.76

N.D: not detected. <sup>a</sup>From drinking water system of urmia, Iran. <sup>b</sup>From vata mineral water. <sup>c</sup>Collected from shahar chay river, Iran. <sup>d</sup>Collected from west water factory of color maral in urmia. <sup>f</sup>Collected from waste-water effluent of Khoi Textile Factory, Iran.

correlation coefficient of 0.999. The calibration equation was  $y = 0.15860x - 0.001$ , where  $y$  is the intensity and  $x$  is the concentration of Methyl violet in the sample solution in

mg l<sup>-1</sup>. The LOD and LOQ, defined as  $3S_b/m$ , and  $10S_b/m$  (where  $S_b$  is the standard deviation of the blank and  $m$  is the slope of the calibration curve), were  $0.08 \mu\text{g l}^{-1}$  and  $0.27$

$\mu\text{g l}^{-1}$ , respectively. In order to study the precision of the method, a series of six solutions containing  $0.08 \text{ mg l}^{-1}$  Methyl violet were measured at the same day. The relative standard deviation (RSD%,  $n = 6$ ) was found to be 1.1%. The recoveries were found  $>99.63 \pm 1.0\%$  dyes on poly (ABA-SMA)  $\text{Fe}_3\text{O}_4$  nanosorbent. Also, the pre-concentration factors were found to be 200 for Methyl violet (Table 3).

### Comparison of the Proposed Methods with other Pre-concentration Methods

Comparison between the presented magnetic nanosorbent and some other reported different sorbents for pre-concentration of Methyl violet is summarized in Table 4. The presented method has relatively low LOD and high enrichment factor. Values in parentheses are the CV concentration for which the RSD was obtained.

### Method Validation and Analysis of Real Samples

The presented procedure was applied to determine Methyl violet in several water samples such as tap water, underground water and sea water. In order to verify the accuracy of the established procedure, recovery experiments were also carried out by spiking the samples with different amounts of dye before any pretreatment. Concentration of Methyl violet (10B) in different samples and relative recoveries were evaluated and the results are shown in Table 5.

### CONCLUSIONS

In this research, a nanosorbent from poly (ABA-SMA) ligand group has been reported. Poly (ABA-SMA) ligand can be regarded as a class of materials that are simply synthesized in the laboratory. It was found that the nanometer-sized particles of poly(ABA-SMA)  $\text{Fe}_3\text{O}_4$  nanosorbent is stable and has a great potential as a sorbent for the removal of dyes from aqueous solutions. Poly (ABA-SMA)  $\text{Fe}_3\text{O}_4$  nanosorbent has also a high retention capacity regarding Methyl violet (10B) dye, and the retained analyte can be easily stripped with  $\text{HNO}_3$ . On the other hand, the coupling of poly (ABA-SMA)  $\text{Fe}_3\text{O}_4$  nanosorbent for SPE procedure with spectrophotometric detection exhibits a sensitive, reproducible, simple, and low cost

technique that can be used for the separation and determination of methyl violet (10B) dye in textile wastewater effluents.

High selectivity and precision of the proposed method have made it a suitable and selective method for extraction and pre-concentration of cationic dye (methyl violet 10B) from aqueous solutions by adjusting pH. The presented procedure is simple and fast for sorption and pre-concentration of the cationic dye without using any chelating agent and organic solvents. The simplicity of  $\text{Fe}_3\text{O}_4$  modification with the poly (ABA-SMA) ligand group, easy separation, and high capacity factor improves the application of this compound as special and unique solid phase for magnetic solid phase for Methyl violet extraction. Compared to the other reported procedures, this method has lower detection limit and is more conventional (easy sorbent separation by magnet), however, its pre-concentration factor is more than that of some other methods. The presented method possesses some advantages such as: simplicity, high kinetic sorption of the target analyte, low detection limit ( $0.08 \mu\text{g l}^{-1}$ ), good precision (RSD = 1.1%) and high sorption capacity ( $167.3 \text{ mg g}^{-1}$ ).

### REFERENCES

- [1] L.E. Gaini, M. Lakraimi, E. Sebbar, A. Meghea, M. Bakasse, *J. Hazard. Mater.* 161 (2009) 627.
- [2] D. Master, M. Mehta, *Eng. Sci. Res. Technol.* (2014) 417.
- [3] Y. Safa, H.N. Bhatti, *Chem. Eng. J.* 167 (2011) 35.
- [4] Y. Lin, X. He, G. Han, Q. Tian, W. Hu, *Environ. Sci.* 23 (2011) 1.
- [5] K. Mohanty, J.Th. Naidu, B.C. Meikap, M.N. Biswas, *Ind. Eng. Chem. Res.* 4 (2006) 5165.
- [6] S. Senthilkumar, P. Kalaamani, C.V. Subburaam, *J. Hazard. Mater. B* 136 (2006) 800.
- [7] Sh. Li, *Bioresour. Technol.* 101 (2010) 2197.
- [8] A. Mittal, J. Mittal, A. Malviya, D. Kaur, V.K. Gupta, *Colloid Interface Sci.* 343 (2010) 463.
- [9] Y.M. Slokar, A.M. Marechal, *Dyes Pigm.* 37 (1998) 335.
- [10] J.A Bumpus, B.J. Brock, *Appl. Environ. Microbiol.* 54 (1988) 1143.
- [11] Y. Tao, D. Chen, X. Chao, H. Yu, P. Yuanhu, Zh. Liu,

- Li. Huang, Y. Wang, Z. Yuan, *Food Control*. 22 (2011) 1246.
- [12] S.J. Allen, G. McKay, J.F. Porter, *J Colloid Interface Sci.* 280 (2004) 322.
- [13] G.O. El-Sayed, *Desalination* 272 (2011) 225.
- [14] A. Adak, M. Bandyopadhyay, A. Pal, *Dyes Pigm.* 69 (2006) 245.
- [15] A. Babana, A. Yedilerb, D. Lienert, N. Kemerdeera, A. Kettrup, *Dyes Pigm.* 58 (2003) 93.
- [16] R.E. Palma-Goyes, F.L. Guzmán-Duque, G. Peñuela, I. González, J.L. Nava, R.A. Torres-Palma, *Chemosphere* 81 (2010) 26.
- [17] G. Crini, *Bioresour. Technol.* 97 (2006) 1061.
- [18] L. An, J. Deng, Li. Zhou, H. Li, F. Chen, H. Wang, Y. Liu, *Hazard. Mater.* 175 (2010) 883.
- [19] G. Li, X. Zhang, L. Zhang, Sh. Xu, Ch. Li, *Chromatographia* 78 (2015) 979.
- [20] V. Manzo, O. Navarro, L. Honda, K. Sánchez, P. Richter, *Talanta* 106 (2013) 305.
- [21] M. Wierucka, M. Biziuk, *Anal. Chem.* 59 (2014) 50.
- [22] P. Rai, R.K. Gautam, S. Banerjee, V. Rawat, M.C. Chattopadhyaya, *Environ. Chem. Eng.* 3 (2015) 2281.
- [23] H. Chen, Sh. Yang, J. Chang, K. Yu, D. Li, *Chemosphere* 89 (2012) 185.
- [24] A. Adak, A. Pa, *Environ. Sci. Health A* 41 (2006) 1.
- [25] Q. Han, Z. Wang, J. Xia, S. Chen, X. Zhang, M. Ding, *Talanta* 101 (2012) 388.
- [26] I. Safarik, M. Safarikova, *Water Res.* 36 (2002) 196.
- [27] I.G. Dakova, I.B. Karadjova, V.T. Georgieva, G.S. Georgiev, *Micro. Chim. Acta* 164 (2009) 55.
- [28] O. Sadeghi, M.M. Amini, M.F.B. Bazargani, *Int. J. Polym. Mater.* 22 (2012) 530.
- [29] R. Dhodapkar, N.N. Rao, S.P. Pande, S.N. Kaul, *Bioresour. Technol* 97 (2006) 877.
- [30] G. Crini, P.M. Badot, *Prog. Polym. Sci.* 33 (2008) 399.
- [31] P. Sittner, V. Michaud, J. Schrooten, *Mater. Trans.* 43 (2002) 984.
- [32] S.M. Henry, M.E.H. El-Sayed, Ch.M. Pirie, *Biomacromolecules* 7 (2006) 2407.
- [33] I. Donati, A. Gamini, A. Vetere, C. Campa, S. Paoletti, *Biomacromolecules* 3 (2002) 805.
- [34] A. Masoumi, M. Ghaemy, A. Nik Bakht, *Ind. Eng. Chem. Res.* 53 (2014) 8188.
- [35] N. Samadi, R. Hasanzadeh, M. Rasad, *Appl. Polym. Sci.* 41642 (2015) 1.
- [36] R. Hasanzadeh, P.N. Moghadam, N. Samadi, *Polym. Adv. Technol.* 24 (2014) 34.
- [37] Yu. Rong, H. Zh. Chen, *Colloids Surf. A* 242 (2004) 17.
- [38] N. Samadi, R. Ansari, B. Khodavirdilo, *Eng. Adv. Technol.* 4 (2015) 11.
- [39] M. Eisapour, F. Shemirani, B. Majidi, *Anal. Methods* 5 (2013) 5731.
- [40] L. Zaijun, Ch. Jie, Sh. Haixia, P. Jiaomai, *Anal. Chem.* 26 (2015) 109.
- [41] X. Wua, G. Zhanga, Y. Wua, X.H.Z. Yuanb, *Chromatogr. A* 1172 (2007) 121.
- [42] K.A. Sagar, M.R. Smyth, M. Rodriguez, P.T. Blanco, *Talanta* 42 (1995) 235.
- [43] A. Azarkohan, F. Shemirani, M. Alvand, *Hindawi Publishing Corporation* (2013) 1.