



Synthesis of SDS micelles-coated $\text{Fe}_3\text{O}_4/\text{SiO}_2$ magnetic nanoparticles as an excellent adsorbent for facile removal and concentration of crystal violet from natural water samples

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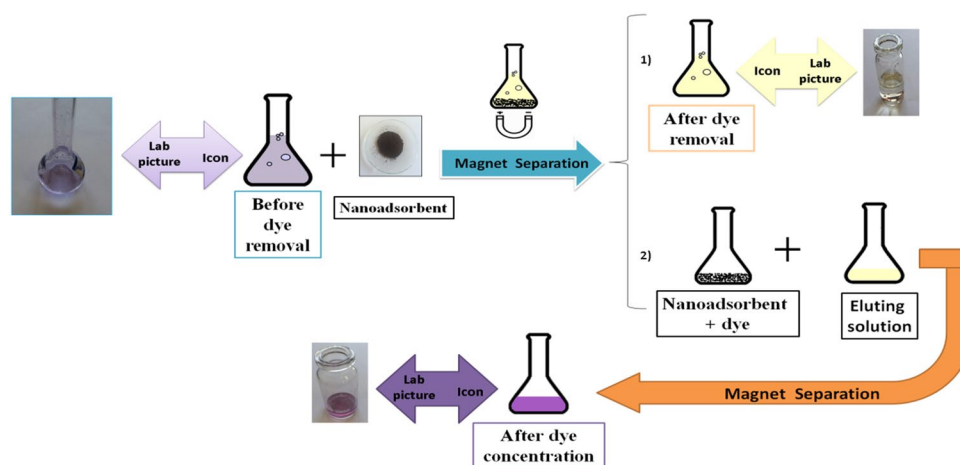
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Abstract

In this research, a simple and rapid method for the separation and preconcentration of trace amounts of crystal violet (CV) from aqueous sample solutions by modified magnetic nano-particles (MNPs) has been developed. The modification of magnetite nanoparticles was conducted by tetra ethoxysilane (TEOS) followed by micelles of anionic surfactant (SDS) to enhance the preconcentration of CV. To characterize the shape and structure of the nanoadsorbent, FT-IR and XRD procedures were used. Also, the average size of the synthesized nanoparticles was achieved between 30 and 40 nm by TEM technique. The effects of some important parameters such as: aqueous solution pH, adsorbent dosage, contact time, temperature and desorption conditions on the separation and concentration of CV were investigated. So, under optimal experimental conditions: aqueous solution pH 6, solution temperature = 20 °C, 7 mg of adsorbent, 1 mL of eluent (0.8 mL of acetonitrile + 0.2 mL of acetic acid), the recovery of CV from river water samples was achieved $98.32 \pm 0.056\%$ ($n=5$) in two short periods of time for extraction (5 min) and elution (2 min). The maximum sorption capacity of the nano-composite was determined to be 16.37 mg/g. Also linear dynamic range and limit of detection were calculated to be 10–2500 ppb and 1.82 ppb, respectively. Finally, the proposed method was successfully applied for the separation and concentration of CV from the real water samples and the results were satisfied.

Graphical abstract

Under optimal conditions, a significant amount of nanocomposite was added to the dye solution. After dye removal in a short time, the nanoadsorbent-containing dye was magnetically separated from the solution and then the adsorbed dye was eluted into low volume of a suitable eluting solution.



Keywords Crystal violet · Fast removal, SDS micelle-coated MNP · Concentration · Magnetic nanoparticles

Introduction

Natural and synthetic dyes are heavily used in many industries including food, cosmetics, textiles, pharmaceuticals, and leather tanning [1]. According to their chemical structures, dyes can be classified as acidic and basic dyes. Basic dyes (cationic dyes) are soluble in water with positive charge which are widely applied to acrylic fibers and paper but rarely applied to wool and silk. Cationic dyes are toxic even at trace levels [1]. Usually, cationic dyes are present in natural and treated wastewater and even in potable waters at μg or ng per liter [2, 3].

Crystal violet is one of the cationic dyes which cause adverse effects on human health. It may cause eye burn leading to permanent cornea/eye damage. Its inhalation gives rise to a short period of rapid or difficult breathing, nausea, vomiting, profuse sweating, hypermotility, diarrhea, and abdominal pain [4]. Therefore, a preliminary preconcentration step is an essential step before analysis by sensitive instruments.

Several methods for preconcentration of dyes include dispersive liquid liquid microextraction (DLLME), cloud point extraction (CPE), solid phase extraction (SPE), and rotating disk sportive extraction (RDSE) [5–8]. Among these techniques, SPE procedures are considered superior to other procedures, because these techniques have many advantages over others, such as: low running cost, high speed, low solvent consumption, and higher enrichment factors [9]. The effectiveness of dyes removal in SPE procedures depends strongly on the nature of adsorbent being used, because the analytical sensitivity, affinity, capacity, and precision of the procedure can be usually estimated by the adsorbent action during separation process [10–13].

Recently, many research groups have explored the application of several nanosized SPE adsorbents such as nanoparticles (NPs) and nanotubes. Meanwhile, the magnetic nanoparticles are one of the most popular materials in analytical biochemistry, medicine, and biotechnology. Also, they have been increasingly applied to immobilize proteins, enzymes, and other bioactive agents [14].

Nanomaterials can offer several advantages over traditional SPE adsorbents, such as having a short diffusion route and very high surface areas and extraction capacity, which result in their rapid extraction dynamics and high extraction efficiencies [15]. Moreover, by using superparamagnetic nanoparticles (NPs), such as Fe_3O_4 , a shorter analysis time can be achieved. It is mainly due to their easy isolation by an external magnetic field which is applied outside the extraction container [16].

However, pure magnetic particles are prone to form aggregates and their magnetic properties can be altered in complex environmental and biological systems. To solve the above problems, a suitable protective coating on a magnetic core is often used. The core–shell magnetic nanoparticles have high surface areas. Between some protective coatings, silica has been considered as one of the most ideal shell materials. This is mainly due to its reliable chemical stability, biocompatibility, and versatility in surface modification [17, 18].

Recent studies on the use of surfactant-coated mineral oxides have demonstrated that these new adsorbent materials, which are shielded with hemimicelles/or admicelles, can be promising tools for the extraction/preconcentration of ionic and non-ionic compounds [18–20]. In comparison with the other ordinary adsorbents, one feature of the surfactant-coated adsorbents is that the outer surfaces of hemimicelles and admicelles are hydrophobic and ionic, respectively. Therefore, it makes them as a proper adsorbent, which offers different mechanisms for extraction processes [18]. Moreover, since the surfactants are commercially available, the hydrophobicity and the charge of the adsorbent can be easily modified according to the nature of the analytes. So, using mixed hemimicelles/admicelles in SPE has many advantages, such as, high extraction yields, high breakthrough volumes, and rapid elution of analytes [18].

In this study, the chemical synthesis of Fe_3O_4 MNPs and the surface modification of synthesized MNPs with silica and micelles of sodium dodecyl sulfate (SDS) have been described. So, bilayer coatings of silica and SDS micelle in the first and second layers surrounded the Fe_3O_4 nanoparticle core, respectively. The shape and structure of the synthesized nanomaterials were studied by FTIR, XRD, and TEM techniques. Also, the capability of SDS micelles-coated $\text{Fe}_3\text{O}_4/\text{SiO}_2$ magnetic nanoparticles to separate crystal violet (CV) from water samples was investigated and then the dye was concentrated into the eluting solution.

Experimental

Reagents and materials

Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), sodium hydroxide, ammonia, ethanol, acetone, sodium dodecyl sulfate (SDS), tetra ethoxysilane (TEOS) (98%), sodium chloride and hydrochloric acid were all analytical grade from Merck (Darmstadt, Germany). Crystal violet, $\text{C}_{25}\text{H}_{30}\text{N}_3\text{Cl}$, was purchased from

Sigma-Aldrich Company. The chemical structure of the dye is presented in Fig. 1.

Instrumentation

The dye concentrations were measured by a double-beam UV/Vis spectrophotometer (Shimadzu, Model UV 1601, Japan) at a wavelength of 582 nm. The phase purity was characterized by X-ray powder diffraction (XRD) (bruker AXS GmbH, Karlsruhe, Germany) using Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$). Transmission electron microscopy was carried out using a Zeiss-EM10C operated at a 100-kV accelerating voltage. The pH values were measured with a Consort C860 multi-parameter analyzer. The FTIR spectra were recorded on a Perkinelmer FTIR 100 spectrometer and using standard KBr pellet technique.

Adsorbent preparation

Synthesis of Fe₃O₄ nanoparticles

The chemical co-precipitation method was used in the preparation of the Fe₃O₄ NPs with some modifications [16]. At first for preparing a stock solution, 5.4 g of FeCl₃·6H₂O and 2.0 g of FeCl₂·4H₂O were dissolved in 25 mL of deionized distilled water and 25 mL of 2 M HCl was added to the solution in a beaker. The stock solution was stirred under argon gas protection for 10 min. Then, its temperature was adjusted in 80 °C in a reactor and 40 mL of concentrated ammonia solution was added dropwise under vigorous stirring (1000 rpm) and argon gas protection in 30 min. After adding ammonia to the solution, it was rapidly stirred for 60 min. Then, the solution was cooled to room temperature and the Fe₃O₄ NPs were produced. The magnetic precipitate was isolated with a permanent magnet and then washed three times with 150 mL of deionized water and absolute alcohol. Finally, the black powder Fe₃O₄ nanoparticles were dried under vacuum at 50 °C during 24 h.

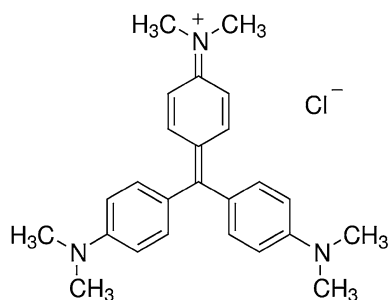


Fig. 1 Chemical structure of crystal violet (CV)

Modification of Fe₃O₄ nanoparticles with SiO₂ groups

Fe₃O₄/SiO₂ NPs were synthesized according to the previously reported method with some modifications [21]. So, 1 g of the Fe₃O₄ nanoparticles was suspended in 200 mL of pure ethanol under sonication and argon gas protection for 1 h. Then, 22.5 mL of concentrated ammonia, 18.75 mL of deionized water, and 0.5 mL of TEOS were added, in sequence, to the suspension and the mixture was sonicated for 1 h. To achieve complete silica-coated magnetic nanoparticles, the suspension was stirred for another 8 h. The silica-modified nanoparticles were isolated by a permanent magnet and rinsed with deionized water three times and then dried during 24 h.

Preparation of SDS micelle-bound SiO₂-coated magnetic NPs

To coat the SiO₂-modified magnetic nanoparticles by micelles of SDS, 10 mL of 5% w/v SDS solution (> CMC of SDS) was added to about 1.0 g of silica-modified MNPs, in a beaker. Then, the solution was vigorously stirred for 1 min with a glass rod and then the beaker was placed on a magnetic field. After completing the grounding of the SDS micelles-bound silica-coated magnetic nanoparticles (SDS micelle-SCMNPs), the solution was decanted and the dark brown modified NPs were washed three times with distilled water, to eliminate the extra amount of surfactant [21].

Procedure

Preconcentration of crystal violet by SDS micelle-coated Fe₃O₄/SiO₂ MNPs has been studied in batch experiments. A known amount of nanoadsorbent (7 mg) was added to 20 mL of 1 mg L⁻¹ aqueous crystal violet solution at pH 6 and it was shaken for 5 min at 20 °C. 5 min and 20 °C are contact time and temperature, respectively. To isolate the modified MNPs containing the adsorbed dye, from the remaining solution, a strong magnetic field was used and so the supernatant liquid phase was magnetically decanted. Finally, the adsorbed target analyte (CV) on the SDS micelle-coated Fe₃O₄/SiO₂ MNPs was eluted with 1.0 mL of 1:4 v/v solution of acetic acid: acetonitrile under shaking in 2 min, elution time, and exposed to a permanent magnet. The clear solution of the eluent containing the eluted crystal violet was transferred to the glass tube. Then, analyte absorbance in the eluent was determined by a UV spectrophotometer at 589 nm against blank.



Calculation of extraction recovery (response) and relative recovery

To evaluate the efficiency of the method and obtain optimum conditions, the extraction recovery of the analyte was determined. The extraction recovery (ER%) was defined as the percentage of total analyte (n_0) that was extracted into the sedimented phase (n_{sed}) and presented in the following equation:

$$\text{ER}\% = \frac{n_{\text{sed}}}{n_0} \times 100 = \frac{V_{\text{sed}} \times C_{\text{sed}}}{V_{\text{aq}} \times C_0} \times 100, \quad (1)$$

where C_{sed} is the concentration of analyte in the sedimented phase after extraction, and C_0 is the initial concentration of analyte in the aqueous phase. V_{sed} and V_{aq} are the volume of sedimented phase and the volume of aqueous phase, respectively. N_0 and n_{sed} are the initial moles of analyte in the aqueous phase and its extracted moles into the sedimented phase, respectively.

To assess the matrix effect of real samples on the proposed method, the relative recovery (RR) was determined using Eq. (2):

$$\text{RR}\% = \frac{n_{\text{measured}} - n_{\text{real}}}{n_{\text{added}}} \times 100, \quad (2)$$

where n_{measured} is the moles of analyte after addition of a known amount of standard in the real sample, n_{real} is the initial moles of analyte in real sample and n_{added} is the moles of the spiked standard to the real sample.

Results and discussion

Characterization of the synthesized nanoadsorbent

X-ray powder diffraction (XRD)

XRD analysis was used to investigate the crystalline structure of synthesized nanoparticles (Fig. 2). The Joint Committee on Powder Diffraction Standards (JCPDS) reference pattern of magnetite (No. 19-629) was used for comparison. As could be seen in Fig. 2, the XRD pattern of functionalized magnetite nanoparticles (SDS micelle coated $\text{Fe}_3\text{O}_4/\text{SiO}_2$ MNPs) was matched well with that of the standard Fe_3O_4 structure. This indicated that the SiO_2 and SDS micelles coating did not cause the phase change in Fe_3O_4 NPs structure [22]. On the other hand, the sharp and narrow peaks also indicate that SDS micelle-coated $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanoparticles have high crystallinity and purity [23–25].

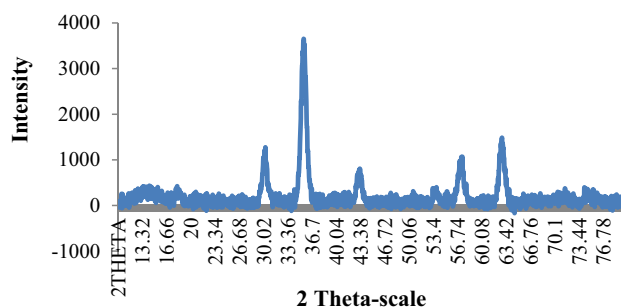


Fig. 2 XRD pattern of synthesized SDS micelle coated $\text{Fe}_3\text{O}_4/\text{SiO}_2$ MNPs

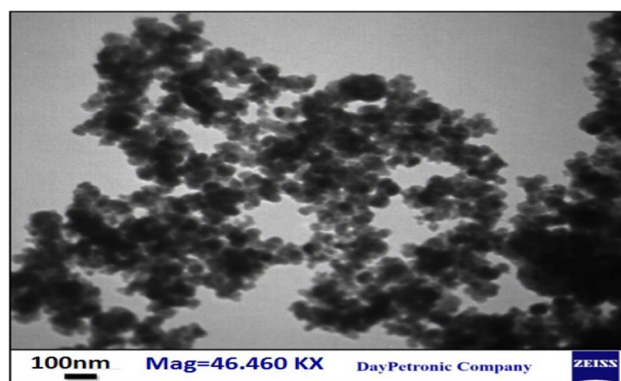


Fig. 3 TEM micrograph of synthesized SDS micelle coated $\text{Fe}_3\text{O}_4/\text{SiO}_2$ MNPs

The introduction of SiO_2 and SDS micelle onto the magnetite nanoparticles was approved by TEM results (Fig. 3). As seen in Fig. 3, the dark nano- Fe_3O_4 cores have been surrounded by a gray shell of SDS micelle and SiO_2 coating, and also little agglomeration can be observed [13]. Moreover, from TEM report, the particles have an approximate spherical shape and an average size of 30–40 nm.

FT-IR spectrum

FT-IR is a reliable technique for the monitoring of the variations in the functional groups. So, the structures of the Fe_3O_4 MNPs, $\text{Fe}_3\text{O}_4/\text{SiO}_2$ and the SDS micelle-coated $\text{Fe}_3\text{O}_4/\text{SiO}_2$ MNPs were characterized by FTIR spectroscopy. The results are shown in Fig. 4. The main absorption bands of OH ($3300\text{--}3500\text{ cm}^{-1}$) and Fe–O (589 cm^{-1}) groups are observed in all samples. Fe–O stretching band at 589 cm^{-1} is the characteristic peak of magnetite. The characteristic band of Si–O is at 1066 cm^{-1} , which confirmed that the Fe_3O_4 NPs were protected by silica coating. On the other hand, the absorption band at 1067 cm^{-1} could be attributed to the stretching vibration of S=O

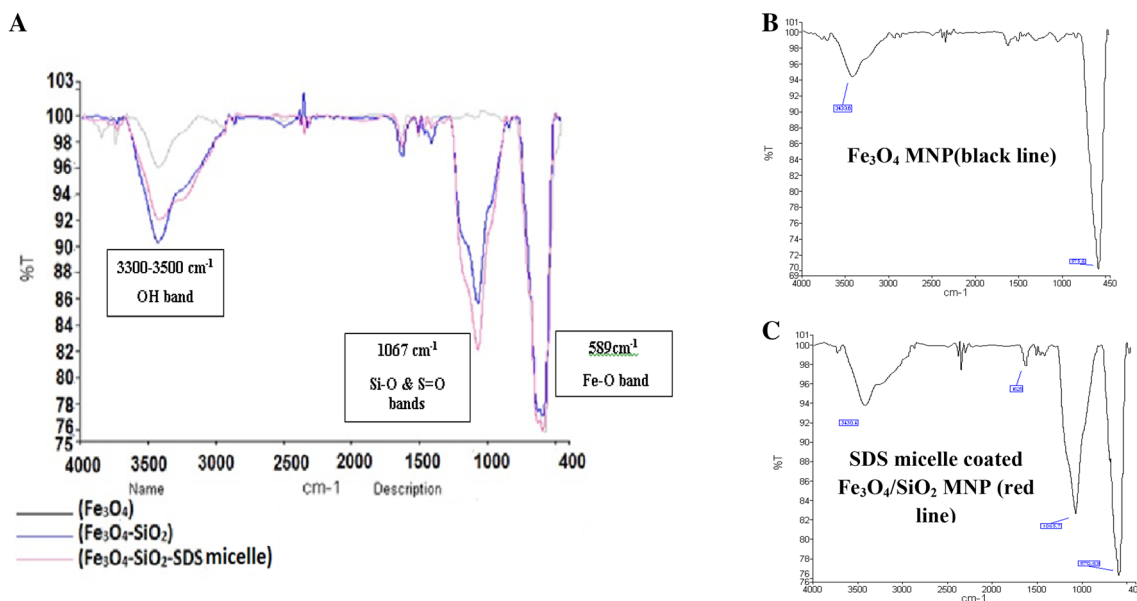


Fig. 4 **a** IR spectrum of the Fe_3O_4 MNPs (black line), $\text{Fe}_3\text{O}_4/\text{SiO}_2$ (blue line), and the SDS micelle-coated $\text{Fe}_3\text{O}_4/\text{SiO}_2$ MNPs (red line). **b** Separate IR spectrum of the Fe_3O_4 MNPs (black line). **c** Separate IR spectrum of the SDS micelle coated $\text{Fe}_3\text{O}_4/\text{SiO}_2$ MNPs (red line)

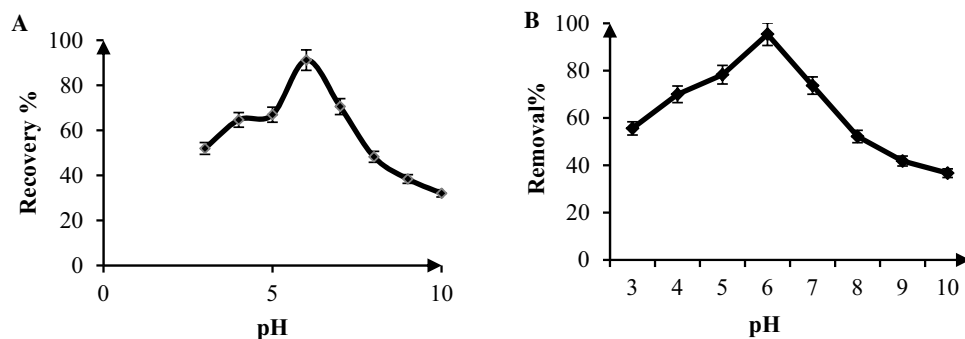
band, which showed that the surface of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ MNPs was successfully modified with SDS micelles. Also as reported by T. Liu and co-workers, there are some peaks at $3400\text{--}3500\text{ cm}^{-1}$, $550\text{--}600\text{ cm}^{-1}$, 1220 cm^{-1} , and 1084 cm^{-1} for pure SDS and when the SDS adsorbs on the surface of a solid phase (like colophane), these main peaks can shift a little [26]. Therefore, the main peak of the stretching vibration of $\text{S}=\text{O}$ at 1220 cm^{-1} for pure SDS has shifted a little and is observed at 1067 cm^{-1} . Since the peak at $1066\text{--}1067\text{ cm}^{-1}$ belongs to the stretching vibrations of the both of $\text{Si}\text{--}\text{O}$ and $\text{S}=\text{O}$ bands and the two peaks overlapped, this peak in the red line is more intense than that of in blue one (Fig. 4). So, the results in Fig. 4 show that the both of SDS micelles and SiO_2 coatings are adsorbed on Fe_3O_4 MNPs via purely physical adsorptions [26].

Optimization of various parameters

Effect of pH

It is well known that the pH of the sample solution is one of the prime factors influencing on the states of species (as ions or neutral forms). Also, adsorption behavior of an adsorbent system can be affected by pH aqueous solution. For instance, at different working pH values, there is different charge density on the $\text{Fe}_3\text{O}_4/\text{SiO}_2$ MNP surface [27]. In this study, the sorption behavior of crystal violet on the modified nano-adsorbent from water samples was investigated, in the solution pH range of 3.0–10.0. The pH of the solution was adjusted at the required value by the addition of 1.0 mol L^{-1} NaOH or 1.0 mol L^{-1} HCl. As shown in Fig. 5a, b, by increasing the solution pH, from 3 to 6, the adsorption efficiency of dye was improved and reached a maximum at pH about 6 and then decreased at higher pH values. At low pH (about

Fig. 5 Effect of pH on the recovery (a) and removal (b) of crystal violet. Experimental conditions: 20 mL of 1 mg L^{-1} dye solution at different pHs (3.0–10.0) in $25\text{ }^\circ\text{C}$, 7 mg of nano-adsorbent, and contact time was 5 min, elution conditions: mixture of 0.8 mL of acetonitrile + 0.2 mL of acetic acid, as eluting solution, and elution time was 2 min



3), the negative charge density on the SDS micelle coating $\text{Fe}_3\text{O}_4/\text{SiO}_2$ MNPs is decreased [28]. This is mainly due to the high free proton ion concentration in the solution, which makes the neutralization of the negative charge on the SDS micelle-coated $\text{Fe}_3\text{O}_4/\text{SiO}_2$ MNPs. So, the tendency of the cationic dye toward the nanoadsorbent is reduced. Then, by increasing the pH value up to 6, H^+ ions concentration is diminished and so the removal percentage of CV on the surface of the nanocomposite is improved. But at higher pH (> 6), a significant decrease in the dye removal and recovery percentage is observed (Fig. 5). Since the point of zero charge (PZC) of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ was reported about 3.3 [29], at higher pH and free hydroxide ion concentration, the SDS micelle-surrounded $\text{Fe}_3\text{O}_4/\text{SiO}_2$ MNPs may be substituted by OH^- ions. So, under this circumstance, the prolapse of SDS micelle from the $\text{Fe}_3\text{O}_4/\text{SiO}_2$ MNPs may happen [30, 31]. On the other hand, the positive charge of the cationic dye can be neutralized by OH^- groups in basic conditions. Thus, pH of the solution was adjusted at pH 6.0, as optimum value, for further experiments.

Effect of nanoadsorbent dosage

Compared to ordinary adsorbents (micron-size particle adsorbents), NP adsorbents have higher surface areas. Therefore, satisfactory results can be achieved by fewer amounts of NP adsorbents [27, 32, 33]. In this study, the effect of the amount of modified nanoparticles on the quantitative

extraction of crystal violet was investigated, by varying the amounts of the modified nanoparticles from 0.5 to 17 mg. It can be seen from Fig. 6a, b that the highest recovery and removal of crystal violet has been obtained with increasing of modified nanoparticles amount up to 5 mg and remained constant at higher amounts of nanocomposite. This is mainly due to the higher collision probability between CV and SDS micelles-coated $\text{Fe}_3\text{O}_4/\text{SiO}_2$ MNPs in higher dosage of nanocomposite. Therefore, 7 mg of the modified nanoparticles was selected as the optimum value for further experiments.

Effect of contact time

The effect of contact time on the overall extraction efficiency of the crystal violet was studied, by varying the contact time between adsorbent and dye sample solution in the range of 1–15 min. As shown in Fig. 7a, b, the adsorption efficiency of crystal violet has been improved by increasing the contact time up to 5 min and remained nearly constant in more than 5 min. Therefore, a short contact time of 5 min was selected for the adsorption of CV on the SDS micelle-coated $\text{Fe}_3\text{O}_4/\text{SiO}_2$ MNPs.

Effect of temperature

In this study, the effect of temperature on the adsorption of crystal violet on the SDS micelle-coated $\text{Fe}_3\text{O}_4/\text{SiO}_2$ NPs was investigated, in the range of 5–40 °C under optimal

Fig. 6 Effect of nanosorbent dosage on the recovery (a) and removal (b) of crystal violet. Experimental conditions: 20 mL of 1 mg L^{-1} dye solution at pH 6 in 25 °C, different amounts of nanosorbent were used and contact time was 5 min, elution conditions: mixture of 0.8 mL of acetonitrile + 0.2 mL of acetic acid, as eluting solution, and elution time was 2 min

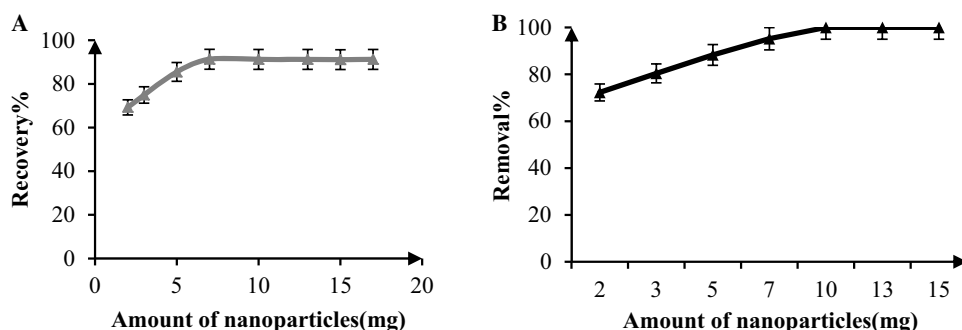


Fig. 7 Effect of contact time on the recovery (a) and removal (b) of crystal violet. Experimental conditions: 20 mL of 1 mg L^{-1} dye solution at pH 6 in 25 °C, 7 mg of nanoadsorbent and contact time was varied between 1 and 15 min, elution condition: mixture of 0.8 mL of acetonitrile + 0.2 mL of acetic acid, as eluting solution, and elution time was 2 min

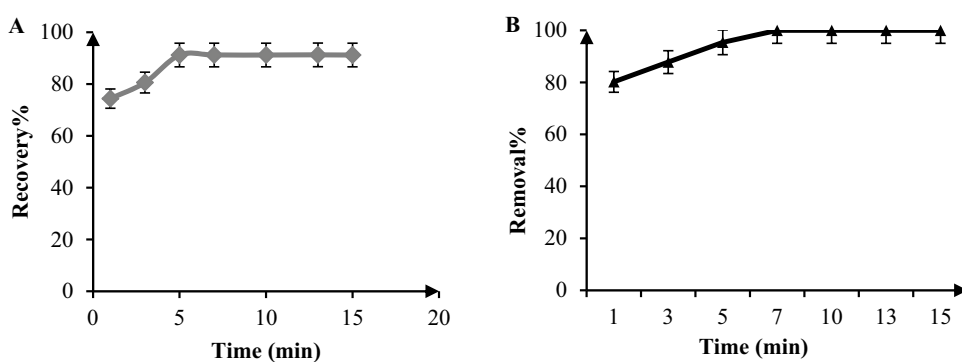
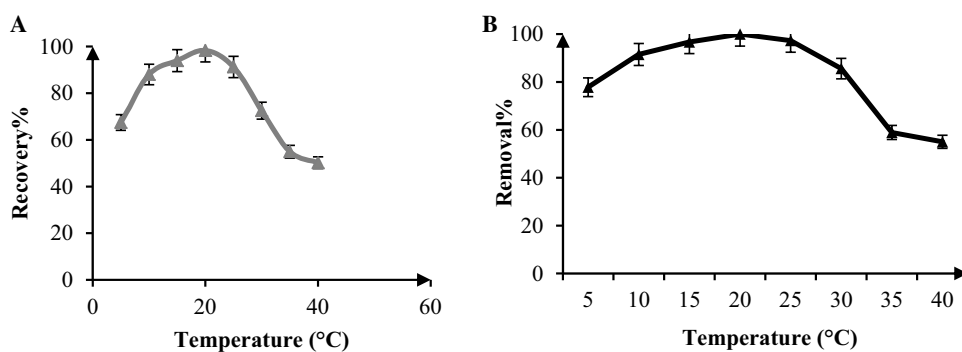


Fig. 8 Effect of temperature on the recovery (a) and removal (b) of crystal violet. Experimental conditions: 20 mL of 1 mg L⁻¹ dye solution at pH 6 in different temperatures, 7 mg of nanoadsorbent and contact time was 5 min, elution condition: mixture of 0.8 mL of acetonitrile + 0.2 mL of acetic acid, as eluting solution, and elution time was 2 min



conditions (i.e., contact time: 5 min, pH 6 and adsorbent dosage: 7 mg). It can be seen from Fig. 8a, b, by increasing the temperature from 5 to 20 °C, the adsorption and recovery efficiencies of the crystal violet have been increased nearly 100% and 98.32%, respectively. But at higher temperatures (25–40 °C), the separation and recovery efficiencies of CV have been diminished. This might be due to the fact that the critical micelle concentration (CMC) of SDS and consequently its micellization can be varied as a function of temperature [34]. For ionic surfactant, the temperature has strong effect on the hydrophobic and hydrophilic interaction behavior of micelles. According to the CMC versus temperature studies for ionic surfactants, CMC decreased to a minimum value and then increased, by increasing the temperature. Therefore, a U-shape behavior was observed [34]. Since the minimum CMC value of SDS was achieved at 21 °C, the maximum micellization could be occurred around this temperature [34]. So, maximum recovery and extraction efficiencies of the crystal violet (98% and 100%) can be seen at 20 °C, because of the maximum micellization of SDS at this temperature [34].

Desorption condition

Organic solvents can rapidly and completely disrupt the micelles and therefore the analyte is removed from the surface of NPs [14, 35]. By carrying out some experiments we found that desorption ability of acetonitrile was improved, when acetic acid was added into the acetonitrile [18]. Thus, different volumes of the mixed solutions of acetonitrile and acetic acid were studied for desorption of analytes from the SDS micelle coated Fe₃O₄/SiO₂ MNPs. The results are presented in Table 1. It was resulted that among the testing solvents, the highest recoveries (91.32%) were achieved using 1 mL of the mixture of acetic acid: acetonitrile (1:4, v/v) at ambient temperature (~25 °C). Therefore, it was selected as the elution solvent for desorption of the analyte from the surface of the modified magnetic nanoparticles. Also, the elution time in the range of 1–7 min was investigated and the results showed that the recovery of CV was quantitative

Table 1 Effect of different mixture of eluting solution on the recovery efficiency of crystal violet. Experimental conditions: 20 mL of 1 mg L⁻¹ CV at pH 6 in ambient temperature, 7 mg of nanoadsorbent, and contact time was 5 min. Elution conditions: different mixtures of acetonitrile and acetic acid solutions, elution time was 2 min

Eluent	Volume (mL)	Recovery (%)
Acetonitrile + CH ₃ COOH	0.7 + 0.3	85.27
Acetonitrile + CH ₃ COOH	0.8 + 0.2	91.32
Acetonitrile + CH ₃ COOH	0.3 + 0.7	91.0
Acetonitrile + CH ₃ COOH	0.2 + 0.8	88.2
Acetonitrile + CH ₃ COOH	0.5 + 0.5	79.2
Acetonitrile + CH ₃ COOH	1.0 + 1.0	70.75
Acetonitrile + CH ₃ COOH	0.5 + 1.5	63.5
Acetonitrile + CH ₃ COOH	1.5 + 0.5	60.15

Table 2 Adsorption isotherm parameters of crystal violet onto SDS micelle-coated Fe₃O₄/SiO₂ MNPs

Freundlich model			Langmuir model		
R ²	Log K _F	1/n	R ²	q _m (mg g ⁻¹)	K _L (L mg ⁻¹)
0.9473	0.56	0.174	0.9992	16.37	-0.23

(91.32%) in 2 min. So, 2 min was selected as the optimal elution time in other experiments.

Adsorption capacity and isotherms

To study the adsorption capacity and isotherms of SDS micelle-coated Fe₃O₄/SiO₂ MNPs, 7 mg of the adsorbent was added to 20 mL of different concentrations of dye, in the range of 1–20 mg L⁻¹, at pH 6.0 and 20 °C. After shaking for 5 min, the supernatant was decanted by applying an external magnetic field and the remaining crystal violet in the supernatant solution was determined by a UV spectrophotometer at 589 nm against blank. The adsorption capacity (q_E, mg g⁻¹) was calculated as:

$$q_E = \frac{(C_0 - C_E)V}{m}, \quad (3)$$



where C_0 and C_E are the initial and equilibrium concentrations (mg L^{-1}) of crystal violet in the solution, respectively. V is the volume of dye solution in mL and m is the amount of adsorbent in mg.

Two more common adsorption isotherms, Langmuir and Freundlich, were studied [36]. The results are summarized in Table 2. As seen in Table 2, the Langmuir model has been fitted better ($R^2=0.9992$) than the Freundlich model ($R^2=0.9473$). Therefore, monolayer adsorption of dye on the homogeneous surface of SDS micelle-coated $\text{Fe}_3\text{O}_4/\text{SiO}_2$ MNP has been considered. Since the constant $1/n$ is 0.174, proper physical adsorption of dye on the nanoadsorbent is concluded [13]. On the other hands, the results showed that the maximum capacity of the SDS micelle-coated $\text{Fe}_3\text{O}_4/\text{SiO}_2$ MNPs was 16.37 mg g^{-1} for the removal of crystal violet.

Also, the effect of initial dye concentration, in the range of $1\text{--}20 \text{ mg L}^{-1}$, on its removal percentage was studied. The results are shown in Fig. 9. As indicated in Fig. 9, by increasing the initial concentration of crystal violet in the aqueous solution, the dye removal is diminished. This is mainly due to the finite capacity of nanoadsorbent [13].

Analytical performance

Under optimal conditions: 20 mL of 1 mg L^{-1} of CV solution at pH 6 in 20°C , 7 mg of nanoadsorbent, contact time = 5 min, eluting solution = mixture of 0.8 mL of acetonitrile + 0.2 mL of acetic acid, and elution time = 2 min, the analytical parameters such as: linear dynamic range (LDR), correlation coefficient (R^2), limit of detection (LOD), and relative standard deviation (RSD) were

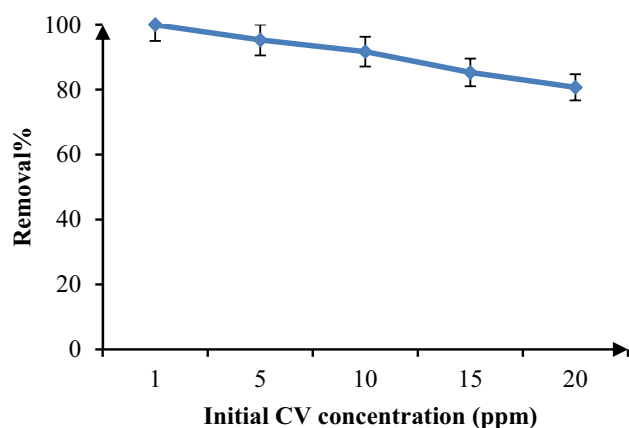


Fig. 9 Effect of initial concentration of crystal violet (CV) on its removal. Experimental conditions: 20 mL of different concentrations of dye solution ($1\text{--}20 \text{ mg L}^{-1}$) at pH 6 in 20°C , 7 mg of nanoadsorbent and contact time was 5 min, elution condition: mixture of 0.8 mL of acetonitrile + 0.2 mL of acetic acid, as eluting solution, and elution time was 2 min

Table 3 Analytical figures of merit of the proposed method

	Crystal violet
LDR ($\mu\text{g L}^{-1}$) ^a	10–2500
R^2	0.9991
LOD ($\mu\text{g L}^{-1}$) ^b	1.82
SD % ($n=7$) ^c	0.056
Enrichment factor ^d	20

^aLinear dynamic range

^bLimit of detection

^cStandard deviation

^dRatio of the initial volume to the final volume

determined and summarized in Table 3. The calibration curve of crystal violet was constructed in the range of $10\text{--}2500 \mu\text{g L}^{-1}$ and characterized with a high correlation coefficient ($R^2=0.9991$) under optimum conditions. Based on $C_{\text{LOD}}=3S_b/m$ equation, C_{LOD} , S_b and m are limit of detection, standard deviation of blank, and slope of the calibration curve, respectively. The limit of detection (LOD) of crystal violet was achieved $1.82 \mu\text{g L}^{-1}$. Standard deviation (SD) of the method was 0.056% ($n=7$) under optimal conditions. After measuring the amount of crystal violet in the 1 mL of eluent, preconcentration/or enrichment factor was achieved 20.

Also, the ultraviolet/visible spectrums of crystal violet before and after removal and also after concentration, via proposed method, were investigated, under optimal conditions (Fig. 10).

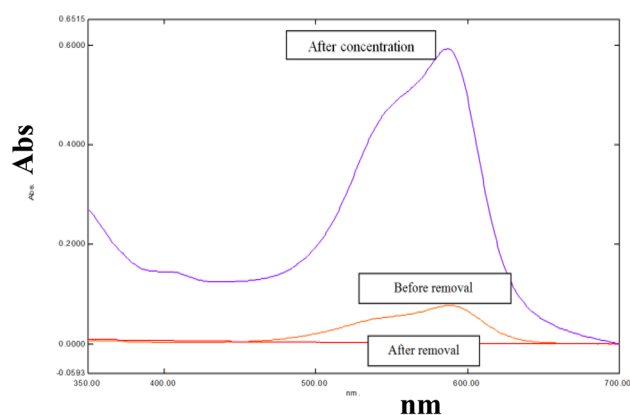


Fig. 10 UV/Vis spectra of crystal violet (CV) before and after removal and concentration under optimal conditions: 20 mL of 0.7 mg L^{-1} dye (CV) solution at pH 6 in 20°C , 7 mg of nanosorbent and contact time was 5 min, elution condition: mixture of 0.8 mL of acetonitrile + 0.2 mL of acetic acid, as eluting solution, and elution time was 2 min

Real sample analysis

The proposed method was applied to determine the extraction and concentration of crystal violet from river water samples. Since the concentration of CV in river water samples was at very low levels and could not be determined, two different amounts of standard dye solution were spiked to two river water samples, 0.5 and 1 mg L⁻¹, and the recovery percentage of dye was investigated. The results are shown in Table 4. As it is seen in Table 4, recovery percentage of dye from matrices was obtained about 97.1% and 97.7% when 0.5 and 1 mg L⁻¹ crystal violet was spiked into two river water samples, respectively. As a result, the complexity of the medium did not have significant effect on the efficiency of dye recovery with the proposed method under optimum conditions.

Table 4 The recovery of crystal violet from river water samples. Experimental conditions: 0.5 and 1 mg L⁻¹ crystal violet were spiked into two river samples at pH 6 in 20 °C, 7 mg of nanoadsorbent, and the contact time was 5 min, and elution conditions: mixture of 0.8 mL of acetonitrile + 0.2 mL of acetic acid, as eluting solution, and elution time was 2 min

Sample	Added (mg L ⁻¹)	Found ^a (mg L ⁻¹)	Recovery (%)
River water ^b	0	n.d. ^c	–
	0.50	0.49 ± 0.05 (n = 5)	97.1
	1.00	1.01 ± 0.05 (n = 5)	97.7

^aMean ± SD % (n = 5)

^bThe water sample was collected from Baraghan river (Alborz province, Iran)

^cNot detected

Table 5 Comparison of the proposed method with other reported preconcentration methods for extraction and concentration of crystal violet

Sorbent	Time ^a (min)	PF ^b	LOD (µg L ⁻¹)	SD %	Detection	References
SDS micelle coated Fe ₃ O ₄ /SiO ₂	5	20	1.82	0.056	UV–Vis	This work
Nanoporous silica SBA-3	2	200	1.3	< 1.3	FO-LADSc	[37]
Diatomite	–	89–96	28	2.3	UV–Vis	[7]
GO ^d	15	19.6	9	1.99	UV–Vis	[38]
RDSEe	100	–	1.8	< 8.4	UV–Vis	[8]

^aExtraction time

^bPreconcentration Factor

^cFiber optic-linear array detection spectrophotometry

^dGraphene Oxide

^eRotating disk sorptive extraction with a layer of polydimethylsiloxane

Comparison with other preconcentration methods

A comparison of the proposed method with other reported preconcentration methods for extraction of crystal violet is given in Table 5. As seen in Table 5, the LOD (1.8 µg L⁻¹), standard deviation (SD %) and contact time of the proposed method are comparable to or better than those of some previously reported preconcentration methods.

Conclusion

This study proved that SDS micelle-coated Fe₃O₄/SiO₂ nanoadsorbent, with average size of 30–40 nm, can act as an effective solid phase for the adsorption of crystal violet (CV) from water samples. This may be due to the strong electrostatic interactions between negatively charged SDS micelle-coated Fe₃O₄/SiO₂ nanoparticles and the positively charged dye under optimal conditions. One of the most important characteristics of the synthesized SDS micelle-coated Fe₃O₄/SiO₂ nanoadsorbent is its magnetically assisted separation of analytes from the aqueous sample solutions, while shorter analysis time can be achieved. On the other hand, the larger surface area of nanomaterials results in the higher adsorption capacity. So, lower amounts of SDS micelle-coated Fe₃O₄/SiO₂ nanoadsorbent are needed than those of other ordinary adsorbents and the extraction process was done in less time. Also, crystal violet was concentrated into low volume of eluting solution in a very short time. Therefore, fast removal and concentration of dye was performed via proposed method, in less than 10 min.

The SDS micelle-coated Fe₃O₄/SiO₂ NPs, as an efficient adsorbent, were used to remove the crystal violet dye from river water samples and the results proved the reliability of the proposed method.



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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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References

- Crini, G.: Non-conventional low-cost adsorbents for dye removal: a review. *Bioresour. Technol.* **97**, 1061–1085 (2006)
- Šafařík, I., Šafaříková, M.: Detection of low concentrations of malachite green and crystal violet in water. *Water Res.* **36**, 196–200 (2002)
- Sharma, A.K., Bhalla, P., Kaith, B.S., Bajaja, S., Bhatia, J.K., Panchal, S., Sharma, N., Tanwar, V.: Efficient capture of eosin yellow and crystal violet with high performance xanthan-acacia hybrid super-adsorbent optimized using response surface methodology. *Colloids Surf. B Biointerfaces* **175**, 314–323 (2019)
- Otero, M., Rozada, F., Calvo, L.F., Gracia, A.I., Morán, A.: Elimination of organic water pollutants using adsorbents obtained from sewage sludge. *Dyes Pigments* **57**, 55–65 (2003)
- Sadeghi, S., Nasehi, Z.: Simultaneous determination of brilliant green and crystal violet dyes in fish and water samples with dispersive liquid–liquid micro-extraction using ionic liquid followed by zero crossing first derivative spectrophotometric analysis method. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **201**, 134–142 (2018)
- An, L., Deng, J., Zhou, L., Li, H., Chen, F., Wang, H., Liu, Y.: 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**, 883–888 (2010)
- Al-Degs, Y.S., Sweileh, J.A.: Simultaneous determination of five commercial cationic dyes in stream waters using diatomite solid-phase extractant and multivariate calibration. *Arab. J. Chem.* **5**, 219–224 (2012)
- Manzo, V., Navarro, O., Honda, L., Sánchez, K., Toral, M.I., Richter, P.: Determination of crystal violet in water by direct solid phase spectrophotometry after rotating disk sorptive extraction. *Talanta* **106**, 305–308 (2013)
- Korn, M., Andrade, J., Jesus, D., Lemos, V., Bandeira, M., dos Santos, W., Bezerra, M., Amorim, F., Souza, A., Ferreira, S.: Separation and preconcentration procedures for the determination of lead using spectrometric techniques: a review. *Talanta* **69**, 16–24 (2006)
- Tian, M., Yan, H., Row, K.H.: Solid-phase extraction of tanshinones from *Salvia Miltiorrhiza* Bunge using ionic liquid modified silica sorbents. *J. Chromatogr B.* **877**, 738–742 (2009)
- Falaki, F., Fakhri, A.: Study of the adsorption of methyl orange from aqueous solution using nickel oxide nanoparticles: equilibrium and kinetics studies. *J. Phys. Theor. Chem.* **10**(2), 117–124 (2013)
- Falaki, F., Fakhri, A.: Adsorption properties of nickel oxide nanoparticles for removal of congo red from aqueous solution. *J. Phys. Theor. Chem.* **10**(4), 255–262 (2014)
- Helmi, H., Falaki, F., Karimi, M., Babaloi, F.: Highly facile removal of acid red 88 from aqueous samples by using synthesized iron oxide magnetic nanoparticles and 1-butyl-3-methylimidazolium tetrachloroferrate magnetic ionic liquid. *Desalin. Water Treat.* **90**, 331–340 (2017)
- Zhao, X., Shi, Y., Cai, Y., Mou, S.: Cetyltrimethylammonium bromide-coated magnetic nanoparticles for the preconcentration of phenolic compounds from environmental water samples. *Environ. Sci. Technol.* **42**, 1201–1206 (2008)
- Faraji, M., Yamini, Y., Rezaee, M.: Magnetic nanoparticles: synthesis, stabilization, functionalization, characterization, and applications. *J. Iran. Chem. Soc.* **7**, 1 (2010)
- Falaki, F., Berijani, S.: Aspartic acid-modified magnetic nanoparticles as an ideal sorbent for solid phase extraction of Pb in water samples prior to ICP-OES determination. *Desalin. Wat. Treat.* **57**, 25765–25772 (2016)
- Zhang, Z., Zhang, L., Chen, L., Chen, L., Wan, Q.H.: Synthesis of novel porous magnetic silica microspheres as adsorbents for isolation of genomic DNA. *Biotechnol. Prog.* **22**, 514–518 (2006)
- Zhu, L., Pan, D., Ding, L., Tang, F., Zhang, Q., Liu, Q., Yao, S.: Mixed hemimicelles SPE based on CTAB-coated Fe₃O₄/SiO₂ NPs for the determination of herbal bioactive constituents from biological samples. *Talanta* **80**, 1873–1880 (2010)
- Ezoddin, M., Shemirani, F., Abdi, Kh., Khosravi Saghezchi, M., Jamali, M.R.: Application of modified nano-alumina as a solid phase extraction sorbent for the preconcentration of Cd and Pb in water and herbal samples prior to flame atomic absorption spectrometry determination. *J. Hazard. Mater.* **178**, 900–905 (2010)
- Keyhanian, F., Shariati, S., Faraji, M., Hesabi, M.: Magnetite nanoparticles with surface modification for removal of methyl violet from aqueous solutions. *Arab. J. Chem.* **9**, S348–S354 (2016)
- Davudabadi Farahani, M., Shemirani, F.: Mixed hemi-micelle solid-phase extraction based on modified magnetic nanoparticles for extraction of cadmium and lead from food and water samples. *J. AOAC Int.* **97**(6), 1682–1688 (2014)
- Suyanta, Kunarti, E.S., Muzakir, M., Pertiwi, C., Pertiwi, D.: Comparative study of methods in the synthesis of magnetite (Fe₃O₄). In: *Proceedings of the International Conference on Research, Implementation and Education of Mathematics And Sciences 2014*, Yogyakarta State University, pp. 18–20 (2014)
- Ramimoghadam, D., Bin Hussein, M.Z., Taufiq-Yap, Y.H.: The effect of sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) on the properties of ZnO synthesized by hydrothermal method. *Int. J. Mol. Sci.* **13**, 13275–13293 (2012)
- Sharma, A.K., Bhalla, P., Kaith, B.S., Panchal, S., Bhatia, J.K., Bajaj, S., Tanwar, V., Sharma, N.: Response surface methodology directed synthesis of luminescent nanocomposite hydrogel for trapping anionic dyes. *J. Environ. Manag.* **231**, 380–390 (2019)
- Bhalla, P., Kaith, B.S., Shanker, U., Gupta, B.: One-pot green synthesis of polymeric nanocomposite: biodegradation studies and application in sorption-degradation of organic pollutants. *J. Environ. Manag.* **234**, 345–356 (2019)
- Sun, K., Liu, T., Zhang, Y., Liu, X., Wang, B., Xu, C.: Application and mechanism of anionic collector sodium dodecyl sulfate (SDS) in phosphate beneficiation. *Minerals* **7**(29), 1–13 (2017)
- Bavili Tabrizi, A., Dehghani Teymurlouie, N.: Application of sodium dodecyl sulfate coated iron oxide magnetic nanoparticles for the extraction and spectrofluorimetric determination of propranolol in different biological samples. *J. Mex. Chem. Soc.* **60**, 108–116 (2016)

28. Rahman, A.: Effect of pH on the critical micelle concentration of sodium dodecyl sulphate. *J. Appl. Polym. Sci.* **28**, 1331–1334 (1983)
29. Esmaeili-Shahri, E., Es'haghi, Z.: Superparamagnetic Fe₃O₄@SiO₂ core-shell composite nanoparticles for the mixed hemimicelle solid-phase extraction of benzodiazepines from hair and wastewater samples before high-performance liquid chromatography analysis. *J. Sep. Sci.* **38**, 4095–4104 (2015)
30. Shariati, S., Faraji, M., Yamini, Y., Rajabi, A.A.: Fe₃O₄ magnetic nanoparticles modified with sodium dodecyl sulfate for removal of safranin O dye from aqueous solutions. *Desalination* **270**, 160–165 (2011)
31. Ghanbari Adivi, F., Hashemi, P., Dadkhah Tehrani, A.: Agarose-coated Fe₃O₄@SiO₂ magnetic nanoparticles modified with sodium dodecyl sulfate, a new promising sorbent for fast adsorption/desorption of cationic drugs. *Polym. Bull.* **75**(3), 1239–1256 (2019)
32. Bagheri, H., Zandi, O., Aghakhani, A.: Extraction of fluoxetine from aquatic and urine samples using sodium dodecyl sulfate-coated iron oxide magnetic nanoparticles followed by spectrofluorimetric determination. *Anal. Chim. Acta* **716**, 61–65 (2012)
33. Tavakoli, M., Shemirani, F., Hajimahmoodi, M.: Magnetic mixed hemimicelles solid-phase extraction of three food colorants from real samples. *Food Anal. Methods* **7**, 100–108 (2014)
34. Dehghan Noudeh, G., Housaindokht, M., Fazly Bazzaz, B.S.: The effect of temperature on thermodynamic parameters of micellization of some surfactants. *J. Appl. Sci.* **7**, 47–52 (2007)
35. Zhao, X., Shi, Y., Wang, T., Cai, Y., Jiang, G.: Preparation of silica-magnetite nanoparticle mixed hemimicelle sorbents for extraction of several typical phenolic compounds from environmental water samples. *J. Chromatogr. A.* **1188**, 140–147 (2008)
36. Sharma, A.K., Bhalla, P., Kaith, B.S., Sharma, N., Bhatia, J.K., Tanwar, V., Panchal, S., Bajaj, S.: Selective removal of cationic dyes using response surface methodology optimized gum acacia sodium alginate blended superadsorbent. *Int. J. Biol. Macromol.* **124**, 331–345 (2019)
37. Azarkohan, A., Shemirani, F., Alvand, M.: Fast analysis of water samples for trace amount of crystal violet dye based on solid phase extraction using nanoporous SBA-3 prior to determination by fiber optic-linear array detection spectrophotometry. *J. Chem.* (accepted 28 Oct 2013)
38. Razi-Asrami, M., Ghasemi, J.B., Amiri, N., Sadeghi, S.J.: Simultaneous spectrophotometric determination of crystal violet and malachite green in water samples using partial least squares regression and central composite design after preconcentration by dispersive solid-phase extraction. *Environ. Monit. Assess.* **189**, 196 (2017)

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