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

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ABSTRACT

A novel and sensitive extraction procedure using maghemite nanoparticles (γ-Fe$_2$O$_3$) modified with sodium dodecyl sulfate (SDS), as an efficient solid phase, was developed for removal, preconcentration and spectrophotometric determination of trace amounts of malachite green (MG) and leuco-malachite green (LMG). Combination of nanoparticle adsorption and easily magnetic separation was used to extraction and desorption of MG and LMG. The adsorption capacity was evaluated using both the Langmuir and Freundlich adsorption isotherm models. Maghemite nanoparticles were prepared by co-precipitation method and their surfaces were modified by SDS. The size and properties of the produced maghemite nanoparticles was determined by X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM) and BET analysis. MG and LMG became adsorbed at pH 3.0. LMG was oxidized to MG by adsorption on maghemite nanoparticles. The adsorbed MG was then desorbed and determined spectrophotometrically. The calibration graph was linear in the range 0.50–250.00 ng mL^{-1} of MG and LMG with a correlation coefficient of 0.9991. The detection limit of the method for determination of MG was 0.28 ng mL^{-1} and the relative standard deviation (R.S.D.) for 10.00 and 50.00 ng mL^{-1} of malachite green was 1.60% ($n = 3$) and 0.86% ($n = 5$), respectively. A preconcentration factor of 50 was achieved in this method. The Langmuir adsorption capacity (q_{max}) was found to be 227.3 mg g^{-1} of the adsorbent. The method was applied to the determination of MG in fish farming water samples.

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1. Introduction

Malachite green (MG) has close structural similarity to carcinogenic triphenylmethane dyes that can undergo chemical and metabolic reduction to a leuco derivative inside the cell which have a much longer tissue half-life [1]. Although MG has an extremely effective application as an antifungal, antimicrobial and anti-parasitic agent since 1930s in food industry or as a therapeutic agent in aquaculture [2–5], the chemical causes serious side effects. MG and leuco-malachite green (LMG) have toxic effects to human cells and mutagenic and carcinogenic properties as well, like causing liver tumor formation, hepatic and renal tumors formation in rodents [6,7] and reproductive abnormalities in rabbits and fishes. Therefore its use has been banned in many countries [8]. But, due to its ease and low cost to manufacture, high efficiency against fungus, bacteria and parasite, it is still used in certain countries with less restrictive laws for non-aquaculture purposes [9,10]. The European minimum required performance limit, a qual-

ity parameter for residue laboratories, is set as the sum of MG and LMG at 2.00 μg kg^{-1} [2,11–13]. Therefore MG is not authorized by the European Union and the US Food and Drug Administration (FDA) [6]. Consequently, it is of great importance that any related enforcement is being focused on the determination of the lowest concentrations for both of MG and LMG [14].

Until now, different methods have been reported for the determination of MG and LMG such as high performance liquid chromatography [5,14–20], spectrophotometry [21,22], capillary electrophoresis [23] and electrochemical determinations [9,24]. Also different adsorbents have been reported for removal of these materials.

In the past decade, the synthesis of spinel magnetite and maghemite nanoparticles has been intensively developed not only for its great fundamental scientific interest but also for many technological applications in biology, such as extraction of genomic DNA [25], contrast agents in magnetic resonance imaging (MRI) [26,27], medical applications (such as targeted drug delivery) [28–30], bioseparation [31]; and separation and preconcentration of various anions and cations [32–35], due to their novel structural, electronic, magnetic and catalytic properties. Recently, nano-sized iron oxide particles were widely used in different industrial pro-

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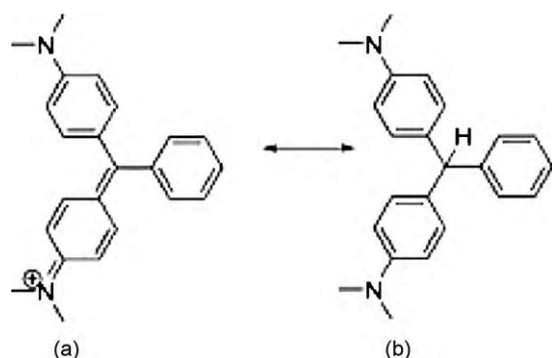
Scheme 1. Molecular structure of (a) malachite green (MG) and (b) leuco-malachite green (LMG).

cesses like manufacturing semiconductors, recording materials, catalysts, gas sensor materials and other applications [25,30,36].

In the present paper sodium dodecyl sulfate (SDS) modified maghemite nanoparticles was employed for preconcentration of MG and LMG followed by their determination by spectrophotometric method. The technique was found to be very useful and cost effective for a better removal and determination of this dye and its metabolite and can be used as an effective adsorbent in the wastewater treatment. These particles showed the highest adsorption capacities of MG compared to the reported adsorbents.

2. Experimental

2.1. Reagents and materials

All the chemicals and reagents used in this work were of analytical grade and purchased from Merck (Merck, Darmstadt, Germany). Double distilled water (DDW) was used throughout the study. The leuco form of MG was prepared by reduction of MG using Na_2SO_3 as a reducing agent.

The stock solutions (1000 mg L^{-1}) of MG and LMG (the structures was shown in Scheme 1) were prepared in DDW and experimental solutions of their desired concentrations were obtained by successive dilutions of the stock solution with DDW.

2.2. Instrumentation

A Metrohm model 713 pH-meter was used for pH measurements. A single beam Agilent 8453 UV–Vis spectrophotometer was used for determination of MG concentration in the solutions. Scanning electron microscope (SEM, Philips, XL30, Netherlands) was used for preparation of SEM images. The crystal structure of synthesized materials was determined by an X-ray diffractometer (XRD) (38066 RIVA, d/G. Via M. Misone, 11/D (TN), Italy) at ambient temperature. A $40 \pm 5\%$ kHz (power: 100 W) ultrasonic water bath (DSA100-SK$_2$, Korea) was used in this work. The BET surface area, pore volume and pore size distribution of the catalyst were measured using N_2 adsorption/desorption technique at 77 K on a Belsorp adsorption/desorption using data analysis software (Bel Japan, Inc.).

2.3. Synthesis of maghemite

The maghemite nanoparticles were synthesized according to a previous work [32] and the coating of nanoparticles by SDS was performed according to the method proposed elsewhere [37]. Firstly, 1.5 mL of SDS solution (5%, m/v) was added to about 0.1 g of nanoparticles in a beaker. T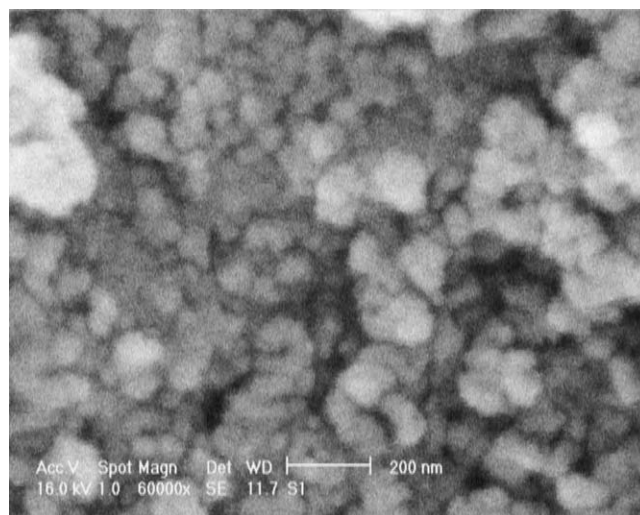he solution was stirred for 1 min on the stirrer and the beaker was then placed on the magnet and the ferrofluid was washed with DDW for several times.

Fig. 1. SEM image of SDS-coated maghemite nanoparticles.

2.4. Recommended procedure

Adsorption studies were performed by adding 100.0 mL of the solution containing 0.50–250.00 ng mL^{-1} of MG and/or LMG to 0.1 g of SDS-loaded maghemite nanoparticles in a beaker. The pH of the solutions and maghemite nanoparticles were separately adjusted at 3.0 using 0.1 mol L^{-1} HCl and/or 0.1 mol L^{-1} NaOH and the solutions were stirred for 90 s. The concentration of MG decreased with time due to its adsorption by SDS-loaded maghemite nanoparticles. Then MG loaded nanoparticles were separated with magnetic decantation. Desorption process were performed on loaded nanoparticles with 2.0 mL of pure acetic acid. The concentration of MG in the solution was then measured spectrophotometrically at 627 nm (λ_{max}) after desorption. Also the concentration of LMG could be determined upon the oxidation of the former solution to MG. It is mentionable that LMG can be easily oxidized to MG in the presence of maghemite nanoparticles, because Fe^{3+} can perform as an oxidizing agent. So the total concentration of MG and LMG was detected.

The concentration of MG in the stripped solutions was also monitored spectrophotometrically by measuring the absorbance of the solution at 627 nm.

3. Results and discussion

3.1. Characterization of the adsorbent

The SEM image of the SDS-coated nanoparticles, as shown in Fig. 1, revealed the diameter of maghemite nanoparticles synthesized were around 38–45 nm. The typical XRD profile of maghemite nanoparticles is shown in Fig. 2. The crystallite size was obtained around 8.78 nm from the XRD pattern according to Scherrer equation [32]. As the results show, the particle dimension obtained by SEM is higher than the corresponding crystallite size. This difference may be explained due to the presence of aggregates in SEM grain consisting of several crystallites and/or poor crystallinity [32]. The specific surface area of maghemite nanoparticles, obtained by BET analysis, was found to be 81.61 m^2 g^{-1}, and the mean pore diameter was obtained as 10.37 nm, with a total pore volume of 0.2116 cm^3 g^{-1}.

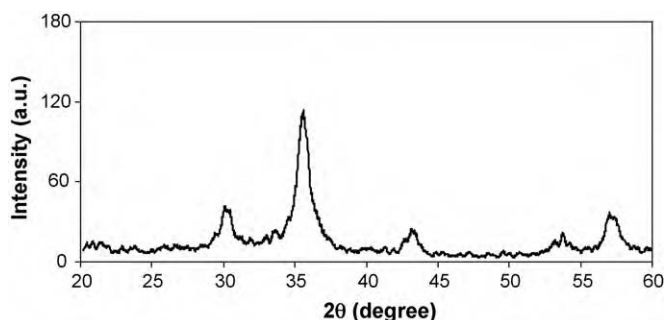Fig. 2. XRD patterns of the maghemite nanoparticles.

Table 1
Parameters of Langmuir and Freundlich isotherm equations, regression coefficients (r) for the adsorption of MG on maghemite nanoparticles at 25 °C and at pH 3.0.

Langmuir				
a_L (L mg^{-1})	K_L (L g^{-1})	K_L/a_L [$=q_m$] (mg g^{-1})	R_L[a]	r
0.0484	11.01	227.3	0.1711	0.9935
Freundlich				
K_f (mg$^{1-1/n}$ L$^{1/n}$ g^{-1})		1/n		r
26.24		0.4001		0.9806

[a] For MG concentration of 100 mg L^{-1}.

3.2. Effect of SDS

It was observed that maghemite nanoparticles cannot adsorb MG from aqueous solution at all, while their SDS modified form adsorbed MG efficiently. The surfaces of metal oxides (γ-Fe$_2$O$_3$ suspension) are generally covered with hydroxyl groups that vary in forms at different pHs. Below the pH of zero point charge, pH$_{zpc}$, that is around 6.3 for maghemite nanoparticles [32], the adsorbent surface is positively charged and hydrophilic. Therefore, adsorption of MG onto the adsorbent does not take place. Anionic surfactants such as SDS molecules will adsorb onto the surface of maghemite through the negative moiety sulfate [38] and makes the surface of adsorbent hydrophobic. The dye could be trapped into the aggregates of SDS on adsorbent [39].

In order to optimize the amount of SDS for coating nanoparticles different volumes of 5% (m/v) SDS solution was tested and a volume of 1.5 mL of 5% (m/v) SDS was chosen as the most suitable.

The effect of different amounts of SDS modified maghemite nanoparticles on the adsorption of MG was studied to determine the optimum amount for removal of MG in a 20.0 mL of 10.0 mg L^{-1} MG solution at pH 4.7 (Fig. 3). As Fig. 3 shows the percent of adsorption of MG increased by increasing adsorbent up to 0.05 g and remained nearly constant at higher values. Therefore a 0.10 g of adsorbent was used as optimal value.

3.3. Effect of pH

The effect of pH on the removal of MG, in the range 2.0–7.2, was investigated using 0.1 mol L^{-1} HCl or NaOH solutions for pH adjustment, with the initial MG concentration fixed at 10.0 mg L^{-1}. The percent adsorption increased by increasing pH and reached maximum at pH 3.0, and remained nearly constant up to pH 5 and decreased at higher pH values. Thus pH 3.0 was selected for future studies. The pK_a value for MG is 6.9 and in aqueous solutions it can occur in two cationic and colorless carbinol forms [40]. The balance between these two forms depends on the pH of the solution. Lower
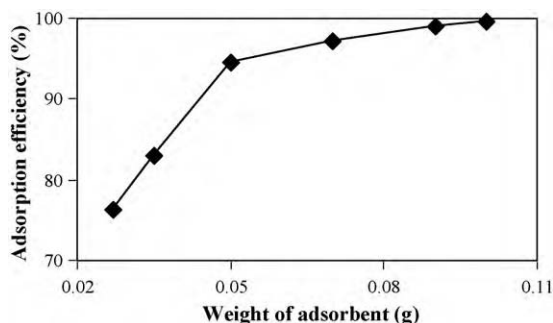

Fig. 3. Removal of MG from 20 mL of 10 mg L^{-1} MG at pH 4.7 in various amounts of adsorbent.

removal at pH values lower than 3.0 can be due to the dissolution of Fe$_2$O$_3$ nanoparticles [33]. At higher pHs, the decrease in the positive charge of adsorbent surface sites can cause a decrease in the adsorption of SDS.

3.4. Adsorption isotherms

The equilibrium adsorption isotherm model which is the number of mg adsorbed per gram of adsorbent (q_e) vs. 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 MG (2.5–450.0 mg L^{-1}) at 25 °C and at pH 3.0. Two models were used to analyze the equilibrium adsorption data: Langmuir [41] and Freundlich [42].

The general form of the Langmuir isotherm is:

$$\frac{q_e a_L}{K_L} = \frac{K_L C_e}{1 + K_L C_e} \tag{2}$$

where C_e is the equilibrium concentration of the MG in the solution (mg L^{-1}), q_e is the amount of MG adsorbed per unit mass of adsorbent (mg g^{-1}), at equilibrium concentration, C_e, a_L (L mg^{-1}) and K_L (L g^{-1}) are the Langmuir constants with a_L related to the adsorption energy and q_m [$=K_L/a_L$] signifies the maximum adsorption capacity (mg g^{-1}), which depends on the number of adsorption sites.

By linearization of the Langmuir isotherm we obtain:

$$\frac{C_e}{q_e} = C_e \left(\frac{a_L}{K_L}\right) + \left(\frac{1}{K_L}\right) \tag{3}$$

The values of a_L and K_L are calculated from the slope and intercept of the plot of C_e/q_e vs. C_e. The amount of MG adsorbed (mg g^{-1}) was calculated based on a mass balance equation as given below:

$$q_e = \frac{V(C_0 - C_e)}{m} \tag{4}$$

where C_0 is the initial concentration of MG in mg L^{-1}, V is the volume of experimental solution in L, and m is the dry weight of nanoparticles in g. The parameters of the Langmuir equation were calculated and are given in Table 1. Table 1 indicates that the maximum adsorption capacity of modified maghemite nanoparticles, q_m, is 227.3 mg g^{-1}. The essential feature of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor (R_L) given by the following equation:

$$R_L = \frac{1}{1 + a_L C_0} \tag{5}$$

R_L values within the range $0 < R_L < 1$ indicate favorable adsorption [43]. In this study, R_L value of maghemite nanoparticles for the initial MG concentration of 100.0 mg L^{-1}, obtained as 0.1711, indicate favorable adsorption of MG onto them.

Table 2
Summary of MG adsorption capacities of some various adsorbents.

Type of adsorbent	q_{max} (mg g^{-1})	Reference
Cellulose	2.422	[44]
Hen feathers	26.1	[45]
Iron humate	19.2	[46]
Arundo donax root carbon	8.69	[47]
Bentonite	7.72	[48]
Sugar cane dust	4.88	[49]
Activated charcoal	0.180	[50]
EDTAD-modified Sugarcane Bagasse	157.2	[51]
Eucalyptus bark	59.88	[52]
Neem sawdust	4.354	[53]
Maghemite nanoparticles	227.3	Present work

The Freundlich empirical model is represented by:

$$q_e = K_f C_e^{1/n} \tag{6}$$

where C_e is the equilibrium concentration (mg L^{-1}), q_e is the amount adsorbed at equilibrium (mg g^{-1}), and K_f (mg$^{1-1/n}$ L$^{1/n}$ 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 indicates the adsorption capacity. The linearized form of the Freundlich adsorption isotherm equation is

$$\ln q_e = \ln K_f + \left(\frac{1}{n}\right) \ln C_e \tag{7}$$

The values of K_f and $1/n$ calculated from the intercept and slope of the plot of $\ln q_e$ vs. $\ln C_e$ are listed in Table 1. Table 1 shows that the values of correlation coefficient, r, for the fit of experimental isotherm data to Langmuir equation is more close to 1.0000 than that for Freundlich equation. Therefore, the Langmuir model represents the experimental data better on the basis of values of regression coefficients.

The maximum adsorption capacity (q_{max}) for the adsorption of MG on SDS modified γ-Fe$_2$O$_3$ nanoparticles calculated from the Langmuir isotherm model is listed in Table 2 together with literature values of q_{max} for other MG adsorbents. All of the adsorbents used for MG adsorption have considerably lower q_{max} values than SDS modified γ-Fe$_2$O$_3$ 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.

3.5. Desorption of MG

Different solvents for desorbing MG from MG loaded SDS modified maghemite nanoparticles were investigated. Desorption process was performed on loaded nanoparticles by mixing 0.1 g MG loaded adsorbent with 2.0 mL of EtOH, MeOH, 10% MeOH in water, 0.1 mol L^{-1} HCl and NaOH solutions, 10% acetic acid in water, and pure acetic acid. The desorbed MG was then determined and

Table 3
The effect of foreign ions on the determination of 10.0 ng mL^{-1} of MG, optimum conditions and 0.05 g nanoparticles.

Foreign ions	Tolerance ratio (w_{ion}/w_{MG})
Co^{2+}, Cu^{2+}, Cd^{2+}, Al^{3+}, NH$_4^+$, Pb^{2+}, Ca^{2+}, K$^+$, Cl$^-$, NO$_3^-$	800
Hg^{2+}, Zn^{2+}, Na$^+$, Ba^{2+}, SCN$^-$	700
Ni^{2+}	600
S$_2$O$_3^{2-}$	50

the desorption efficiency for them was calculated as 4.1, 3.1, 11.9, ∼0, 12.7 and 100%, respectively. Thus, 2.0 mL of acetic acid, as the most effective eluent, was used for desorption of MG from modified maghemite nanoparticles.

3.6. Effect of sample volume

Effect of sample volume on the adsorption of MG was studied in the range 20.0–300.0 mL. In order to study the effect of sample volume, 20.0 mL of 10.0 mg L^{-1} MG was diluted to 20.0, 100.0, 200.0, and 300.0 mL with DDW. Then adsorption and desorption processes was performed under the optimum conditions (pH 3.0, 1.5 mL SDS) using 0.05 g maghemite as described in experimental section. The results showed that the MG present in the volumes up to 100.0 mL was completely and quantitatively adsorbed with nanoparticles. The adsorption then decreased at higher volumes. Therefore, for determination of trace quantities of MG in samples, a sample volume of 100.0 mL was selected in order to increase the preconcentration factor.

3.7. Interference studies

The survey of matrix effects validated the selectivity of the procedure for MG adsorption due to the competition of foreign ions for available adsorption on the nanoparticles. In this study, the tolerance limit was defined as the amount of foreign ion causing a change in the absorbance of less than ±5%. The effect of some common ions coexisting with MG, on the adsorption of 10.0 mg L^{-1} MG with 0.05 g maghemite nanoparticles at pH 3.0 was investigated and the results are shown in Table 3. As Table 3 shows, most of the investigated species did not interfere even when present 600–800-fold excess over MG. Sulfite ion interfered at concentrations higher than 50 µg mL^{-1}. The results confirm good selectivity of the proposed method and applicability of the method to the accurate determination of MG in real samples.

3.8. Analytical parameters and applications

Calibration graph was constructed from spectrophotometric measurements performed under the optimum conditions described above. The calibration graph was linear in the range 0.5–250.0 ng mL^{-1} for a sample volume of 100.0 mL. The calibration equation is $A = 0.0023C + 0.031$ with a correlation coefficient of

Table 4
Determination of sum of MG and LMG in Fish farming water samples.

Sample	MG added (ng mL^{-1})	LMG added (ng mL^{-1})	MG + LMG found[a] (ng mL^{-1})	R.S.D. (%)	Recovery (%)
1	–	–	30.6 ± 4.5	5.9	–
	20.0	–	51.5 ± 2.7	2.1	104.5
	–	20.0	49.1 ± 4.5	3.8	92.5
	20.0	20.0	70.5 ± 4.1	2.5	99.8
2	–	–	ND[b]	–	–
	0.25	0.250	0.470 ± 0.016	1.39	93.7
	0.500	0.500	0.991 ± 0.066	2.70	99.3

[a] Mean $\pm ts/\sqrt{n}$ at 95% confidence ($n = 3$).
[b] Not detected.

0.9994 ($n = 7$), where A is the absorbance of the eluate at 627 nm and C is the concentration of MG in the sample solution in ng mL^{-1}. The limit of detection, defined as $C_L = 3S_b/m$, where C_L, S_b and m are the limit of detection, standard deviation of the blank and the slope of the calibration graph, respectively, was 0.3 ng mL^{-1} of MG. The relative standard deviation (R.S.D.) for 10.0 and 50.0 ng mL^{-1} of MG was 1.60% ($n = 3$) and 0.86% ($n = 5$), respectively. As the amount of MG in 100.0 mL of the solution was concentrated to 2.0 mL, a preconcentration factor of 50.0 was achieved in this method.

In order to evaluate the analytical applicability of the proposed method, it was applied to the determination of MG and LMG in fish farming water samples. The water samples were also analyzed after spiking different amounts of MG and/or LMG to them. The results are given in Table 4 that shows the good recoveries are obtained from the procedure. The obtained R.S.D. values were ≤5.4% and the obtained recoveries were in the ranges of 93.7–104.5%.

4. Conclusion

In summary, SDS modified γ-Fe$_2$O$_3$ nanoparticles by high adsorption capacity, acceptable sensitivity and simply synthesis with easy separation of maghemite nanoparticles, are so good industrial candidate for removal and hence for determination of traces amount of MG and LMG, as well. Therefore here is a novel and convenient procedure that has been developed as a safe, rapid and inexpensive methodology for preconcentration, determination and infiltration of MG and LMG as toxic compounds from fish farming or other samples compared to the other previous troublesome methods. The method was applied to the fast removal and determination of trace amounts of LMG and MG totally in fish farming water samples with satisfactory results.

The results also shows that the proposed adsorbent can be used as an effective adsorbent in the simple and rapid removal of MG and LMG from water and wastewaters.

Acknowledgements

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