Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.890549

54 (2015) 758–768
April

Taylor & Francis
Taylor & Francis Group

Application of modified nano-γ-alumina as an efficient adsorbent for removing malachite green (MG) from aqueous solution

Ehsan Mohammadifar[a], Farzaneh Shemirani[a,*], Behrooz Majidi[b], Maryam Ezoddin[c]

[a]*Faculty of Chemistry, Department of Analytical Chemistry, University College of Science, University of Tehran, Tehran P.O. Box 14155-6455, Iran*
Email: shemiran@khayam.ut.ac.ir
[b]*Faculty of Sciences, Department of Chemistry, Mahabad Branch, Islamic Azad University, Mahabad 59135-443, Iran*
[c]*Department of Chemistry, Payame Noor University, P.O. BOX 19395-3697 Tehran, Iran*

Received 15 November 2013; Accepted 13 January 2014

ABSTRACT

This study describes a simple, inexpensive and sensitive extraction procedure using γ-Al_2O_3 nanoparticles modified with sodiumdodecylsulfate, as an efficient solid phase, for removal, preconcentration and spectrophotometric determination of trace amounts of malachite green (MG) by fiber optic-linear array detection spectrophotometry. The properties of the produced modified nanoparticles were determined by FESEM and TEM. Various effective parameters on the preconcentration of MG, such as pH, sample volume, amount of sorbent, type, concentration, contact time, temperature, and volume of eluent were investigated. Under the optimized operating conditions, the calibration graph was linear over the range of 1.2–250 $\mu g\,L^{-1}$ and relative standard deviation of 1.50% at 100 $\mu g\,L^{-1}$ were obtained ($n = 5$). The limit of detection ($S/N = 3$) was obtained 0.34 $\mu g\,L^{-1}$. The Langmuir adsorption capacity (q_{max}) was found to be 72.4 $mg\,g^{-1}$ of the adsorbent. The method has been successfully used to determine of MG in fish farming water with satisfactory results.

Keywords: Malachite green; Field emission scanning electron microscopy; Fiber optic-linear array detection spectrophotometry; γ-Al_2O_3 nanoparticles; Fish-farming water

---

1. Introduction

Color removal from wastes has been the target of great attention in the past few years. Some cationic (basic) dyes have been reported to cause eye irritation, cancer, allergic dermatitis, skin irritation and even mutation in humans. The inherent carcinogenic nature of many of these dyes endangers living organisms [1,2]. There are several techniques, which are aimed to preferential removal of different types of dyes from wastewater. The wastewater treatment through adsorption is better than other physical techniques like, flocculation, froth flotation, etc. because of its efficiency and economy. In the last few years, several workers have tried different adsorbents for the dye removal from wastewater [3–11]. malachite green (MG) is a cationic triphenylmethane dye (Fig. 1) that widely used for coloring silk, wool, jute, leather, cotton, paper and acrylic. Another application of MG is the use as biocide in the aquaculture industry because it is an efficient fungicide and parasiticide. MG can readily adsorbed by fish organisms and metabolically reduced to the lipophilic leuco-malachite green, which

---

*Corresponding author.

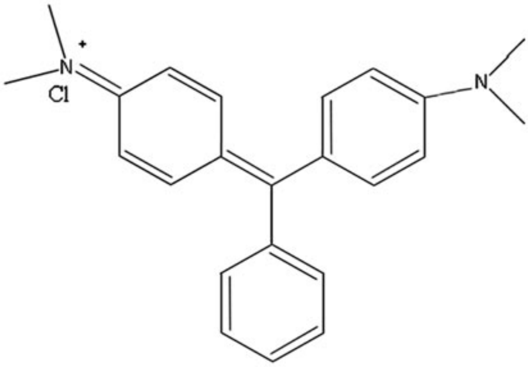

Fig. 1. Structural formula of MG.

presents a long residence time in edible fish tissues and hereby enters to the body of fish consumers [12]. Although MG is effective against protozoan and fungal infections, it is toxic to microbial and mammalian cells, promotion of the hepatic tumor formation in rodents and fishes and also causes serious problems on human immune system and reproductive system [13]. Therefore, the use of MG in aquatic food animals is highly restricted or banned in many countries, including the European Union (EU), Canada, and United States (US Food and Drug Administration banned its use in fisheries in 1991), due to its potential carcinogenic, genotoxic, mutagenic and teratogenic properties [14]. Despite MG is not verified for using in aquaculture, this harmful dye is still used and will probably continue to be used in some parts of the world due to its low-cost and high efficiency. Therefore, the development of sensitive, rapid, inexpensive, and reliable method is necessary for the determination of MG in the aquatic environment. Several analytical methods for the determination of MG have been reported. Liquid chromatography (LC) with visible absorbance (LC-VIS) [15] or LC–mass spectrometry (LC–MS) detection [16], high-performance LC [17,18], spectrophotometric methods after solid-phase extraction (SPE) [19–21], GC–MS [22], and capillary electrophoresis (CE) [23] are among these methods. Although these methods are sensitive and selective, but majority of them require sophisticated and expensive instruments like LC–MS and professional operators. Laborious sample preparation procedure and the manipulation of highly toxic solvents are other problems of these methods.

A growing public concern over protecting our environment obligate chemists, including analytical chemists to change their activities in such a way, that they will be conducted in an environmentally friendly manner. The irony is that the analytical methods used to assess the state of environmental pollution may in fact be the source of significant pollution. A greater concern over the usually toxic solvents discarded and their impact on the environment has led to the development of cleaner extraction methods [24,25].

SPE has been demonstrated to be an effective preconcentration method and environment friendship. This method in comparison with liquid–liquid extraction methods is simpler, faster and reduced organic solvent consumption [26]. Various adsorbents for solid-phase extraction of MG have been used such as diatomite [27], strong cation-exchange solid-phase column [28], polyurethane foam [12], alumina [19], rotating disk sorbent [29], etc. Nowadays, nanometer-sized materials have gained more attention due to their special properties.

One of the most interesting properties is that most atoms are on the surface of the nanoparticles. The unsaturated surface atoms can bind other atoms possessing strong chemical activities that produce a high adsorption capacity. γ-Al_2O_3 nanoparticle is a promising material as a solid-phase adsorbent because of its large specific surface area, high adsorption capacity, mechanical strength, high chemical activity, enhanced sorption kinetics, and low-temperature modification [30–32]. Electrostatic attractive interactions between the head group of ionic surfactants and oppositely charged groups on the nanoalumina result in the formation of mixed hemimicelles assemblies. Besides, a ligand can be effectively adsorbed on the formed hemi and ad-micelles on the nano-alumina surface, through the hydrophobic interactions between hydrocarbon tail-groups of surfactant and hydrocarbon groups of ligand, which give a number of advantages, such as high selectivity, high breakthrough volumes, easy elution of analytes and high flow rate for sample loading.

Because of very low concentration of MG in fish-farming water, we need a high preconcentration factor prior to spectrophotometric determination. In this work, sodium dodecyl sulfate (SDS)-modified γ-alumina nanoparticle was employed for the separation and preconcentration of MG in fish farming water followed by its determination with fiber optic-linear array detection spectrophotometry (FO-LADS).

2. Experimental

2.1. Apparatus

The UV–vis light source, optical fiber and spectrograph model 2048 were prepared from Avantes (Eerbeek, the Netherland) for FO-LADS with charge-coupled device (CCD) detector. Microcell was from Starna Scientific (Essex, England, Cat. No.

16.40F-Q-10/Z15). The pH-meter model 692 from Metrohm (Herisau, Switzerland) with combined glass electrode and a universal pH indicator (pH 0–14) from Merck (Darmstadt, Germany) were used for the pH measurements. Separation was assisted using a refrigerated centrifuge (Hettich, Universal 320 R) equipped with an angle rotor (6-place, 9,000 rpm, Cat. No. 1620A). Field emission scanning electron microscope (FESEM, Hitachi, S-4160, and Japan) was used for the preparation of SEM images. The size, morphology and structure of the nanoparticles were characterized by transmission electronic microscopy (TEM, Philips, CM10, 100 kV).

2.2. Standard solutions and reagents

All reagents were analytical grade and used without further purification. A stock solution of 1,000 mg L^{-1} of MG (Merck) was prepared by dissolving 0.1 g of the reagent in water and diluting to 100 mL in a volumetric flask. The desired concentrations were obtained by successive dilutions. nano-γ-alumina (purity:> 99% Nano Amor, Los Alamos, NM, USA) was activated by shaking with 5 mol L^{-1} nitric acid and washed three times with distilled water. SDS (Schuchardt, Germany) was prepared by dissolving certain amounts with double-distilled water in 100-mL volumetric flask and stored at 4°C. Also, ethanol, acetic acid, acetonitrile, hydrochloric acid, and sodium hydroxide were all purchased from Merck (Darmstadt, Germany).

2.3. Preparation of modified nano-γ-alumina

About 1.5 g of γ-alumina nanoparticles was added to 50 mL of 5 mol L^{-1} HNO_3 in a beaker and stirred for 3 min on the stirrer. Then, nanoparticles were washed three times with double-distilled water and suspended in 50 mL of water and were mixed with 100 mg of SDS in a flask. The pH of solution was adjusted to 2–2.5 with 0.1 mol L^{-1} HCl solutions, and then, the flask was stirred mechanically for 15 min. Then, nanoparticles were separated from solution and were stored for next experiments.

2.4. Preconcentration procedure

Eighty milligrams of modified γ-alumina nanoparticles was added to a known volume of sample solution containing MG in the range of 1.2–250 ng mL^{-1} in a screw-capped polypropylene tube, and pH value was adjusted to about 3.0 with 0.1 mol L^{-1} HCl and 0.1 mol L^{-1} NaOH, and the solutions were stirred for about 3 min for dispersion of nanoparticles thorough the solution. After adsorbing the MG on the surface of nanoparticles, the solid phase was separated by centrifuging for 5 min at 4,000 rpm. Adsorbed MG was then eluted with 1.0 mL of 4 mol L^{-1} acetic acid and concentration of MG in solution was determined by FO-LADS at $\lambda_{max} = 630$ nm.

3. Result and discussion

3.1. The effect of SDS concentration and mechanism of the adsorption

Preliminary experiments showed that alumina nanoparticles have a low tendency for the retention of MG adsorption (less than 10%). According to these results, there is dependence of the use of SDS on the kinetics of the sorption, indicating lower affinity between the dye and nanoalumina, compared with modified nanoalumina. The modified nanoparticles have a greater affinity for the adsorption of MG with higher recovery values. Therefore, the effect of the SDS concentration was studied in the range 0–600 mg. It was found that with the increasing SDS concentration, the MG adsorption amount increased remarkably. The increase in adsorption can be explained by the gradual formation of mixed hemimicelles on the nanoalumina surface, and then, the adsorbed MG amount increased gradually. As shown in Fig. 2, it is evident that by increasing the amount of surfactant in the range of 100–300 mg, the efficiency of removal of dye was nearly constant. But at higher amount, clearly the equilibrium sorption decreased as the SDS amount increased. Quantitative recovery (>95%) was obtained when SDS added was in the range of 100–300 mg. Therefore, 100 mg of SDS was accepted as the optimum amount to

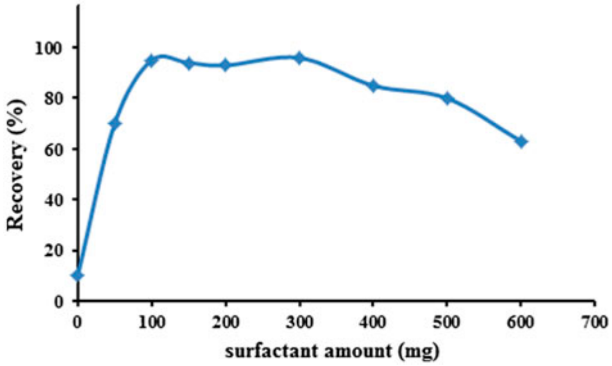

Fig. 2. Effect of amount of surfactant on efficiency of removal of dye. Conditions: 80 mg of modified γ-alumina nanoparticles, MG: 100 ng mL^{-1} of dye, agitation time of 3 min, temperature: 25°C.

desorb the dye. The surfaces of metal oxides (γ-Al_2O_3 suspension) are generally covered with hydroxyl groups that vary in forms at different pH values. Below the pH of zero point charge (pH_{zpc}) that is around 8.5 for γ-alumina nanoparticles [33], the adsorbent surface is positively charged and hydrophilic. Therefore, adsorption of MG onto the adsorbent does not take place. Anionic surfactants like SDS will adsorb onto the surface of γ-alumina nanoparticles through the negative moiety sulfate and makes the surface of adsorbent hydrophilic. The dye could be trapped into the aggregates of SDS on adsorbent [34] and separated from the bulk of the solutions.

3.2. Characterization of the adsorbent

In Fig. 3(a) and (b), the FESEM images show the difference between size of alumina nanoparticles before and after modification by SDS. It is possible to see the naked alumina nanoparticles have smaller mean diameter in comparison with modified nanoparticles, so this significant enlargement reveals that SDS has been adsorbed multilayer. It can be found from these images that the alumina nanoparticles have been completely coated by SDS.

The particle size and morphology of nano-γ-alumina and modified nano-γ-alumina were evaluated from TEM micrographs. From Fig. 4(a), it was clear that the naked nano-γ-alumina particles were essentially fine and had a mean diameter of about 30 nm. After coating with SDS (Fig. 4(b)), the mean diameter of particles increased to about 40 nm. This revealed that the coating process did not significantly result in the agglomeration and the change in size of the particles. This revealed that the coating process did not significantly result in the agglomeration and the change in size of the particles. Although some agglomerations of the nanoparticles, which causes irregularity of the shape and size of the nanoparticles, can also be observed from Fig. 4(a), it was found that these agglomerations had not obvious effect on adsorbing applications of the nanoparticles. It was clear that modified nanoparticles had a mean diameter of 40 nm since the agglomeration is not serious.

3.3. Effect of pH

Solution pH is an important parameter that affects adsorption of dye molecules onto alumina nanoparticles. To study the effect of pH on the removal of MG, the pH adjusted 50 mL of sample solution containing 100 ng mL^{-1} MG in the range 2.0–8.0, using 0.1 mol L^{-1} HCl or NaOH solutions. The amount of MG adsorbed (mg g^{-1}) was calculated using Eq. (1):

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where q_e is the amount of MG adsorbed per unit mass of adsorbent (mg g^{-1}) at equilibrium concentration, V is the volume of experimental solution in L, m is the dry weight of nanoparticles in g, C_0 and C_e are the initial and equilibrium concentrations (mg L^{-1}) of MG in the solution, respectively. As shown in Fig. 5, it is evident that the amount of MG adsorbed (mg g^{-1}) increased by increasing pH and reached maximum at pH 3.0 and slowly decreased at higher pH values. The pK_a value for MG is 6.9, and in aqueous solutions, it can occur in two cationic and colorless carbinol forms. The balance between these two forms depends on the pH of the solution [35]. When the pH was adjusted below 3, there was a decrease in the adsorption of the dye by the nanoalumina. At higher pH values, there

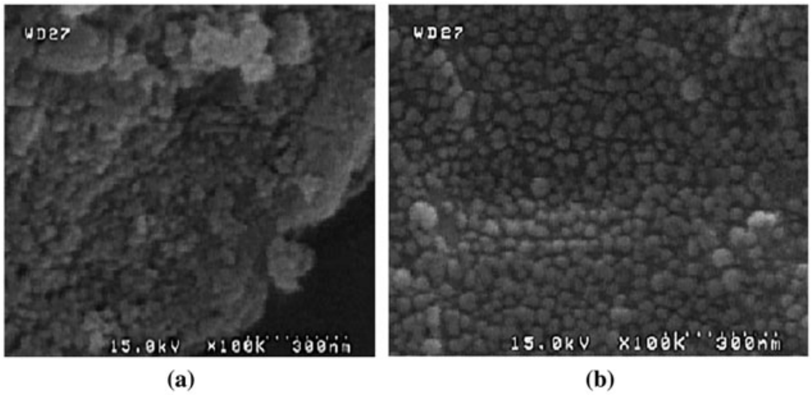

Fig. 3. The FESEM image of naked γ-alumina nanoparticles (a) and SDS modified γ-alumina nanoparticles (b).

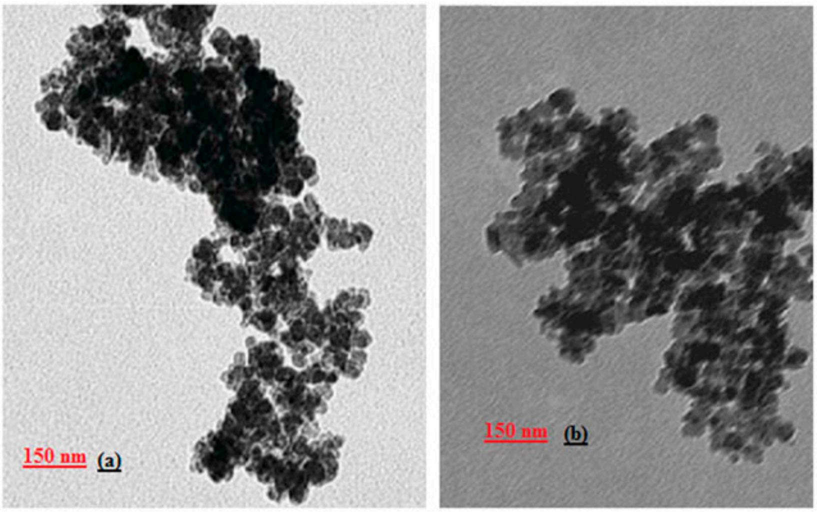

Fig. 4. TEM images of image of naked γ-alumina nanoparticles (a) and SDS modified γ-alumina nanoparticles (b).

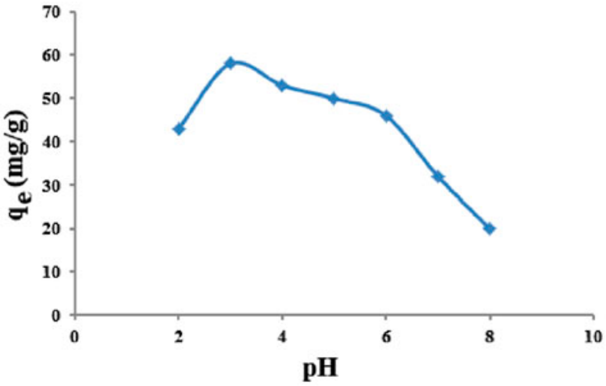

Fig. 5. Effect of pH on MG adsorbed (mg g^{-1}). Conditions: 80 mg of modified γ-alumina nanoparticles, MG: 100 ng mL^{-1} of dye, agitation time of 3 min, temperature: 25°C.

was almost complete bleaching of dye solution, so MG takes its hydroxyl form called carbinol. Therefore, pH 3.0 was selected for next experiments.

3.4. Choice of type and concentration of eluent

Some experiments were carried out in order to choose a proper eluent for the adsorbed MG by modified nano-γ-alumina. The MG was desorbed with 1 mL of different solvents such as acetonitrile, ethanol and different concentrations of HCl, HNO_3 and acetic acid. The results showed that 4 mol L^{-1} acetic acid is most efficient eluent for this aim.

3.5. Effect of sample volume and temperature on dye adsorption

Sample volume is one of the important parameters for obtaining high preconcentration factor. For this purpose, the effect of sample volume on the adsorption of MG on modified nano-γ-alumina was investigated in the range of 25–250 mL while keeping the total amount of loaded MG fixed at 2.0 μg. As shown in Fig. 6, it is evident that the recovery of MG is quantitative (>95%) up to 100 mL sample volume. Hence, 100 mL was chosen as the largest sample volume to work. By applying of 100 mL sample volume under optimum conditions and desorbing of MG with 1 mL of acetic acid, the preconcentration factor of 100 was obtained. Effect of temperature on the adsorption of MG at equilibrium was investigated at three different temperatures, viz, 10, 25 and 35°C at the initial MG concentration of 100 ng mL^{-1}, pH 3.0 and the adsorbent dose of 0.80 g L^{-1} (Fig. 7). The adsorption of MG was noted to enhance with the increase in temperature indicating that higher temperature favored the removal of dye by sorption onto modified nano-γ-alumina.

3.6. Interference studies

Before the application of proposed method on real samples, it was necessary to investigate the effect of some of the interfering ions on the adsorption of MG on γ-alumina nanoparticles. The tolerance limit was defined as the amount of the foreign ion causing a change of ±5% in the absorbance reading. Solutions containing 100 ng mL^{-1} of MG and different amounts

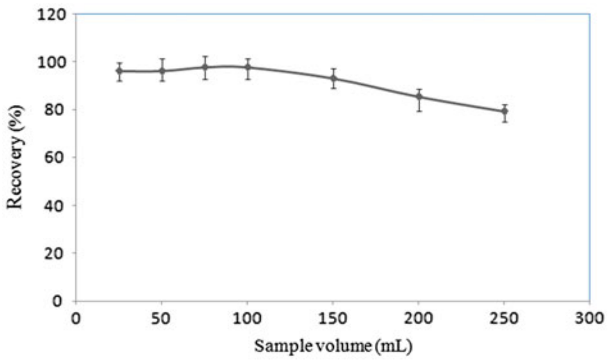

Fig. 6. Effect of sample volume on MG adsorption recovery. Conditions: 80 mg of modified γ-alumina nanoparticles, MG: 100 ng mL^{-1} of dye, agitation time of 3 min, temperature: 25 °C.

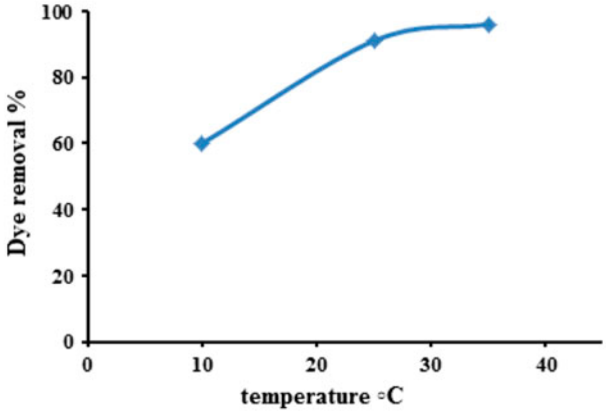

Fig. 7. Effect of temperature on the dy removal of MG. Conditions: 80 mg of modified γ-alumina nanoparticles, MG: 100 ng mL^{-1} of dye, agitation time of 3 min.

of foreign ions were prepared, and the general procedure was performed. The Pb^{2+} is tolerable up to 700-times higher amounts than that of MG; Co^{2+}, Zn^{2+}, Cu^{2+}, and Ca^{2+} more than 800-times, Na^{+}, Ba^{2+}, Hg^{2+}, Ni^{2+} and SCN^{-} 700-times, SO_{4-2} and S_2O_{3-2} 500 times. The obtained results indicate that this method is useful for determining MG in real water samples.

3.7. Absorption isotherms

The relationship between the amount of analyte adsorbed per unit mass of adsorbent and its concentration in the equilibrium solution at constant temperature is called the adsorption isotherm [36]. The milligram of MG absorbed per gram of sorbent, q_e, versus equilibrium concentration as adsorption isotherm is plotted. As seen in Fig. 8, the sorption of MG increases with increase in its initial concentration and reaches to a constant and maximum value.

Analysis of isotherm data is important for the design of an adsorption system. Two models described by Freundlich [37] and Langmuir were used to analyze the equilibrium adsorption data [38].

The widely used empirical Freundlich equation, based on sorption on a heterogeneous surface, is given using Eq. (2):

$$q_e = K_F C_e^{1/n} \tag{2}$$

This equation can be expressed in a linear form using Eq. (3):

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{3}$$

where q_e is the amount of MG adsorbed per unit mass of adsorbent (mg g^{-1}) at equilibrium concentration, C_e is the equilibrium concentration of MG, K_F and n are Freundlich constants indicating adsorption capacity and intensity, respectively, which can be calculated from linear plot of ln q_e against ln C_e (Fig. 9).

The Langmuir isotherm is valid for monolayer sorption onto a surface containing a finite number of homogeneous sites. It can be represented using Eq. (4):

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{q_{\max} K_{ads}} \tag{4}$$

where $q_{\max}$ is the maximum amount of MG adsorbed per unit weight of adsorbent (mg g^{-1}), C_e is the equilibrium concentration of MG, q_e is the amount of MG adsorbed per unit weight of adsorbent at equilibrium

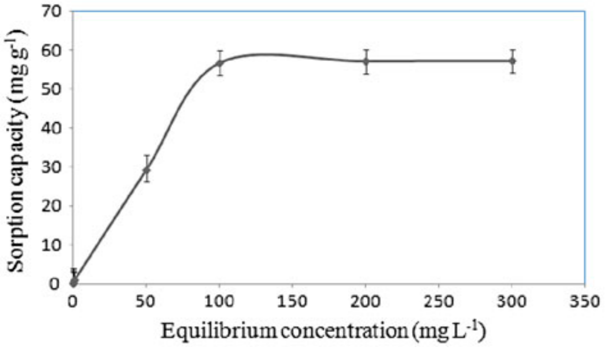

Fig. 8. Adsorption isotherm of MG from aqueous solution on the surface of sorbent.

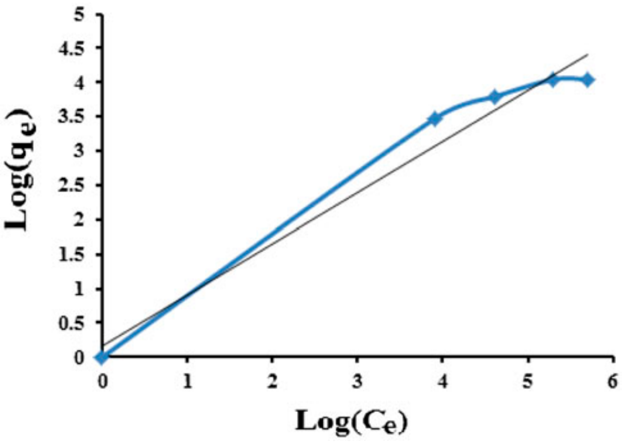

Fig. 9. Freundlich adsorption isotherm for MG (100 ng mL^{-1}, pH 3.0), γ-alumina nanoparticles (of 0.80 g L^{-1}). System at 25℃ temperatures.

concentration (mg g^{-1}), and K_{ads} is the Langmuir constant related to the affinity of binding sites (L mg^{-1}). A linearized plot of C_e/q_e against C_e gives q_{max} and K_{ads} (Fig. 10).

The Langmuir and Freundlich isotherms obtained at temperatures of 25℃ are found linear in both the cases. It was found (Table 1) that the value of correlation coefficient for the fit of experimental isotherm data to Langmuir equation is more close to 1.0 than that for Freundlich equation. Therefore, the Langmuir model agrees with the adsorption of MG onto modified nanoalumina in our adsorption experiment. The maximum sorption capacity (q_{max}) and binding constant (K_{ads}) were calculated 72.4 mg g^{-1} and 0.0145 L mg^{-1}, respectively. The favorability of the dye adsorption process onto modified nano-γ-alumina was evaluated using a dimensionless parameter (R_L) derived from the Langmuir expression. It is defined as follows:

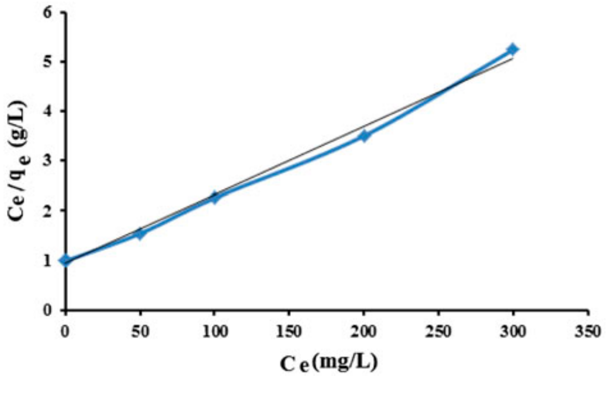

Fig. 10. Langmuir adsorption isotherm for MG (100 ng mL^{-1}, pH 3.0), γ-alumina nanoparticles (of 0.80 g L^{-1}). System at 25℃ temperature.

Table 1
Parameters of Langmuir and Freundlich isotherm equations, regression coefficients (r) for the adsorption of MG on modified nanoalumina at 25℃ and at pH 3

Langmuir		
K_{ads} (L mg^{-1})	$q_{\max}$ (mg g^{-1})	r
0.0145	72.4	0.9948
Freundlich		
K_F (mg$^{1-1/n}$ L$^{1/n}$ g^{-1})	$1/n$	r
1.17	0.8485	0.9697

$$R_L = \frac{1}{(1 + bC_0)} \tag{5}$$

where b is the Langmuir constant and C_0 is the initial concentration. The adsorption process can be defined as irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$) in terms of R_L. The calculated values of R_L for the adsorption of 100 mg L^{-1} of MG are 0.408 that this fall between 0 and 1, and thus, the adsorption of the dyes onto modified nano-γ-alumina is favorable.

On the other hand, thermodynamic parameters change in free energy (ΔG°), change in enthalpy (ΔH°), and change in entropy (ΔS°) were calculated using following equations:

$$\Delta G^\circ = -RT \ln b \tag{6}$$

$$\Delta H^\circ = -R \times \frac{T_2 T_1}{T_2 - T_1} \ln \frac{K_2}{K_1} \tag{7}$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \tag{8}$$

where K_1 and K_2 are the equilibrium constants at 25℃ and 35℃, respectively. The evaluated thermodynamic parameters are presented in Table 2 The negative values of free energy (ΔG°) indicate the feasibility and spontaneous nature of the ongoing process. The value of change in enthalpy (ΔH°) is found to be positive confirms the endothermic nature of the process. The positive value of change in entropy (ΔS°) is evident for increased randomness in the adsorption process and reveals good affinity towards the dye molecule [3].

3.8. Effect of contact time

The contact time between adsorbate and adsorbent is one of the most important design parameter that affects the performance of adsorption processes. The

Table 2
Calculated thermodynamic parameters for the adsorption of MG (pH 3.0) over modified nanoalumina (0.8 mg/L)

$-\Delta G^\circ$ (kJ mol^{-1})		ΔH° (kJ mol$^{-1)}$)	ΔS° (Jk^{-1} mol^{-1})
25℃	35℃		
21.56	24.67	105.78	282.61

effect of contact time on the performance of modified nano-γ-alumina in adsorbing the dyes was also investigated. The solution pH, adsorbent dosage and SDS amount were fixed at their obtained optimum values. The initial dye concentrations for all test solutions were 100 ng mL^{-1}. The results showed that the shaking time from 3 to 20 min has no effect on the extraction recovery of MG. The results indicated that the adsorption of dye started immediately upon adding the modified nano-γ-alumina to dye solution. After 3 min, modified nano-γ-alumina removed the dyes from the solutions quantitatively. Therefore, the optimum contact time for the adsorption of the test dyes was considered as 3 min. The removal of the dyes was very fast. Such the fast adsorption rates could be referred to the absence of internal diffusion resistance.

According to the Brykina method [39], the sorption rate constant k can be calculated from following equation:

$$-\ln(1-F) = kt + B \tag{9}$$

where $F = q_t/q_e$ and q_t and q_e are, respectively, the sorption amounts at time t and at equilibrium. The sorption rate constant can be calculated from the slope of the straight line plot of −ln $(1-F)$ vs. t. The calculated sorption rate constants (k) were found to be 6.21×10^{-2} s^{-1}. It is expected that external mass transfer resistance in the aqueous phase will be negligible, which is reasonable in well-shaken adsorption systems. Furthermore, it was concluded such an extraordinary fast rate of initial color removal may also manifest a fast chemical ion surface attachment.

3.9. Effect of the amount of modified nano-γ-alumina

To choose the optimum amount of adsorbent (nano-γ-alumina) required for quantitative recoveries for MG, different values of γ-alumina nanoparticles were used in the range of 10.0–200.0 mg. The maximum recovery percentage (>95%) was obtained at 80.0 mg of nanoparticles. The amount of extracted MG increased by increasing amount of modified nanoparticles due to the greater availability of the surface area at high amounts of the sorbent. About 80.0 mg of the recovery percentage remained nearly constant up to 160.0 mg and then started to decrease. When the amount of eluent is constant, and amount of sorbent is increasing after certain amount of sorbent, eluent is not adequate for desorbing the MG entirely.

3.10. Figures of merit

Under the optimum experimental conditions, quantitative parameters such as linear range, correlation coefficient, detection limit, quantification limits and preconcentration factor were evaluated. Excellent linearity was observed over the concentration 1.2–250 ng mL^{-1} with favorable coefficient of correlation (r^2) 0.9977. Relative standard deviation (RSD) for five replicate measurements of 100 ng mL^{-1} MG was 1.50%. The limit of detection defined as $\mathrm{LOD} = 3S_b/m$, (where LOD, S_b and m are the limit of detection, standard deviation of the blank and the slope of the calibration graph), respectively, was found to be 0.34 ng mL^{-1}. As the amount of MG in 100 mL of the solution was concentrated to 1.0 mL, a preconcentration factor (PF) of 100 was achieved in this method. The results are shown in Table 3.

3.11. Application to environmental water samples

The proposed method was applied to the remove and preconcentration of MG in two fish-farming water samples collected from different fish-farming ponds. The samples were filtered before analysis through a 0.45-μm membrane filter and stored in polyethylene container for subsequent usage. The results of the real sample analysis are summarized in Table 4 All the real water samples were spiked with the MG standard solutions at different concentration levels to assess the matrix effects. As can be seen, the method was validated after spiking different amounts of MG to the samples, and the relative recoveries of MG from mentioned water samples at various spiking levels were between 95 and 104%. The obtained relative recoveries indicates that matrix does not influence the microextraction efficiency in the mentioned samples (no serious interferences); therefore, there was not any obligation to remove interferences.

3.12. Comparison of analytical performance data with literatures

A comparison of the represented method with other SPE methods with different adsorbents reported in the literature was given in Table 5. As can be seen from the Table 5, high preconcentration factor, low detection limit, low amount of sorbent and good RSD values are some of the advantages of the proposed method.

Table 3
Analytical characteristics of proposed method at the optimum conditions

Analyte	LOD (ng mL^{-1})	LOQ (ng mL^{-1})	R^2	Linear range (ng mL^{-1})	Regression equation	RSD (%$n = 5$)[a]	PF[b]
Malachite green	0.34	1.2	0.9977	1.2–250	$A = 0.0036C + 0.0242$	1.50	100

[a]Value in parenthesis is malachite green concentration (100 ng mL^{-1}) for which the RSD was obtained.
[b]Ratio of the initial volume to the final volume.

Table 4
Determination of MG in Fish-farming water samples

Sample	MG added (ng mL^{-1})	MG found (ng mL^{-1})	RSD[a] (%)	Recovery[b] (%)
Fish-farming water 1	0.0	15.4	1.7	–
	10.0	24.9	1.6	95
	20.0	35.8	1.8	102
Fish-farming water 2	0.0	10.7	2.3	–
	10.0	21.1	2.1	104
	20.0	30.6	2.0	99.5

[a]Relative standard deviation ($n = 3$).
[b]Collected from trout fish-farming pools, Arak, Iran.

Table 5
Comparison of the preconcentration methods for MG with the proposed method

Method	Technique	EF[a]	Volum sample (mL)	LOD (ng mL^{-1})	RSD (%)	Linearly range (ng mL^{-1})	Sorbent (mg)	Ref
Modified maghemite nanoparticle	HPLC-UV	50	100	0.28	1.60	0.5–250	100	[35]
Diatomite	Spectrophotometer	80–92	1,000	67	<3	210–8,000	300	[27]
Teflon	Spectrophotometer	–	100	1.4	8.1	5–50	–	[29]
Poly urethane foam	Spectrophotometer	–	200	2.2	8.5	50–250	200	[12]
Alumina	Spectrophotometer	250	250	3.2	<4	5–500	500	[19]
Modified nanoalumina	FO-LADS	100	100	0.34	1.50	1.2–250	80	This work

[a]Enrichment factor

Modifying nano-sized alumina is very simple and takes a short time. Therefore, alumina nanoparticles are a good choice for the separation and preconcentration of dyes in environmental samples due to its low cost when compared to commercially available sorbents.

4. Conclusions

This work proved that the γ-alumina nanoparticles modified with SDS can act as a convenient solid phase for the sorption and remove of MG. It was found that modification of alumina nanoparticles prevents agglomeration of these particles. This modified sorbent is stable and can be stored for long time without decrease in its analytical performance. Isotherm modeling revealed that the Langmuir equation could better describe the adsorption of the dyes onto the modified nano-γ-alumina as compared to Freundlich model. Because of the high specific surface area and nanoscale particle size, modified nano-γ-alumina indicated favorable adsorption behavior for MG. The proposed method is simple, fast and accurate for the spectrophotometric determination of trace amount of MG in water samples. The presented SPE method has some advantages in comparison with other methods such as high preconcentration factor and high tolerance to interferences from the matrix ions. Very high surface area and good dispersion of γ-alumina nanoparticles make method more efficient for thorough adsorbing of MG from the solution. The proposed method can be applied to the determination of MG in various fish farming waters samples.

References

[1] E. Forgacs, T. Cserháti, G. Oros, Removal of synthetic dyes from wastewaters: A review, Environ. Int. 30(7) (2004) 953–971.

[2] A. Mittal, V.K. Gupta, A. Malviya, J. Mittal, Process development for the batch and bulk removal and recovery of a hazardous, water-soluble azo dye (Metanil Yellow) by adsorption over waste materials (Bottom Ash and De-Oiled Soya), J. Hazard. Mater. 151(2–3) (2008) 821–832.

[3] A. Mittal, V. Thakur, J. Mittal, H. Vardhan, Process development for the removal of hazardous anionic azo dye Congo red from wastewater by using hen feather as potential adsorbent, Desal. Wat. Treat. 52 (2014) 227–237.

[4] A. Mittal, Removal of the dye, amaranth from waste water using hen feathers as potential adsorbent, Electro. J. Environ. Agric. Food Chem. 5(2) (2006) 1296–1305.

[5] A. Mittal, J. Mittal, L. Kurup, Utilization of hen feathers for the adsorption of a hazardous dye, indigo carmine from its simulated effluent, J. Environ. Protect. Sci. 1 (2007) 92–100.

[6] A. Mittal, D. Jhare, J. Mittal, V.K. Gupta, Batch and bulk removal of hazardous colouring agent rose bengal by adsorption over bottom ash, RSC Advances 2(22) (2012) 8381–8389.

[7] A. Mittal, R. Jain, Jyoti Mittal, S. Varshney, Shalini Sikarwar, Removal of yellow ME 7 GL from industrial effluent using electrochemical and adsorption techniques, Int. J. Environ. Pollut. 43(4) (2010) 308–323.

[8] A. Mittal, R. Jain, J. Mittal, M. Shrivastava, Adsorptive removal of hazardous dye quinoline yellow from waste water using coconut-husk as potential adsorbent, Fres. Environ. Bull. 19(6) (2010) 1–9.

[9] A. Mittal, D. Jhare, J. Mittal, Adsorption of hazardous dye Eosin Yellow from aqueous solution onto waste material De-oiled Soya: Isotherm, kinetics and bulk removal, J. Mol. Liq. 179 (2013) 133–140.

[10] H. Daraei, A. Mittal, M. Noorisepehr, J. Mittal, Separation of chromium from water samples using eggshell powder as a low-cost sorbent: Kinetic and thermodynamic studies, Desal. Wat. Treat. (2013). doi:10.1080/19443994.2013.837011.

[11] H. Daraei, A. Mittal, J. Mittal, H. Kamali, Optimization of Cr(VI) removal onto biosorbent eggshell membrane: Experimental & theoretical approaches, Desal. Wat. Treat. (2013). doi:10.1080/19443994.2013.787374.

[12] N.F. Robaina, L.G.T.D. Reis, R.J. Cassella, Diffuse reflectance determination of malachite green using polyurethane foam as solid support and sodium dodecylsulfate as counter ion, Talanta 85 (2011) 749–753.

[13] K.C. Lee, Determination of malachite green and leucomalachite green in edible goldfish muscle by liquid chromatography–ion trap mass spectrometry, J. Chromatogr. B 843 (2006) 247–251.

[14] A.A.M. Stolker, T. Zuidema, M.W.F. Nielen, Residue analysis of veterinary drugs and growth-promoting agents, Trends Anal. Chem. 26 (2007) 967–979.

[15] C.-J. Cha, D.R. Doerge, C.E. Cerniglia, Biotransformation of malachite green by the fungus cunninghamella elegans, Appl. Environ. Microbiol. 67 (2001) 4358–4360.

[16] A.B. Aldert, P. Scherpenisse, Determination of residues of malachite greenin aquatic animals, J. Chromatogr. B 788 (2003) 351–359.

[17] D. Arroyo, M.C. Ortiz, L.A. Sarabia, F. Palacios, Advantages of PARAFAC calibration in the determination of malachite green and its metabolite in fish by liquid chromatography–tandem mass spectrometry, J. Chromatogr. A 1187 (2008) 1–10.

[18] C. Long, Z. Mai, Y. Yang, B. Zhu, X. Xu, L. Lu, X. Zou, Determination of multi-residue for malachite green, gentian violet and their metabolites in aquatic products by high-performance liquid chromatography coupled with molecularly imprinted solid-phase extraction, J. Chromatogr. A 1216 (2009) 2275–2281.

[19] K. Farhadi, R. Maleki, N.M. Nezhad, N. Samadi, Spectrophotometric determination of malachite green residue in water samples after preconcentration on surfactant-coated alumina, Spectrosc. Lett. 43 (2010) 101–107.

[20] N. Pourreza, S. Elhami, Spectrophtometric determination of malachite green in fish farming water samples after cloud point extraction using nonionic surfactant Triton X-100, Anal. Chim. Acta 596 (2007) 62–65.

[21] L. An, J. Deng, L. Zhou, H. Li, F. Chen, H. Wang, Y. Liu, Simultaneous spectrophotometric determination of trace amount of malachite green and crystal violet in water after cloud point extraction using partial least squares regression, J. Hazard. Mater. 175 (2010) 883–888.

[22] S.B. Turnipseed, J.E. Roybal, J.A. Hurlbut, A.R. Long, Gas chromatographic/mass spectrometric confirmation of leucomalachite greenin catfish (Ictalurus punctatus) tissue, J. AOAC. Int. 78 (1995) 971–977.

[23] C.H. Tsai, J.D. Lin, C.H. Lin, Optimization of the separation of malachite green in water by capillary electrophoresis Raman spectroscopy (CE-RS) based on the stacking and sweeping modes, Talanta 72 (2007) 368–372.

[24] J. Namieśnik, W. Wardencki, Solventless sample preparation techniques in environmental analysis, J. High Resol. Chromatogr. 23 (2000) 297–303.

[25] W. Wardencki, J. Curyło, J. Namieśnik, Trends in solventless sample preparation techniques for environmental analysis, J. Biochem. Bioph. Methods 70 (2007) 275–288.

[26] M.M. Hassanien, Kh.S. Abou-El-Sherbini, Selective separation of palladium (II) from precious metal ions using thiosemicarbazone derivatives from acidic media by solid phase and solvent extractions, Desal. Wat. Treat. 16 (2010) 329–338.

[27] Y.S. Al-Degs and J.A. Sweileh, Simultaneous determination of five commercial cationic dyes in stream waters using diatomite solid-phase extractant and multivariate calibration, Arabian J. Chim. 5 (2012) 219–224.

[28] G. Stubbings, J. Tarbin, A. Cooper, M. Sharman, T. Bigwood, P. Robb, A multi-residue cation-exchange clean up procedure for basic drugs in produce of animal origin, Anal. Chim. Acta 547 (2005) 262–268.

[29] P. Richter, A. Cañas, C. Muñoz, C. Leiva, I. Ahumada, Rotating disk sorbent extraction for pre-concentration of chromogenic organic compounds and direct determination by solid phase spectrophotometry, Anal. Chim. Acta 695 (2011) 73–76.

[30] A.R. Turker, New sorbents for solid-phase extraction for metal enrichment, Clean 35 (2007) 548–557.

[31] L. Zhang, T. Huang, M. Zhang, X. Guo, Z. Yuan, Studies on the capability and behavior of adsorption of thallium on nano-Al_2O_3, J. Hazard. Mater. 157 (2008) 352–357.

[32] J. Li, Y. Shi, Y. Cai, S. Mou, G. Jiang, Adsorption of di-ethyl-phthalate from aqueous solutions with surfactant-coated nano/microsized alumina, Chem. Eng. J. 140 (2008) 214–220.

[33] A. Afkhami, M. Saber-Tehrani, H. Bagheri, Simultaneous removal of heavy-metal ions in wastewater samples using nano-alumina modified with 2,4-dinitrophenylhydrazine, J. Hazard. Mater. 181 (2010) 836–844.

[34] P. Janoš, V. Šmídová, Effects of surfactants on the adsorptive removal of basic dyes from water using an organomineral sorbent—iron humate, J. Colloid. Interface. Sci. 291 (2005) 19–27.

[35] A. Afkhami, R. Moosavi, T. Madrakian, Preconcentration and spectrophotometric determination of low concentrations of malachite green and leuco-malachite green in water samples by high performance solid phase extraction using maghemite nanoparticles, Talanta 82 (2010) 785–789.

[36] M. Ezoddin, T. Taghizadeh, Kh. Abdi, M. Jamali, Application of modified nano γ-alumina as a solid-phase extraction sorbent combined with high-performance liquid chromatography for determination of phthalate esters in environmental water and soft drink samples, Desal. Wat. Treat (2013). doi:10.1080/19443994.2013.852138.

[37] H. Freundlich, W. Heller, The adsorption of cis- and trans-azobenzene, J. Am. Chem. Soc. 61 (1939) 2228–2230.

[38] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403.

[39] G.D. Brykina, T.V. Marchak, L.S. Krysina, Sorption-photometric determination of copper by using AV-17 anion exchanger modified with 1-(2-thiazolyl-azo)-2-naphthol-3, 6-disulphonic acid, Zh. Anal. Khim. 35 (1980) 2294–2299.