

Spectrophotometric determination of trace amount of malachite green from water with novel magnetic silica nanoparticles

N. Samadi*¹, M. Ahari Salmasi²

¹ Professor, Department of chemistry, Faculty of science, Urmia university, Urmia, Iran

² PhD Student, Department of Chemistry, Faculty of Sciences, Azarabaijan Shahid Madani University, Tabriz, Iran

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

ABSTRACT

A nano-hybrid based on polystyrene derivatives and magnetite was introduced as a new sorbent for pretreatment and determine the trace amount of malachite green from aqueous solution by spectrophotometry after preconcentration by solid phase extraction (SPE). UV-Vis spectrophotometer was used for determination of MG concentration after desorption of the dye by hydrochloric acid solution in the solutions. Different variables affecting the separation/preconcentration conditions, including pH of the sample solution, amount of the sorbent, extraction and desorption times, sample volume, and elution conditions were obtained in the range of 1–2000 ng/mL dye, with the correlation coefficient of 0.998. The enrichment factor of 133 was achieved. The limit of detection was 0.2 ng·mL⁻¹ and the relative standard deviation for the determination of malachite was 1.4 % (n=6). Langmuir, Freundlich, adsorption isotherm models were studied and the experimental results were addressed by Freundlich isotherm model. The maximum sorption capacity of the adsorbent for malachite green was 148.6 mg·g⁻¹, indicating high potential of MSMA in the adsorption of malachite green. The adsorption kinetics was studied with the pseudo-first-order, pseudo-second-order models. The method was successfully applied to determine malachite green in natural waters and satisfactory recoveries were obtained >98 % from this.

Keywords: Nanohybrid, Magnetite, Polystyrene, Magnetic solid phase extraction, Malachite green

1. INTRODUCTION

Malachite green (MG) is tri phenyl methane dye and has been widely used around the world as fungicide, parasiticide and antiseptic in the aquaculture the chemical causes serious side effects. In 1993 the FDA nominated malachite green as a priority chemical for carcinogenicity testing by the National Toxicology Program. The basis for selection was the potential for significant worker and consumer

exposure suggestive evidence of tumor promotion in rodent liver and suspicion of carcinogenicity based on structure activity relationships. So it has toxic effect to human cells and mutagenic and carcinogenic properties as well, like causing liver tumor formation, hepatic and renal tumors formation in rodents [1, 2].

However, due to its low cost and high effectiveness, this harmful dye is still used and will probably continue to be

used in the aquaculture in some parts of the world. Therefore, it is very important to develop sensitive detection methods to simultaneously detect the existence of MG in various water samples. Therefore, the treatment of effluent containing dye pollutions before being discharged to the environment is essential. Until now, different methods have been reported for the determination of MG such as high performance liquid Chromatography [3, 4–6], spectrophotometry [7, 8], capillary electrophoresis Raman spectroscopy (CE-RS) [9] and electrochemical determinations [10, 11]. Among these approaches, absorption is regarded as an easy, economic and desirable process due to its high efficiency and ability to separate a wide range of pollutants from industrial effluents [12] and so Liquid–liquid extraction (LLE) is one of the oldest preconcentration methods in analytical chemistry [13]. Other methods like supercritical fluid extraction (SFE) and solid-phase extraction (SPE) are relatively expensive methods [14]. Solid-phase micro extraction (SPME) [15–17] includes extraction and preconcentration of analytes from aqueous samples or from headspace of the samples is also expensive and at most time the reproducibility of the results is low. In addition, the fiber which is used in SPME is fragile and has a limited lifetime [18]. Single drop microextraction (SDME) is inexpensive and very little solvent is used [18]. Various sample preparation techniques based on solid phase extraction (SPE) systems have been developed to isolate various types of analytes from different matrices. However, in spite of the whole advantages of SPE, it can still be tedious, time consuming, and relatively expensive [19]. Recently, a new mode of SPE called magnetic solid-phase extraction (MSPE) has been developed

[20]. MSPE is based on the combination of magnetic inorganic material and non-magnetic adsorbent material [21]. By taking advantages of the combined benefits of both the materials, the MSPE technology exhibits excellent adsorption efficiency and rapid separation from the crude sample matrix by an external magnetic field [21,22] Various SPE materials have been successfully used for preconcentration and extraction of dyes in trace amounts [23-27]. Like, magnetic nanoparticles [28], modified silica [28], and polymer gels [29] and multi-wall carbon nanotube [30] have been used to modify the surface of Fe_3O_4 magnetic nanoparticles. To improve the dispersibility and stability of adsorbents in aqueous solution, the surface of nanoparticles can be modified with a polymer [31]. A polymeric ligand is applied to selectively bind specific dyes in a mixture to isolate important dyes from wastewater and aqueous media [31-34]. The polymeric ligand is usually applied in an insoluble resin form to separate a specific metal ion from a liquid that containing a mixture of dyes. Among the various types of polymers, MMSMA (modified magnetic styrene maleic anhydride) has attracted intense attention amount of dye. These magnetic nanoparticles could be easily functionalized with desired molecules using silane agents that the silane group will be reacted with active hydroxyl and amine groups on the surface of particles and cause formation of functionalized magnetic nanoparticles [35]. The SMA copolymer is biocompatible compound which has been used in drug delivery and controlled release systems. It can be used in numerous applications but their use in bio applications is proportional to their purity [36, 37]. 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.

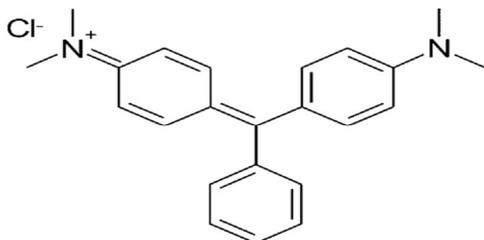


Fig. 1. The chemical structure of malachite green (MG).

However, there has been no report concerning the synthesis of magnetic styrene maleic anhydride nanohybrids. This paper reports on preparation of CSMA(modified magnetic styrene maleic anhydride) coated Fe_3O_4 nanoparticles using an as a magnetic nano hybrid as a sorbent for the separation, preconcentration and determination of malachite green from aqueous solutions by (SPE) adsorption technique, in this research. we were optimized the effects of type, concentration conditions of the analyte, including pH of the sample solution, amount of the sorbent, extraction and desorption times, and elution conditions and sample volume. This method was applied to a numbers of industrial and natural samples. The concentration of MG in the stripped solutions was also monitored spectrophotometrically by measuring the absorbance of the desorbed dye by hydrochloric acid at 618 nm. This paper describes a novel, simple and sensitive method for the determination of malachite green in water samples. The method is based on the extraction of malachite green mediated by sensitive magnetic nanosorbent (poly (styrene-alt-maleic acid)). The extracted dye is dissolved in chloridric acid and measuring its absorbance by spectrophotometry at 618 nm. This polymeric nanosorbent possesses ionic

functional groups and can absorb or traps cationic dyes like malachite green.

2. EXPERIMENTAL

2.1. Standard solutions and reagents

All chemicals were used of analytical–reagent grade and all solutions were prepared with high purity deionized water Artemia research center (Urmia, Iran). A stock standard solution of malachite green (1000 mg.L^{-1}) was prepared by dissolving appropriate amount of malachite green (obtained from Shanghai Chemical Reagent Company, China) 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 (0.1M) was prepared by dissolving appropriate amounts of sodium phosphate (Merck, Germany) in deionized water and adjusting to pH 8 by adding diluted NaOH (Merck, Germany) solution. All reagents and solvents including methanol, ethanol, sulfuric acid, acetic acid, hydrochloric acid, H_2O_2 , THF, SOCl_2 , 3-aminopropyltriethoxysilane (APTES), 1,3-diaminopropane (DAP), triethylamine (TEA), styrene, maleic anhydride (MA), 3-aminbenzoic acid (ABA), benzoyl peroxide (BPO), ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferrous chloride ($\text{FeCl}_2 \cdot 7\text{H}_2\text{O}$), ammonia, and all salts used for the interference study were purchased from Merck. All the plastic and glassware 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. All of the required solutions were prepared using deionized water. The pipettes and vessels used for ultra–trace analysis were kept in 15% (v/v) nitric acid at least overnight and subsequently

washed three times with deionized water before using.

2.2. Instrumentation

A single beam Agilent WPA (Biowave II) UV–Vis spectrophotometer utilizing a 1 cm quartz cell was used for determination of MG concentration in the solutions. In order to structural study of the nano sorbent, Powder X-ray diffraction (XRD) measurements were performed on a Bruker AXS model D8 Advance (Karlsruhe, Germany) instrument with $\text{Cu-K}\alpha$ radiation source (1.54 Å) between 2 and 701 generated at 40 kV and 35 mA at room temperature. Samples for XRD were ground into powder and then pressed flat in the sample slot. In addition, FT-IR spectra (4000–400 cm^{-1}) were recorded on a Bruker model Vector 22 (Ettlingen, Germany) Fourier transforms 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 characteristics 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.

2.3. Synthesis of modified Fe_3O_4 magnetic nano-particles

Magnetic Fe_3O_4 NPs were prepared by chemical co-precipitation method [38]. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (10 mmol, 2.730 g) and

$\text{FeCl}_2 \cdot 7\text{H}_2\text{O}$ (5 mmol, 0.994 g) were dissolved in deionized water (20 mL) and stirred at 80 °C. Then, 80 mL of NH_4OH solution (1.5 mol L^{-1}) was added into the mixture under N_2 atmosphere until the pH reached 10 and the reaction mixture was stirred for 1h. After the formation of a black precipitate, the Fe_3O_4 NPs were collected by a magnet and washed three times using deionized water until the pH reached 7 and then dried in vacuum oven for 24 h.

The synthesized Fe_3O_4 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 °C. Finally, modified APTES- Fe_3O_4 NPs were collected by applying a magnet, washed three times with ethanol, and dried in vacuum at 80 °C.

2.3.1 Synthesis of modified styrene-maleic anhydride (SMA) copolymer

The SMA copolymer was prepared by free radical polymerization of maleic anhydride and styrene at 70 °C in the presence of benzoyl peroxide as initiator [36]. 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 °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 °C.

For synthesis of 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 °C [37, 39]. Next, after adding 2 mL of SOCl_2 , the reaction was continued at 65 °C for 24 h under argon atmosphere. Finally, the precipitation [poly(ABA-SMA)] was separated by filtration and dried in vacuum at 60 °C.

2.3.2 Synthesis of magnetic nano-composite

For synthesis of MNC, the modified APTES- Fe_3O_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- Fe_3O_4 : ABA-SMA) was added into the mixture, and the reaction mixture was sonicated for 24 h at 65 °C. After that, for further cross linking, 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- Fe_3O_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 (Figure 2).

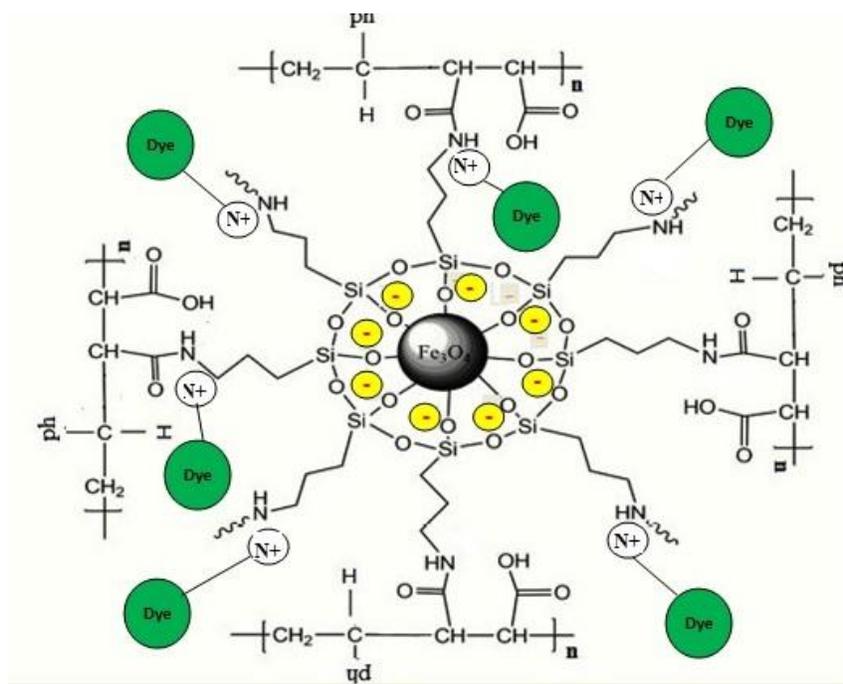


Fig. 2. complexation of the sorbent with malachite green (MG).

2.4 General procedure

25 mL standard solution containing malachite green in the range of 1–2000 μgL^{-1} and 2 mL phosphate buffer (0.1 mol L^{-1} and pH 8) was transferred in a 250 mL glassware beaker. Then, 70 mg

of poly(ABA-SMA)@APTES- Fe_3O_4 MNC nanohybrid as sorbent was added to solution and the mixture was shaken for 10 min at room temperature. Finally, the sorbent was gathered at one

side of the beaker under a strong external magnetic field and the clear supernatant was directly decanted. The isolated sorbent was eluted with 1.5 mL of $1\text{ mol L}^{-1}\text{HCl}$ to desorb the analyte. This step was also done with the help of a magnet. Dye present in clear solution of the eluent was determined by UV-Vis. Finally, this method was applied to separate, preconcentrate and determination of malachite green from the real sample solutions.

2.5 Real Sample preparation

Water samples including tap water, distilled water, sea water, river water and underground water were chosen for the analysis. Each sample was collected from local sources; Underground water from Azarshahr city, river water from Shaharchay and tap water from Azarshahr and Urmia lake. Then, the samples were filtered through Round filter paper (blue band, no. 300210) to remove suspended particulate matter and stored in a refrigerator at 4°C . equal Aliquots of each sample solution was analyzed within 24 hours.

3. RESULTS AND DISCUSSION

3.1 Characterization of the Prepared Magnetic Fe_3O_4

(Figure 3A) shows the FT-IR spectra of (a) Fe_3O_4 nanoparticles, (b) APTES- Fe_3O_4 nanoparticles, (c) MSMA, and (d) poly (SMA). In (Figure 3A(a, b) the absorption bands at around 672 cm^{-1} can be ascribed to the Fe–O stretching vibration of Fe_3O_4 . In addition, O–H stretching vibration around 3422 cm^{-1} and O–H deformed vibration at 1627 cm^{-1} were observed in panels a and (b) of (Figure 1), suggesting that –OH groups coat on the surface of Fe_3O_4 as reported. The presence of APTES on the surface of Fe_3O_4 nanoparticles is also certified by the bands at 1120 and 1027 cm^{-1} which are due to Si–O stretching vibrations. This reveals that

the covalent bonds of Fe–O–Si are formed after modification of Fe_3O_4 through silanization reaction with APTMS (b). The presentation of the broad band at 3421 cm^{-1} 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^{-1} confirm the presence of an anchored propyl group. Comparison of the FT-IR spectrum of poly (MSMA) in Figure (c) and (SMA) in Figure (d) indicates that characteristic absorption bands of the anhydride linkage of poly (SMA) at 1735 , 1784 , and 1856 cm^{-1} disappeared after reaction with the APTES- Fe_3O_4 , and adsorption bands were observed for MSMA at 1728 cm^{-1} related to the amide at 1635 and 3419 cm^{-1} because of carboxylic groups.

(Figure 4) shows XRD patterns of SMA and neat Fe_3O_4 magnetic and SMA/ Fe_3O_4 nano-particles. The diffraction patterns show that the copolymer was amorphous. According to the Spectral data of XRD, The approximate size of particles (However, this method of calculation is not correct because samples are amorphous But due to lack of access SAXD technology This method was used) Calculated by using scherrer equation and the results are listed in the following table, The resulting numbers show the approximate size of particles of synthesized polymer Were 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 (Figure 4a) the diffraction peak at $2\theta =20^{\circ}$ is assigned to the (005) reflection of SMA. The XRD patterns of neat Fe_3O_4 nanoparticles indicate their cubic spine structures. The presence of sharp and intense peaks

confirmed the formation of highly crystalline Fe_3O_4 . (Figure 4b) For synthesized of the SMA/ Fe_3O_4 (Figure 4c) 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_3O_4 (JCPDS No.19-0629). So, the existence of Fe_3O_4 NPs on SMA is confirmed, while the (005) reflection peak of layered SMA almost disappeared. It may be due to the fact that after covering with Fe_3O_4 NPs, the SMA particles cannot pile with each other anymore to form their shapes [40, 41].

For further investigation, we used SEM (emission scanning electron microscopy) to look for morphology and obtain the average diameter of the synthesized SMA and SMA/ Fe_3O_4 copolymers. The morphology of SMA reveals that the copolymer has amorphous nature and Average

diameter of the observed particles in SEM images can be estimated under 100 nm with reasonable monotony and grainy shape. This result indicates that there might be different particle size in these copolymers powder, although more of the grain size could be in nanometer-scale resolution of the SEM [36]. After in situ deposition of Fe_3O_4 NPs onto the surface of the SMA, it was obvious that the distribution of Fe_3O_4 NPs on the surface of SMA is uniform and carefully distributed Fe_3O_4 NPs were densely covered on the surface of SMA and no large lacuna is observed (Figure 3B). The average size of these nano-particles calculated to be around 20 nm according to SEM photograph and the EDX-system that was coupled with SEM for elemental analysis, gave the elemental analysis for SMA/ Fe_3O_4 (C: 11.98, H: 2.14, N: 9.31%) and Si atoms would not decompose in elemental analysis [40, 41].

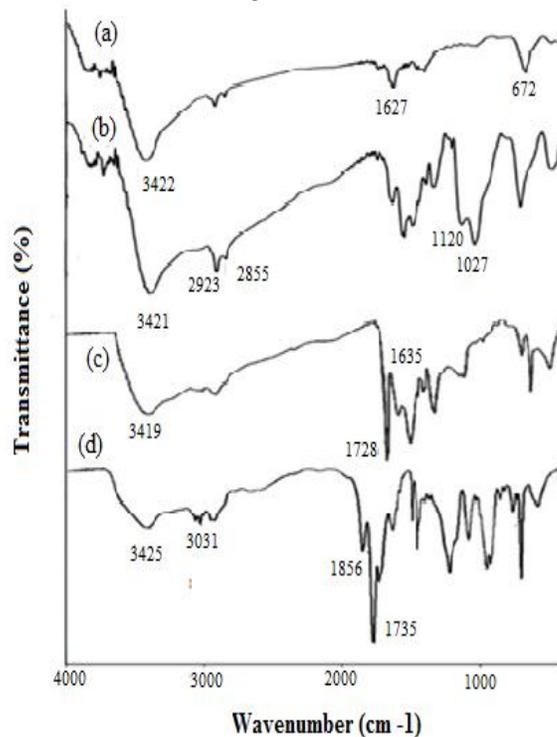


Fig. 3 (A). FT-IR spectrum, a) Fe_3O_4 , b) APTES (3-aminopropyltriethoxysilane), c) APTES/SMA, d) SMA

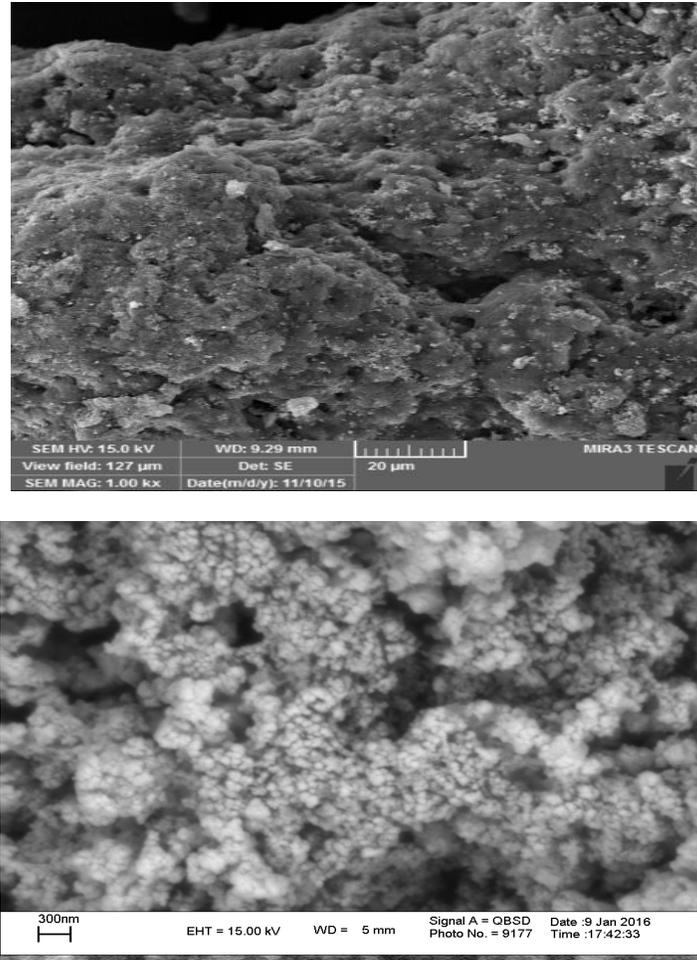


Fig. 3 (B). SEM of MSMA (magnetic styren maleice anhydride)

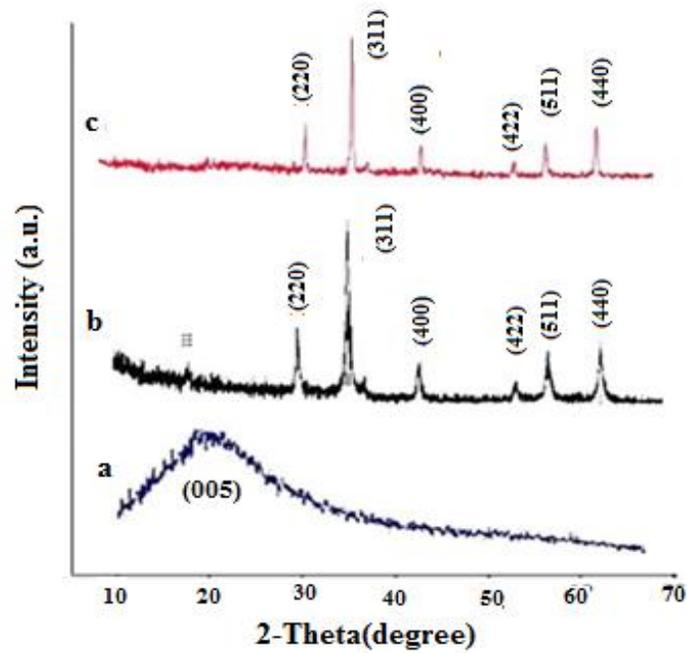


Fig. 4. XRD pattern of SMA and SMA/ Fe_3O_4 and Fe_3O_4 nanohybrid, respectively.

3.2. Optimization of magnetic solid phase extraction conditions

In order to obtain quantitative recoveries of the sorption of silver ions on SMA/Fe₃O₄ nano-sorbent, various analytical parameters were optimized such as, pH of the sample solution, amount of the sorbent, extraction and desorption times and type of eluent and eluent volume and sample volume. The adsorbed dye on poly(ABA-SMA)@APTES-Fe₃O₄ MNC nanohybrid were calculated from the amounts of malachite in the starting sample solution and the amounts of them in the final solution.

3.2.1 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 malachite green was investigated in the pH range 3.0–9.0. In this approach, the preconcentration method has been applied in different pH values and the recoveries were calculated. As the results show, quantitative recovery (>98%) of dye was observed in pH of 7.0–9.0 (Figure 5) For adsorption, the mechanism is different as the amine group should coordinate to malachite green. By increasing the pH, the coordination ability of amine groups will increase and the recovery will be increase (up to 98%). In high alkaline pHs, the dye hydroxide will be precipitate so the recovery will be reduced. Therefore the rest of the studies were carried out at pH 8.0 by using phosphate buffer solution.

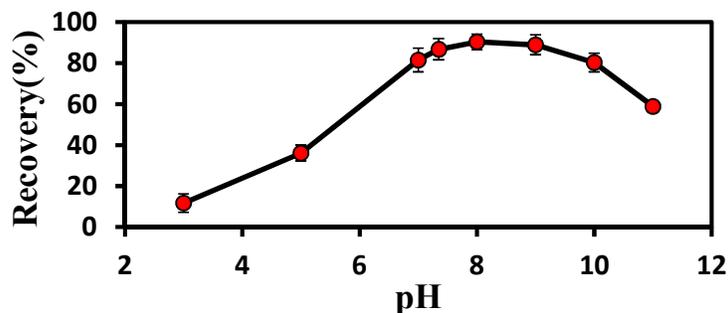


Fig. 5. Effect of pH on the extraction efficiency of malachite green, Utilized conditions: malachite green 1 mg L⁻¹; poly(ABA-SMA)@APTES-Fe₃O₄MNC (magnetic nano sorbent), 100 mg; 3 mL of HCl 1M as eluent; centrifugation time, 20 min.

3.2.2 Effect of amount of nano-sorbent

The amount of poly(ABA-SMA)@APTES-Fe₃O₄ MNC nano-sorbent which is used in this preconcentration 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 nano-sorbent which is necessary for achieving the highest preconcentration factor possible. The variation in the recovery is a function of the amount of nano-sorbent, which was added to 50.0 mL sample, was investigated in the range of 20 to 200 mg. It was observed that the extraction efficiency of the proposed system was remarkably

affected by the nano-sorbent amount. Figure 6. highlights that poly (ABA-SMA)@APTES-Fe₃O₄ MNC magnetic nano-sorbent quantitatively extracts the Malachite green from aqueous sample with amount of 70 mg, using a single step extraction procedure. No significant changes were observed on the extraction efficiency for higher

nano-sorbent amounts. Therefore, in order to achieve a good enrichment factor, 70 mg nano sorbent was chosen as optimum amount. Therefore, the obtained optimum amount of nano sorbent to achieve a good enrichment factor was 70 mg.

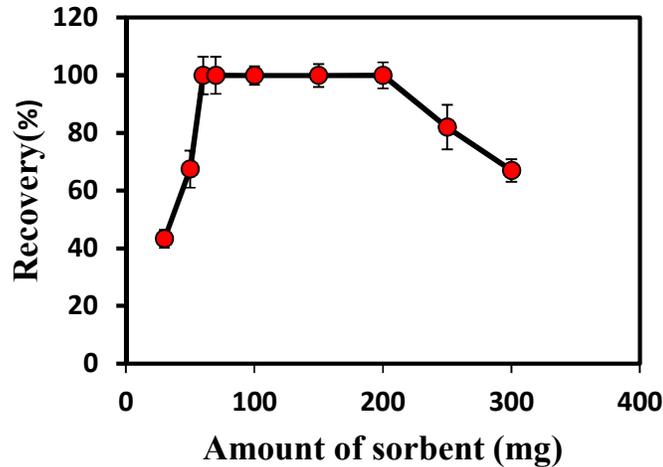


Fig. 6. Effect amount of nano sorbent on the extraction efficiency of malachite green, Utilized conditions: malachite green 1 mg L⁻¹; (pH 8.0); 3 mL of HCL 1M as eluent; centrifugation time, 20 min.

3.2.3 Effect of type and concentration of eluent

The nature of the eluent is prime importance 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 malachite from poly(ABA-SMA)@APTES-Fe₃O₄ MNC surface was examined using various reagent solutions and the results are shown in (Figure 7, 8). As

can be seen, the best recovery was achieved, when HCl 1 mol L⁻¹ was used as an eluent. The effect of elution volume (0.5–4.0 mL) on the recovery was also investigated. The recovery of malachite increased by increasing the volume of HCl up to 1.5 mL and remained constant after ward. So, to achieve the highest preconcentration factor, 1.5 mL of the eluent was chosen as the optimum value.

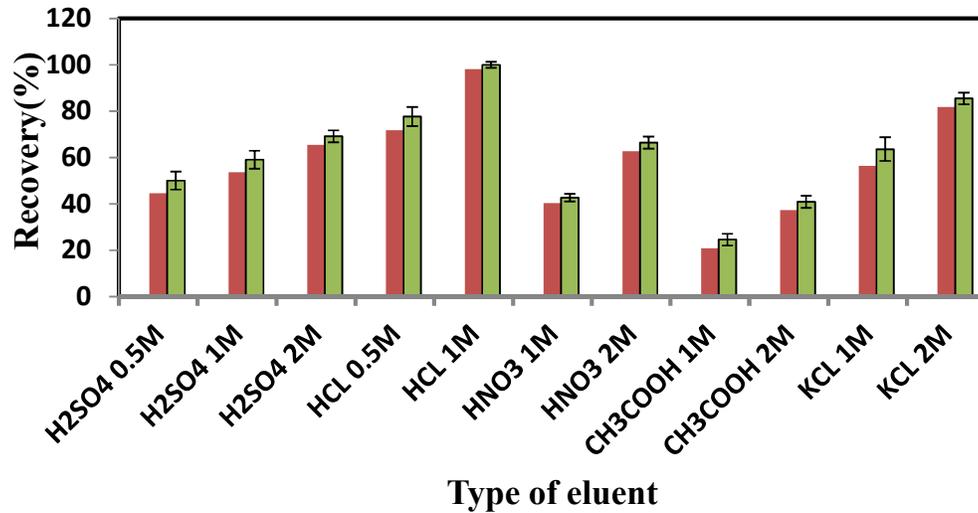


Fig. 7. Effect of eluent type and concentration on the recovery of 1 mg L^{-1} malachite green dye. Experimental conditions: pH; 8, amount of sorbent; 70 mg, sample volume; 50 mL.

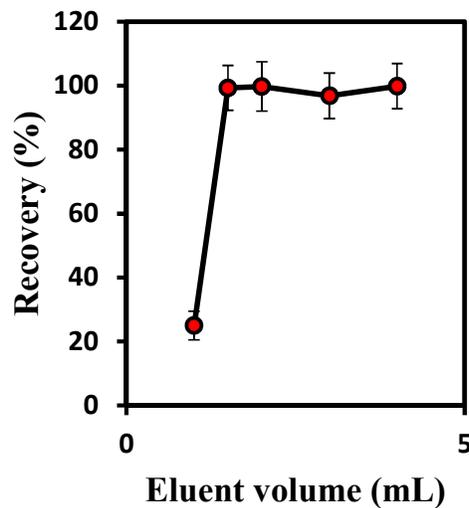


Fig. 8. Effect of eluent volume on the extraction efficiency of malachite green, Utilized conditions: malachite green 1 mg L^{-1} ; poly(ABA-SMA)@APTES-Fe₃O₄MNC (magnetic nano sorbent), 70 mg; (pH 8.0); centrifugation time, 20 min.

3.2.4 Effect of sorption/desorption time

Due to the superparamagnetic property of the poly(ABA-SMA)@APTES-Fe₃O₄ 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 the adsorption and desorption time was varied in the range of 1–20 min. According to the obtained results, 10 min was sufficient for each step (Figure 9).

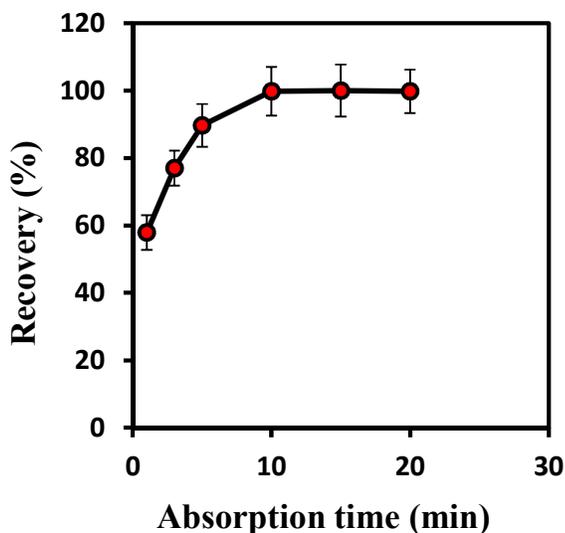


Fig. 9. Effect of sorption time on the recovery of malachite green, Utilized conditions: malachite green 1 mg L^{-1} ; poly(ABA-SMA)@APTES- Fe_3O_4 MNC (magnetic nano sorbent), 70 mg; (pH 8.0); eluent volume 1.5 mL of HCL 1M.

3.2.5 Effect of sample volume

In order to obtain the best pre-concentration factor, the extraction system was studied to allow the highest volume ratio between sample solution and nanosorbent. Thus, the effect of sample volume was examined in a range of 10–300 mL for 1 mg L^{-1} malachite green. After addition of constant amount of nanosorbent into different volumes of aqueous samples, extraction procedure was performed for

each solution. The data is shown in (Figure 10), All solutions were extracted under the optimum conditions by the proposed method. As shown in (Figure 10) quantitative recoveries of malachite obtained up to 200 mL of sample solution. The quantitative recoveries of malachites were obtained by 1.5 mL of eluent, so the pre-concentration factor obtained was 133.3.

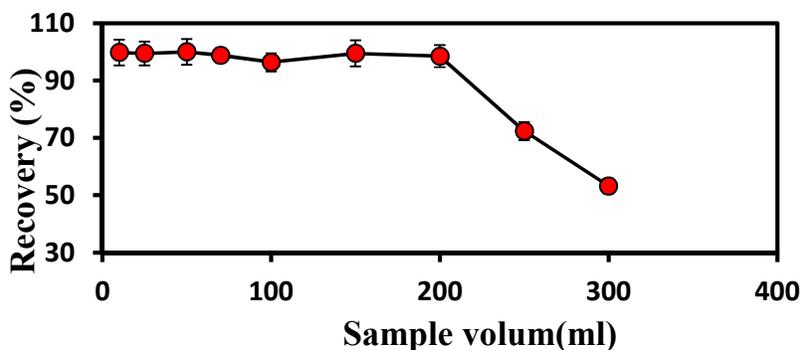


Fig. 10. Evaluation of the extraction efficiency of malachite green by using the different sample volumes and constant amount of poly(ABA-SMA)@APTES- Fe_3O_4 MNC as sorbent. Utilized conditions: malachite green 1 mg L^{-1} ; phosphate buffer (pH 8.0); MNC, 70 mg; eluent volume 1.5 mL of HCL 1M; centrifugation time, 10 min.

3.2.6 Maximum sorption capacity

In order to obtain the maximum sorption capacity, 100 mg of poly(ABA-SMA)@APTES-Fe₃O₄ MNC nano-sorbent was added to 500 mL aqueous solution containing 100 mg of malachite. After 30 min, the sorbent was separated, washed with distilled water and the dyes were eluted with related eluent and its concentration was determined using UV-VIS. The maximum capacities of poly(ABA-SMA)@APTES-Fe₃O₄ MNC magnetic Nano-sorbent, was found to be 148.6 mg.g⁻¹ for malachite solutions. The amount of malachite bounded by the nanoparticles was calculated according to the following formula:

$$Q = (C_0 - C_e) V / W$$

Where Q is the amount of adsorbed malachite (mg.g⁻¹); C₀ (mg L⁻¹) and C_e (mg L⁻¹) 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 amount of nano-sorbent.

3.2.7 Regeneration and reusability of the sorbent

The reusability of this magnetic nano-sorbent was investigated by subsequent sorption and elution cycles for dyes. The results show that there is no significant decrease in malachite recovery (less than 10%) after 80 adsorption-desorption cycles.

3.3 Effect of foreign ions

The effect of typical potential interfering ions and other dyes on the analytical signal was investigated. Different amounts of ions and other dyes like Azo violet, Methyl orange, Congo red, Victoria blue, Alizarine Yellow, Congo red, Thymol blue, Acid orange 7, Ascorbic acid (AA), uric acid (UA), dopamine (DA) were added to the test solution containing malachite and then operated as described previously. A dye was considered to interfere when its presence produced a variation of more than ±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 malachite signal in the UV-VIS system. These results permit the application of the proposed system for interference-free determination of ultra-trace malachite in water samples.

Table 1. Instrumental and experimental conditions for dye determination

FAAS conditions	-	Unit
Wavelength	618	nm
Micro-extraction conditions		
Working pH	8	-
Malachite concentration	1	ppm
Buffer concentration	0.1	M
Shaking time	10	min
Eluent volume (mL)	1.5 1.5	mL mL

Table 2. Tolerance limits of potentially interfering ions in the determination of malachite green.

Interfering ions	Interferent to analyte ratio
Na ⁺ , Cs ⁺ , Mg ⁺² , NO ₃ ⁻ , CO ₃ ⁻ , Sr ⁺² , Sn ⁺² , PO ₄ ⁻² , Cl ⁻ , Br ⁻	
Azo violet, Methyl orange, Congo red, Victoria blue, Alizarine, Yellow, Congo red, Thymol blue, Acid orange 7, Ascorbic acid (AA), uric acid (UA), dopamine (DA)	1000:1
Ca ²⁺ , K ⁺ , F ⁻	800:1
Fe ⁺² , cr ⁺² , so ₃ ⁻²	600:1
cu ⁺² , zn ⁺²	400:1
pb ⁺² , co ⁺² , cd ⁺² , cr ⁺²	100:1

3.4 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 1 and 2000 $\mu\text{g L}^{-1}$ with the correlation coefficient of 0.999. The calibration equation was $y=0.1430 x-0.004$, where y is the intensity and x is the concentration of silver in the sample solution in mgL^{-1} . The LOD and LOQ, defined as $3\text{Sb}/m$, and $10\text{Sb}/m$ (where Sb is the standard deviation of the blank and m is the slope of the calibration curve), were $0.2 \mu\text{gL}^{-1}$ and $0.65 \mu\text{gL}^{-1}$, respectively. In order to study the precision of the method a series of six solutions containing 1mgL^{-1} malachites were measured at the same day. The relative standard deviation (RSD%, $n=6$) was found to be 1.4 %. The recoveries were found to be more than 99% dyes on poly(ABA-SMA)@APTES-Fe₃O₄ MNC. Also, the preconcentration

factors were found to be 133.3 for malachite green.

3.5 Comparison of the proposed methods with other pre-concentration methods

Comparison between the presented magnetic nano-sorbent and some other reported different sorbents for pre-concentration of malachite is summarized in (Table 3). The presented method has relatively low LOD and good enrichment factor.

3.6 Method validation and analysis of real samples

The presented procedure was applied to determination of malachite 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 malachite in different samples and relative recoveries were evaluated and the results are shown in (Table 4).

Table 3. comparison of the presented MSPE method with other pre-concentration methods

Sorbent/Detection	Linear range ($\mu\text{g L}^{-1}$)	LOD ($\mu\text{g L}^{-1}$)	EF	RSD (%)	Ref.
NST / Spectrophotometric cloud point extraction	4-500	1.2	-	1.13	[7]
MWCN / ET determination (mol L^{-1})	5×10^{-8} - 8×10^{-6}	6×10^{-9}	33	5.6	[11]
Spectrophotometric	1-4000	0.175	43.542	3.50	[15]
Spectrophotometric (mol L^{-1})	1×10^{-8} - 5×10^{-7}	4.1×10^{-9}	23	10-7	[18]
PLS / spectrophotometric	9.9-800	2.9	-	-	[42]
(PDMS) / (SERS)	1-100	1-2	-	5	[43]
MSMA/ Spectrophotometric	1-2000	0.2	133.3	1.4	This work

EF: Enrichment factor, ET: electrothermal, NST: nonionic surfactant Tritonx-100, MWCN: multi-wall carbon nanotube modified glassy carbon electrode, PDMS : poly dimethylsiloxane microfluidic, SERS: surface-enhanced Raman spectroscopy.

4. ADSORPTION ISOTHERM

The equilibrium adsorption isotherm model, which is the number of mg adsorbed per gram of adsorbent (q_e). The equilibrium concentration of adsorbate is fundamental in describing the interactive behavior between adsorbate and adsorbent. Analysis of isotherm data is important for predicting the adsorption capacity of the adsorbent, which is one of the main parameters required for the design of an adsorption system. Equilibrium isotherm studies were carried out with different initial concentrations of malachite green ($1-2000 \text{ ng mL}^{-1}$) at 25°C two models (Langmuir, Freundlich) were used to analyze the equilibrium adsorption data [43, 44].

4.1 The Langmuir isotherm

The Langmuir isotherm theory assumes that intermolecular forces decrease rapidly with distance and this leads to the prediction that the maximum adsorption capacity consists of monolayer type, where all sorption sites are identical and energetically equivalent [44]

The general form of the Langmuir isotherm is:

$$q_e = q_m k_L C_e / (1 + k_L C_e)$$

The equation can be linearized to the following equation

$$C_e / q_e = 1 / k_L q_m + C_e / q_m$$

Where C_e is the equilibrium concentration of dye solution (mg L^{-1}), q_e is the equilibrium capacity of dye on

the adsorbent (mg g^{-1}), q_m is the maximum adsorption capacity (mg g^{-1}), k_L is the Langmuir constant related to the energy of adsorption (L mg^{-1}). The Langmuir constants k_L and q_m are calculated from the slope and

intercept of the plot of C_e/q_e versus C_e (Figure 11). The results are listed in (Table 5). The results showed that No good fit was achieved with the Langmuir isotherm equation.

Table 4. Determination of malachite green in water samples (results of recoveries of spiked samples)

Sample	Added (ng mL^{-1})	Found (ng mL^{-1})	Recovery (%)
Distilled Water	0	Not detected	–
	+5	4.90 ± 0.04	98.10
	+10	9.87 ± 0.06	98.70
Tap Water ^a	0	Not detected	–
	+5	4.89 ± 0.05	97.80
	+10	9.90 ± 0.08	99.11
river Water ^b	0	Not detected	–
	+5	4.87 ± 0.05	97.41
	+10	9.94 ± 0.14	98.40
Color Maral factory ^c	0	15.20	–
	+5	19.96 ± 0.06	98.82
	+10	24.60 ± 0.08	98.61
uremia sea Water	0	-	-
	+5	4.91 ± 0.09	98.21
	+10	9.86 ± 0.06	98.63

^a From drinking water system of Azarshahr, Iran.

^b Collected from shaharchay river, Iran.

^c Collected from underground water of Azarshahr, Iran.

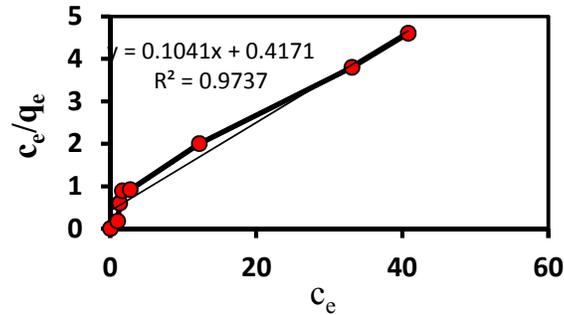


Fig. 11. Adsorption isotherms of the malachite green on to MSMA using Langmuir models

4.2 Freundlich Isotherm

The Freundlich isotherm theory [45] said that the ratio of the amount of solute adsorbed onto a given mass of sorbent to the concentration of the solute in the solution is not constant at different concentrations. The equilibrium capacity of adsorption decreases with increasing the extent of adsorbent and amount of removal increase until 100%. The model of Freundlich adsorption isotherm, which is an indicative of surface heterogeneity of the sorbent, is given by bellow equation.

$$q_e = K_f C_e^{1/n}$$

Where C_e is the equilibrium concentration (mg.L^{-1}), q_e is the amount adsorbed at equilibrium (mg g^{-1}), and K_f ($\text{mg l}^{-1/n} \text{L}^{1/n} \text{g}^{-1}$) and $1/n$ are Freundlich constants depending on the temperature and the given adsorbent-adsorbate couple. n is related to the adsorption energy distribution, and K_f related to the adsorption capacity. The other Freundlich constant n is a measure of the deviation from linearity of the adsorption and used to verify types of adsorption. The values of K_f and $1/n$

calculated from the intercept and slope of the plot of $\ln(q_e)$ versus $\ln(C_e)$ are listed in (Table 5) (Figure 13); In the Freundlich isotherm model, the value of n indicates the type of isotherm. n for this work obtain 0.946. When n is equal to unity, the adsorption is linear. Further, n below unity indicates that adsorption is a chemical process; whereas, n above unity is associated with a favorable adsorption and a physical process [47].

The linearized form of the Freundlich adsorption isotherm equation is

$$\text{Log } q_e = \text{log } K_f + 1/n (\text{log } C_e)$$

(Table 5) show that the values of correlation coefficient, $R^2 = 0.998$, for the fit of experimental isotherm data to Freundlich equation is more close to 1 than that for Langmuir equation ($R^2 = 0.918$) Therefore, the Freundlich model represents the experimental data better on the basis of values of regression coefficients. It can be concluded that Freundlich isotherm model is an appropriate. (Figure 12); Non-linear regression has better performance for analyzing experimental data and Freundlich model was better than Langmuir to represent equilibrium data.

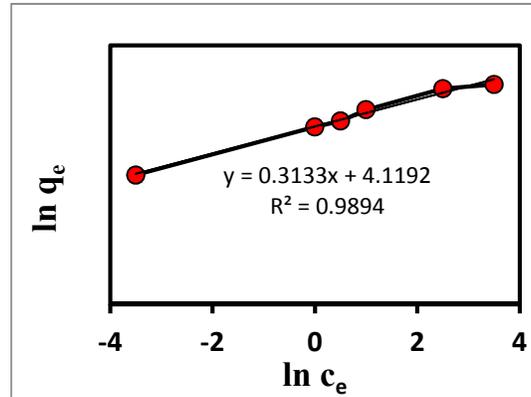


Fig. 12. Adsorption isotherms of the malachite green on to MSMA using Freundlich models

Table 5. Isotherm parameters for the adsorption of malachite green on to magnetic SMA adsorbents

Isotherm	Parameters	Adsorbent (MSMA)
Langmuir $1/q_e = 1/(k_a q_m c_e) + 1/q_m$	q_m (mg g ⁻¹)	120.85
	K_L (L mg ⁻¹)	1.29
	R^2	0.97
Freundlich $\ln q_e = \ln k_F + (1/n) \ln c_e$	n	3.20
	K_F (L mg ⁻¹)	68.09
	R^2	0.99

4.3 Equilibrium Isotherm

The study of equilibrium isotherms was performed by agitating of 0.07 g MSMA nanocomposite in a solution containing various concentrations of dye for 10 min at pH = 8. After shaking for 10 min separated by magnet and absorption measured by spectrophotometry and then the dye concentration according to the calibration curve accepted. The amount of dye adsorbed q_e (mg/g) was determined using the following mass balance relationship $q_e = (C_0 - C_e)V/m$

Where V is the volume of the solution (L); and m is the mass (g) of the adsorbent.

5. ADSORPTION KINETICS

5.1 Pseudo-first order equation

Pseudo-first order equation or Lagergren's kinetics equation [49] when $q_t = 0$ at $t = 0$, Eq can be integrated into following equation:

$$dq_t/dt = k_1(q_e - q_t)$$

$$\text{Log}(q_e - q_t) = \text{Log}(q_e) - k_1 t / 2.303$$

Where q_t is the amount of dye adsorbed per unit of adsorbent (mg g⁻¹) at time t, k_1 is the pseudo-first order rate constant (min⁻¹), and t is the

contact time (min). Values of the rate constant (k_1), equilibrium adsorption capacity ($q_{e,cal}$), the correlation coefficient (R^2) were calculated from the slope and intercept of the plots of $\log(q_e - q_t)$ versus t as shown in (Figure 15) and are presented in Table. 6 The correlation coefficients (R^2) for the pseudo-first-order model are relatively low, and significant differences exist between the calculated q_{cal} values and experimental q_{exp} values. Accordingly, the adsorption of malachite green onto MSMA does not follow the pseudo-first order kinetic model.

5.2 Pseudo-second order equation

The Mckay pseudo-second-order rate equation is represented as [50] when the initial condition is

$q_t = 0$ at $t = 0$, leads to

$$1/(q_e - q_t) = 1/q_e + kt$$

which is the integrated rate law for a pseudo-second order reaction can be rearranged to obtain

$$t/q_t = 1/h + 1t/q_e$$

: where k_2 ($g\ mg^{-1}\ min^{-1}$) is the rate constant of the pseudo second-order adsorption. The constant k_2 is used to calculate the initial sorption rate h ($mg\ g^{-1}\ min^{-1}$), at $t \rightarrow 0$, as follows: where k_2 ($g\ mg^{-1}\ min^{-1}$) is the rate constant of the pseudo second-order adsorption. Values of the rate constant (k_2), equilibrium adsorption capacity (q_e), the correlation coefficient (R^2) were calculated from the slope and intercept of the plots of t/q_t versus t as shown in (Figure 16)

and are presented in (Table 6). For the adsorption of malachite green by MSMA non- linear relationships with high correlation coefficients ($R^2 > 0.997$) between t/q_t and t indicated that

the adsorption process could be well described by the pseudo second-order model. For the pseudo-second-order model, the calculated q_e values agree well with the experimental q_e , exp values. Furthermore, the calculated q_e values agree very well with the experimental q_e ,exp values.

$$dq_t/dt = k_2(q_e - q_t)^2$$

$$t/q_t = 1/k_2q_e^2 + t/q_e$$

$$h = k_2q_e^2$$

For the kinetic studies, the nano composite (0.07 g) with 25 mL samples at the initial concentration of dye (C_0) of 1 mg/L was agitated in a 100 mL beaker. The removal rate of dye was investigated by measurement of dye concentrations after predetermined time intervals by the UV-Vis method. The amount of adsorbed malachite at time t , q_t (mg/g), was calculated by following equation: $q_t = (C_0 - C_t)V/m$ Where the C_t is the concentration of dye in solution at specified time (mg/L).

model to explain the present system. The equilibrium adsorption capacity (q_e) for the adsorption of MG on SMA modified Fe_3O_4 nanoparticles calculated from the Freundlich isotherm model is listed in (Table 6). All of the adsorbents used for MG adsorption have considerably lower q_e values than poly(ABA-SMA)-@APTES- Fe_3O_4 MNC nanoparticles used in this study. Besides that, the simplicity of the preparation method and magnetic and electronic properties that cause simple magnetic separation of MG loaded adsorbent makes these particles as so good candidate for MG adsorption.

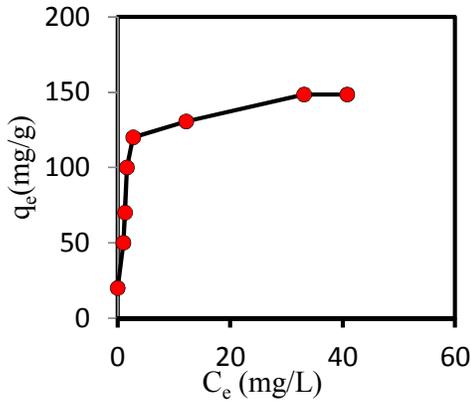


Fig. 13. Sorption isotherm of MG

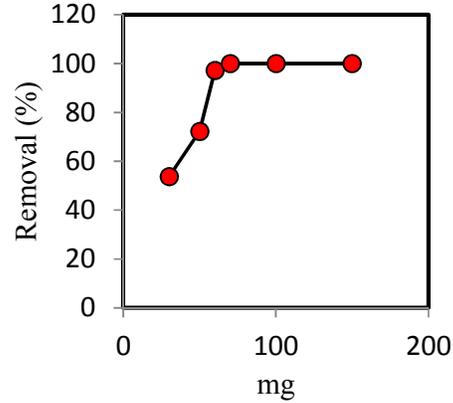


Fig. 14. Dye removal according to increasing amount of sorbente.

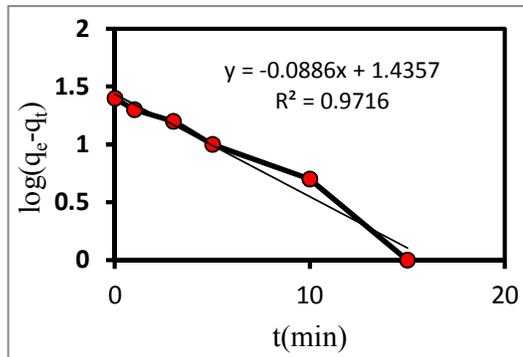


Fig. 15. Kinetics modeling of the adsorption of malachite green reducing pseudo first-order models obtained for MSMA

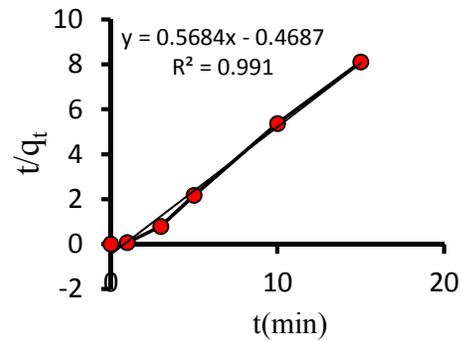


Fig. 16. Kinetics modeling of the adsorption of malachite green reducing pseudo second-order models obtained for MSMA

Table 6. Kinetic parameters for the adsorption of malachite green on the MSMA.

Isotherm	Parameters	Adsorbent
	R^2	0.971
Pseudo-first-order	q_e (mg g ⁻¹)	98.191
	$\log(q_e - q_t) = \log q_e - k_1 t / 2.303$	
	K_1 (min ⁻¹)	0.024
Pseudo-second-order	q_e (mg g ⁻¹)	123.321
	K_2 (mg L ⁻¹ min ⁻¹)	0.003
	$t/q_t = 1/k_2 q_e^2 + t/q_e$	
	R^2	0.991

4. CONCLUSION

In this research, a nano-sorbent from poly(ABA-SMA)@APTES-Fe₃O₄ MNC ligand group has been reported. poly(ABA-SMA)@APTES-Fe₃O₄ MNC ligand can be regarded as a class of materials that are simple to synthesize in the laboratory. It was found that the nanometer-sized on poly(ABA-SMA)@APTES-Fe₃O₄ MNC nano-sorbent is stable and has a great potential as a sorbent for the removal of dyes from aqueous solutions. Also, poly(ABA-SMA)-@APTES-Fe₃O₄ MNC nano-sorbent a high retention capacity regarding (malachite green) dye, and the retained analyte can be easily stripped with HCl. On the other hand, the coupling of poly(ABA-SMA)@APTES-Fe₃O₄ MNC nano-sorbent for SPE procedure with spectrophotometric detection exhibits a sensitive, reproducible, simple, low cost technique that can be used for the separation and determination of malachite green dye in textile wastewater effluents.

High selectivity and accuracy of the proposed method have made it a suitable and selective method for extraction and preconcentration of cationic dye (malachite) from aqueous solutions by changing pHs. The simplicity of Fe₃O₄ modification with the poly(ABA-SMA)@APTES-Fe₃O₄ MNC ligand group, easy separation, and high capacity factor improves the application of this compound as special unique solid phase for magnetic solid phase for malachite extraction. Comparing 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 lower than some methods. The presented method possesses some advantages such as: simplicity, high kinetic sorption of the

target analyte, low detection limit (0.2 ng.mL⁻¹), good precision (RSD=1.4% n=6), excellent accuracy, and high sorption capacity (148.6mg.g⁻¹). Adsorption of malachite green as a sample cationic dye on poly(ABA-SMA)@APTES-Fe₃O₄ MNC was studied. The kinetic studies showed that the malachite dye adsorption process followed pseudo-second order kinetics models. The equilibrium experimental data fit perfectly with the Freundlich isotherm.

ACKNOWLEDGEMENTS

The authors are thankful to Department of chemistry Faculty of science Urmia university for financial support.

REFERENCES

- [1] S. J. Culp and Frederick A. Beland, *American Coll Toxicol*, 15, 219, (1996).
- [2] M. Farré, D. Barceló, *Emerging Journal of Organic Contaminants and Human Health*, 20 ,1, (2012).
- [3] K Mitrowska; A Posyniak; J Zmudzki, *J. Chromatogr. A*, 1089, 187, (2005).
- [4] Z. Lian, J. Wang, *Mar. Pollut. Bull.*, 64, 2656, (2012).
- [5] X. Wu, G. Zhang, Y. Wu, X. Houa, Z. Yuan; *J. Chromatogr. A*, 1172, 121, (2007).
- [6] Ch. Longa, Zh. Maia, Y. Yang, B. Zhub, X. Xu, L. Lu, X. Zou, *J. Chromatogr. A*, 1216, 2275, (2009).
- [7] N. Pourreza, Sh. Elhami, *J. Anal. Chim. Acta*, 596, 62, (2007).
- [8] Safarik, M. Safarikova, *J. Water Res.*, 36, 196, (2002).
- [9] Ch. H. Tsai, J. D. Lin, Ch. H. Lin, *Talanta*, 72, 368, (2007).
- [10] W. Huang, C. Yang, W. Qu, S. Zhang, Russ, *J. Electrochim*, 44, 946, (2008).
- [11] H. Yi, W. Qu, W. Huang, *J. Microchim Acta.*, 160, 291, (2008).
- [12] G. Crini, H. N. Peindy, F. Gimbert, C. Robert, *J. Sep. Purif. Technol*, 53, 99, (2007).

- [13] H. Liu, P. K. Dasgupta, *J. Anal. Chem.*, 68, 1817, (1996).
- [14] M. D. Farahani, F. Shemirani, *J. Colloid Interface Sci.*, 407, 250, (2013).
- [15] A. Asfaram, M. Ghaedi, A. Goudarzi, M. Soylak, S. M. Langroodi, *J. Rsc Adv.*, 39, 9813, (2015).
- [16] L. Chen, Y. Lu, Sh. Li, X. Lin, Zh. Xu, Zh. Dai, *J. Food. Chem.*, 141, 1383, (2013).
- [17] D. Djozan, Y. Assadi, *J. Microchem.*, 63, 276, (1999).
- [18] M. Bahram, F. Keshvari, P. N. Moghaddam, *Talanta*, 85, 891, (2011).
- [19] Q. Wu, M. Liu, X. Ma, W. Wang, C. Wang, X. Zang, Z. Wang, *J. Mikrochim. Acta*, 177, 23, (2012).
- [20] M. Safarokova, I. Safarik, J. M. Mater, *J. Magn. Mater.*, 194, 108, (1999).
- [21] Q. Han, Z. Wang, J. Xia, S. Chen, X. Zhang, *Talanta*, 101, 388, (2012).
- [22] B. Sh. Sha, L. Zhi, Z.X. Huan, W. Chun, W. Zh, *J. Anal. Chem.*, 41, 1177, (2013).
- [23] Y. S. A. Degs, A. H. E. Sheikh, M. A. A. Ghouti, B. Hemmateenejad, G. M. Walker, *Talanta*, 75, 904, (2008).
- [24] M. Taziki, F. Shemirani, B. Majidi, *J. Sep. Purif. Technol.*, 97, 216, (2012).
- [25] M. Soylak, Y. E. Unsal, E. Yilmaz, M. Tuzen, *J. Food. Chem. Toxicol.*, 49, 1796, (2011).
- [26] M. Soylak, Y. E. Unsal, M. Tuzen, *J. Food. Chem. Toxicol.*, 49, 1183, (2011).
- [27] N. Pourreza, S. Rastegarzadeh, A. Larki, *J. Food. Chem.*, 126, 1465, (2011).
- [28] Ch. Jiang, Y. Sun, X. Yu, L. Zhang, X. Sun, Y. Gao, H. Zhang, D. Song, *Talanta*, 89, 38, (2012).
- [29] M. A. Malana, S. Ijaz, M. N. Ashiq, *Desalination*, 263, 249, (2010).
- [30] J. L. Gong, B. Wang, G. M. Zeng, Ch. P. Yang, Ch. G. Niua, Q. Y. Niua, W. J. Zhoua, Y. Liang, *J. Hazard. Mater.*, 164, 1517, (2009).
- [31] M. Q. Caia, X. Q. Weia, Ch. H. Dua, X. M. Maa, M. C. Jin, *J. Chromatogr A*, 1349, 24, (2014).
- [32] V. Bekiari, M. Sotiropoulou, G. Bokias, P. Lianos, *J. Colloids Surf. A*, 312, 214, (2008).
- [33] E. Akceylana, M. Bahadirb, M. Yilmaz, *J. Hazard. Mater.*, 162, 960, (2009).
- [34] G. Crini, P. M. Badot, Application of chitosan, *J. Prog Polym Sci*, 33, 399, (2008).
- [35] X. Liu, J. Xing, Y. Guan, G. Shan, H. Liu, *J. Colloids Surf. A*, 238, 127, (2004).
- [36] R. Hasanzadeh, P. N. Moghadam, N. Samadi, *J. Polym. Adv. Technol.*, 24, 34, (2013).
- [37] N.Samadi, R. Ansari, B.Khodavirdilo, *J. Eng. Adv. Technol.*, 4, 11, (2015).
- [38] A. Masoumi, M. Ghaemy and A. NikBakht, *Ind. Eng. Chem. Res.*, 53, 8188, (2014).
- [39] N.Samadi, R.Hasanzadeh, M. Rasad, *J. Appl. Polym. Sci.*, 41642, 1, (2015).
- [40] R. Liang, C .Liu, X .Meng, J .Wang, J .Qiu, *J. Chromatogr. A*, 1266, 95, (2012).
- [41] X. Liu, L .Yan, W .Yin, L .Zhou, G .Tian, J .Shi, Z .Yang, D .Xiao, Z .Gu, Y .Zhao, *J. Mater. Chem. A*, 2, 12296, (2014)
- [42] L. An, J. Deng, L. Zhou, H. Li, F. Chen, H. Wang, Y. Liu, *J. Hazard. Mater.*, 175, 883, (2010).
- [43] S. Lee, J. Choi, L. Chen, B. Park, J.B. Kyong, G.H. Seong, J. Choo, Y. Lee, K. Shin, E. Kyu Lee, S.W. Joo, K.H. Lee, *Analytica Chimica Acta*, 590, 139, (2007)
- [44] I. Langmuir, *J. Am. Chem. Soc.*, 40, 1361, (1918).
- [45] H. Freundlich, W. Heller, *J. Am. Chem. Soc.*, 61, 2228, (1939).
- [46] A. Afkhami, T. Madrakian, A. Amini, *Desalination*, 243, 258, (2009).
- [47] H. Freundlich, *J. Phys. Chem.*, 57, 384, (1906).
- [48] S. Vasiliu', I. Bunia, S. Racovita, V. Neagu, *J. Carbohydr. Chem.*, 85, 376, (2011).
- [49] M Turabik, *J. Hazard. Mater.*, 158, 52, (2008).
- [50] Y.S. Ho, G. McKay, *J. Process Biochem*, 34, 451, (1999).