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Preconcentration and spectrophotometric determination of oxymetholone in the presence of its main metabolite (mestanolone) using modified maghemite nanoparticles in urine sample

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ABSTRACT

A novel and sensitive extraction procedure using maghemite nanoparticles (γ-Fe_2O_3) modified with sodium dodecyl sulfate (SDS), as an efficient solid phase, was developed for removal, preconcentration and spectrophotometric determination of trace amounts of oxymetholone (OXM), in the presence of mestanolone (MSL). Combination of nanoparticle adsorption and easily magnetic separation was used for the extraction and desorption of OXM. The preparation of γ-Fe_2O_3 nanoparticles were obtained by co-precipitation method and their surfaces were modified by SDS. The size and properties of the produced γ-Fe_2O_3 nanoparticles were determined by X-ray diffraction analysis, FT-IR and scanning electron microscopy measurements. OXM and MSL became adsorbed at pH 3.0. The adsorbed drugs were then desorbed and determined spectrophotometrically using a selective complexation reaction for OXM. The calibration graph was linear in the range 15.0–3300.0 ng mL^{-1} of OXM with a correlation coefficient of 0.9948. The detection limit of the method for determination of OXM was 4.0 ng mL^{-1}. The method was applied for the determination of OXM in human urine samples.

1. Introduction

Oxymetholone (OXM) is a synthetic anabolic steroid; first described by Ringold et al. in 1959 [1]. Anabolic-androgenic steroids (AAS) represent an important class of abused drugs in sport, and are classified as prohibited substances according to World Anti-Doping Agency [2]. The main desired effects of these testosterone-derived compounds are their potential ability to improve physical performance of skeletal muscle and to balance catabolic condition in body after stress [3,4]. In addition, mediated mainly by their androgenic activity, the AAS have the potency also to cause serious health problems as side effects, e.g. cardiovascular or liver diseases [3].

OXM is known to be a potent marrow stimulant, particularly affecting red cell a lesser extent production of neutrophils and platelets output [5]. It has been used for the treatment of anemia caused by red cell production impairment [6], acquired or congenital aplastic anemia [7–9], myelofibrosis [10] and hypoplastic anemias associated with administration of myelotoxic drugs [11]. Actually, because of its anabolic properties, OXM has been studied for the treatment of HIV-associated wasting [12], antithrombin III deficiency [13], growth impairment in children [14], and damaged myocardium in heart failure [15], with varying degrees of success.

On the other hand, OXM is also used as a doping agent [16,17]. Intramuscular or deep subcutaneous injection is the principal route of administration of all the anabolic steroids except the 17-α-substituted steroids as OXM, which are active, orally [18]. This is feasible because substitution at the 17-carbon protects the compound from the rapid hepatic metabolism. Many side-effects have reportedly been associated with chronic use of high doses of all oral anabolic-androgenic hormones including OXM: high blood pressure, water retention, prostate gland enlargement, gynecomastia (abnormal breast tissue growth in males) and liver damage. OXM is the anabolic steroid most associated with premature hair loss [16].

Doping control analyses of anabolic steroids have been mainly carried out on urine because in general it contains relatively high concentrations of the drugs and/or their metabolites. Testing for anabolic steroids in urine samples is mainly carried out by gas chromatography with mass spectrometry (GC–MS) [19–25] and liquid chromatography with tandem mass spectrometry (LC–MS–MS) [26–31]. Gas or liquid chromatography coupled with mass spectrometry has produced accurate and sensitive assays, but chromatographic separations require time. To avoid such tedious and

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lengthy procedures, vacuum matrix-assisted laser desorption ionization coupled with the linear ion trap mass spectrometry technique has been tested for its applicability as a rapid screening technique [32]. In addition, most of the above methods generally require time-consuming sample preparation procedures, such as liquid–liquid extraction or solid phase extraction (SPE) to remove the coexisting substances in urine samples prior to analysis.

Solid phase extraction (SPE) is widely used for the extraction and preconcentration of analytes in various environmental, food and biological samples [33]. Being convenient, simple, fast, and cheap has made it the most popular clean-up technique. It is also the most accepted sample pretreatment method today [34,35]. At present, there are several types of sorbents for SPE including normal-phase, reversed-phase, ionic, and other special sorbents. In addition, due to their unsatisfactory selectivity, these traditional sorbents usually cannot separate analytes efficiently in complex biological or environmental samples [36].

The quest for new adsorbents is an important factor in improving analytical sensitivity and precision in SPE techniques. To date, many adsorbents, such as active carbon [37], modified resin [38], nanometer-sized materials [39], and fullerene [40], have been employed in SPE. These adsorbents are normally modified by attaching organic and inorganic molecules to their surface. Magnetic nanoparticles are widely used for the effective adsorption of different chemical species from water samples [41–45]. Magnetic nanoparticles are widely used in the field of biotechnology and biomedicine [46–49]. These particles are superparamagnetic, which means they are attracted to a magnetic field, but retain no residual magnetism after the field is removed. Therefore, the suspended superparamagnetic particles which are attached to the target can be removed very quickly from a matrix using a magnetic field, but they do not agglomerate after removal from the field.

In the present paper sodium dodecyl sulfate (SDS) modified maghemite nanoparticles were employed for preconcentration of OXM in the presence of MSL, followed by spectrophotometric determination of OMX, after its complexation with Fe(III) in acetonitrile medium. The technique was found to be very useful and cost effective for a better preconcentration and determination of OXM.

2. Experimental

2.1. Reagents and materials

Oxymetholone (USP) and mestanolone (USP) were purchased from (Alborz Bulk Pharmaceutical Co., Iran). All other chemical were of analytical reagent grade available from Merck Company (Darmstadt, Germany) and double distilled water (DDW) was used throughout the study. Scheme 1 shows the structure of the investigated drugs. Stock solutions of drug were prepared by dissolving the powder in methanol and storing it at −20 °C. Drug solutions of different initial concentrations were prepared by diluting the stock solution in appropriate proportions with DDW.

2.2. Apparatus

The size, morphology, and structure of the nanoparticles were characterized by scanning electron microscope (SEM-EDX, XL30, Philips Netherland). 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 Metrohm model 713 pH-meter was used for pH measurements. A single beam UV-mini-WPA spectrophotometer was used for the determination of OXM concentration in the solutions. The mid-infrared spectra of γ-Fe_2O_3, SDS and SDS coated maghemite nanoparticles in the region 4000–400 cm^{-1} were recorded using a Perkin-Elmer FT-IR spectrometer (KBr pellets) Model spectrum GX. A 40 kHz universal ultrasonic cleaner with water bath (RoHS, Korea) was used.

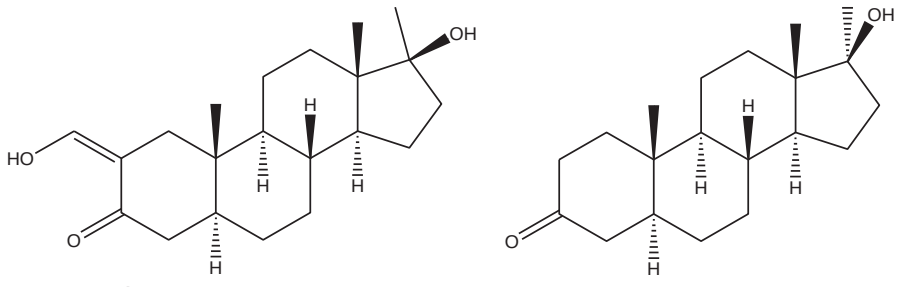
2.3. Synthesis of maghemite nanoparticles (MNPs) and SDS coated maghemite nanoparticles (SDSMNPs)

MNPs were prepared according to the previously reported procedure [50]. SDS coated maghemite nanoparticles (SDSMNPs) were prepared by adding 1.0 mL of 5% (w/v) SDS solution to about 0.1 g of nanoparticles in a beaker. The solution was stirred vigorously for 60 s by a glassy rod and the beaker was then placed on the magnet. After complete precipitation of MNPs, the solution was decanted and modified nanoparticles were washed with DDW four times to eliminate extra amounts of surfactant from nanoparticles.

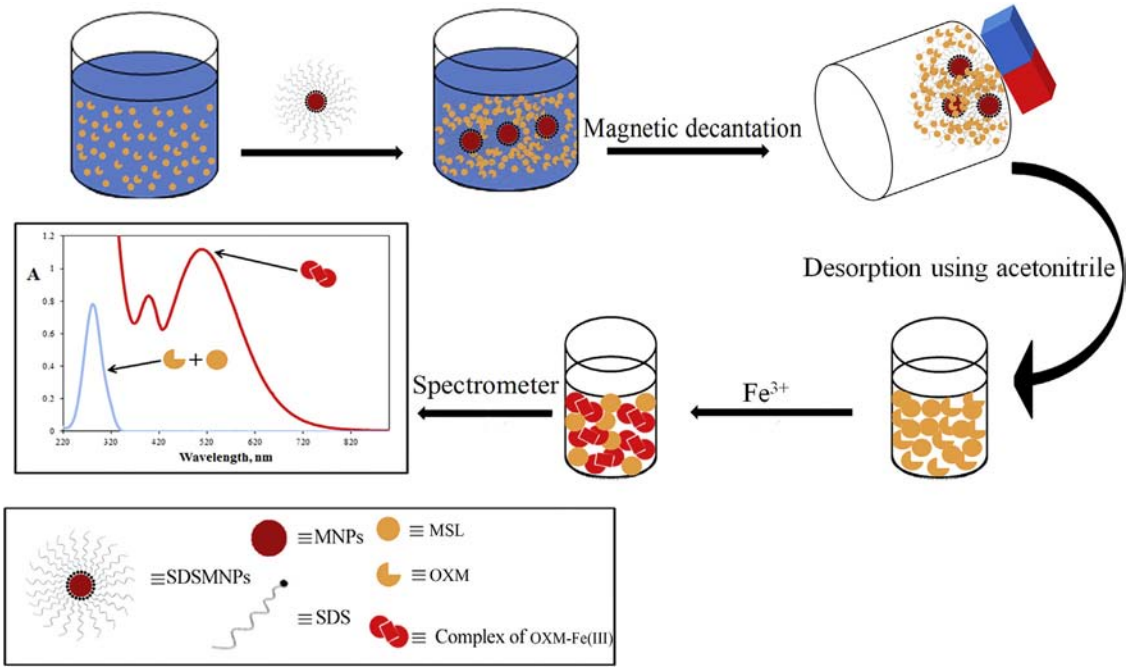
2.4. Recommended procedure

Adsorption studies were performed by adding 25.0 mL of the solution containing 15.0–3300.0 ng mL^{-1} of OXM to 0.05 g of SDSMNPs in a beaker. The pH of the solutions and SDSMNPs 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 30 min. The concentration of OXM decreased with time due to its adsorption by SDSMNPs. Then OXM loaded nanoparticles were separated with magnetic decantation. Desorption process was performed on loaded nanoparticles with 2.0 mL of pure acetonitrile. The concentration of OXM in the solution was then determined after complexation reaction of OXM with Fe^{3+} ions (3.0 mL of 0.01 M of Fe^{3+}) spectrophotometrically at 530 nm (λ_{max} for complex between OXM and Fe^{3+}). A summary of the above procedure is shown schematically in Scheme 2. The adsorption percent, i.e. the drug removal percentage, was determined using the following expression:

$$\%\mathrm{Re} = [(C_o - C_t)/C_o] \times 100 \quad (1)$$



Scheme 1. Structure of investigated drugs.



Scheme 2. Proposed procedure schematic.

where C_o and C_t represent the initial and final (after adsorption) concentration of drug in mg L^{-1}, respectively. All the experiments were performed at room temperature.

2.5. Real sample treatment

The urine samples were collected from three adult volunteers (non-supplemented diet) who participated in this study. The urine samples were collected in disposable polypropylene specimen cups that were rinsed with DDW before use. The samples of 2.0 mL of homogenized urine samples in flasks (50 mL in capacity) were taken. The digestion procedure was carried out by heating the samples at 80 °C for 1 h after the addition of 10 mL concentrated HNO_3 and 2 mL of 70% $HClO_4$. The content of the flasks was diluted with deionized water and filtered through a Whatman no. 4 filter paper into a 25 mL calibrated flask and its pH was adjusted to desired value [51]. Then the procedure as given in the above section was followed.

3. Results and discussion

3.1. Determination of the optimal chemical conditions for OXM complexation

Fig. 1 shows UV–vis spectra of OXM (in acetonitrile solvent) in the absence and presence of Fe(III) cation (Fig. 1a). As can be seen, OXM formed a stable colored complex with ferric ion, whereas we find that MSL did not form such a complex. This matter is the base of selective determination of OXM in the presence of MSL. The effect of presence of MSL on complexation of OXM with Fe^{3+} ions was studied using the addition of equivalent amount of MSL to a mixture of OXM and Fe^{3+} ions (Fig. 1b). The result showed that MSL has no considerable effect on the complexation process.

The optimal chemical conditions (pH and Fe^{3+}/OXM ratio) for the formation of OXM–Fe(III) complex were determined in a mixture of acetonitrile/water solvent (40:60 v/v%). In particular, an optimal pH value of < 3.0 was obtained for OXM complexation, while decomplexation happened at pHs > 4.0. At pH < 3.0, the predominant form of OXM is its neutral form (pK_a for OXM is 4.5 [52]) and interaction of its hydroxyl and carbonyl groups with ferric cations is at the highest level (Scheme 3). Furthermore, at pH > 3 ferric cations precipitated in the form of hydroxide species [53].

It is most conveniently studied by Job's method of continuous variations. The Job's diagram for the complexation of OXM with Fe^{3+} was obtained by plotting the absorbance variation of OXM–Fe^{3+} vs. mole fraction of Fe^{3+} at 530 nm. Fig. 2 shows the Job's diagram for OXM–Fe(III) system in acetonitrile. The plot consists of two straight lines intersecting at mole fraction of Fe^{3+} equal to 0.33, as is typically the case when only a 1:2 complex (Fe(III):OXM) is formed [54].

3.2. Characterization of the adsorbent

The SEM image of the SDS-coated nanoparticles, as shown in Fig. 3, revealed that the diameter of synthesized nanoparticles were around 25–40 nm. The typical XRD profile of synthesized nanoparticles is shown in Fig. 4. The crystallite size was obtained around 11.3 nm from the XRD pattern according to Scherrer equation [55]. As the results show, the particle dimension obtained by SEM is higher than the corresponding crystallite size. This difference may be explained by the presence of aggregates in SEM grain, consisting of several crystallites and/or poor crystallinity [55].

The FT-IR spectra of MNPs, SDS and SDSMNPs are presented in Fig. 5a-c respectively. The characteristic absorption band of Fe–O in γ-Fe_2O_3 (around 580 cm^{-1}) is observed in Fig. 5a and c. New absorption peak at almost 1250 cm^{-1} is observed in Fig. 5c, that was attributed to S=O groups of SDS (in accordance with Fig. 5b) in final product. Moreover, new absorption peaks at 2919 and 2851 cm^{-1} are assigned to stretching mode of the aliphatic C–H groups of SDS (in accordance with Fig. 5b).

Based on the above results, it can be concluded that the fabrication procedure (in Section 2.3) has been successfully performed.

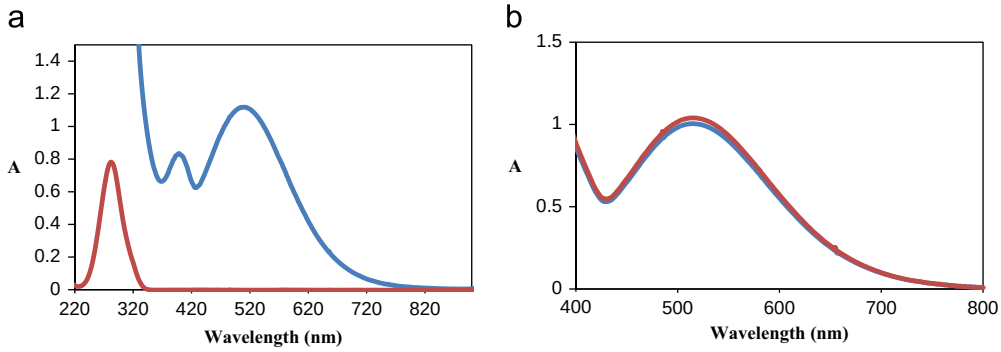
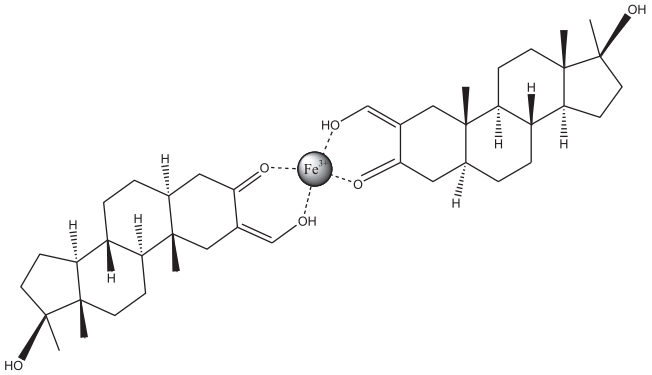


Fig. 1. UV–vis spectra of (a) OXM in the absence (red line) and presence of Fe(III) cation (blue line) and (b) OXM–Fe(III) complex in the absence (blue line) and presence of MSL (red line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Scheme 3. Expectance structure of OXM–Fe(III) complex.

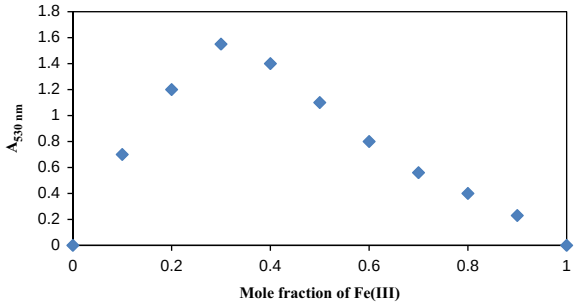


Fig. 2. Job's diagram for OXM–Fe(III) system in acetonitrile at pH 2.5, $\lambda = 530$ nm.

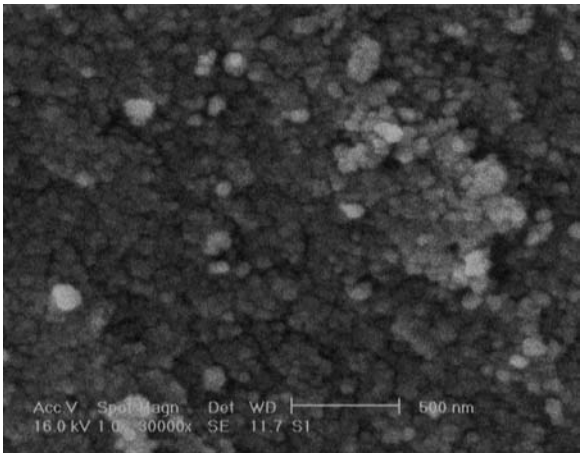


Fig. 3. SEM image of SDS-coated nanoparticles.

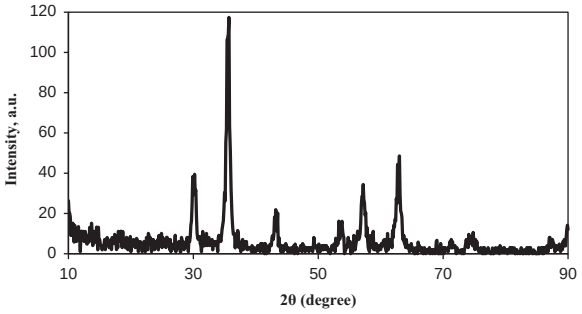


Fig. 4. XRD patterns of the SDSMNPs nanoparticles.

3.3. *Effect of SDS*

The surfaces of metal oxides (γ-Fe_2O_3 suspension) are generally covered with hydroxyl groups that vary in forms at different pHs. Below the pH of zero point charge, pHzpc, that is around 6.3 for maghemite nanoparticles [56], the adsorbent surface is positively charged and hydrophilic. Anionic surfactants such as SDS molecules will adsorb onto the surface of maghemite through the negative moiety of sulfate and make the surface of adsorbent hydrophobic. The drugs could be trapped into the aggregates of SDS on adsorbent [56]. In order to optimize the amount of SDS for coating nanoparticles, different volumes of 5% (w/v) SDS solution were tested and a volume of 3.0 mL of 5% (w/v) SDS was chosen as the most suitable.

3.4. *Effect of adsorbent dosage on drug adsorption*

The adsorbent dosage is an important parameter in adsorption studies because it determines the capacity of adsorbent for a given initial concentration of drug solution. The adsorption percentage increased with the increase in the dosage of SDSMNPs; in addition, the adsorption capacity dropped as the SDSMNPs dosage increased. Increasing the SDSMNPs dosage increases the probability of the SDSMNPs entanglement in the solution, causing adsorption in the interlayer space, and a decrease in the aggregation of drug at the external surface. Accordingly, the adsorption capacity declined as the SDSMNPs dosage increased. Moreover, the high SDSMNPs dosage may influence the physical characteristics of the solid–liquid suspensions, such as increasing the viscosity and inhibiting the diffusion of dye molecules to the surface of the SDSMNPs. Since the concentrations of drug were fixed, the adsorption capacity decreased as the SDSMNPs dosage increased. The increase with SDSMNPs dosage of the amount of drug adsorbed was caused by the availability of more surface area of the SDSMNPs [57].

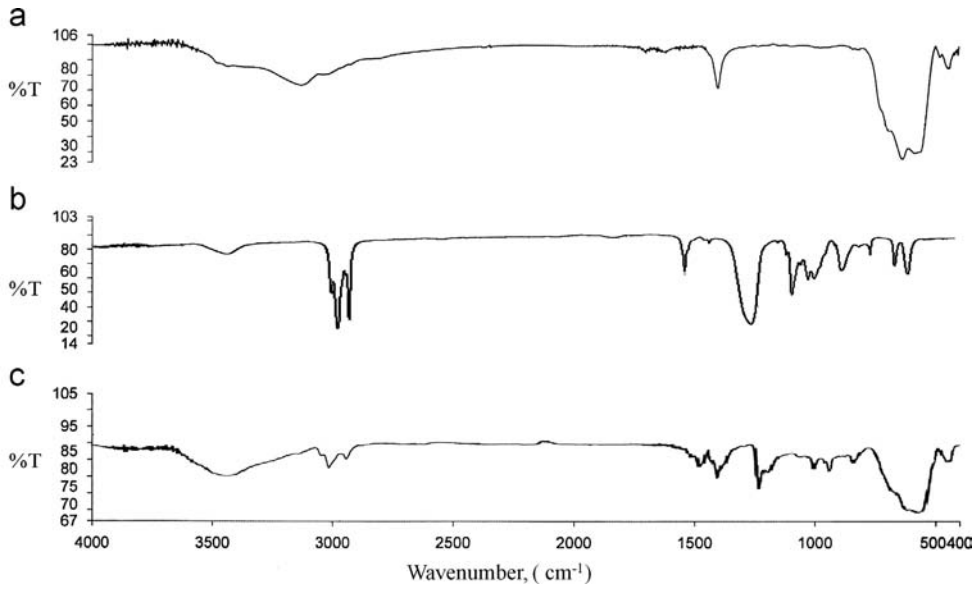


Fig. 5. The FT-IR spectra for (a) MNPs, (b) SDS and (c) SDSMNPs.

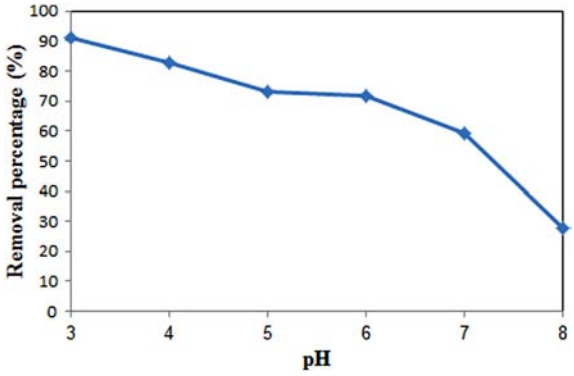


Fig. 6. Removal percent of OXM at different pHs (conditions: 0.05 g of SDSMNPs, 25 mL of 33.0 mg L^{-1} of OXM, agitation time of 30 min).

3.5. Effect of pH and contact time

Solution pH is an important parameter that affects the adsorption process of the drug. The solution pH would affect both aqueous chemistry and surface binding-sites of the adsorbent. The effect of pH in the range of 3.0–8.0 with a stirring time of 30 min on the removal of drug was investigated using 0.1 mol L^{-1} HCl or NaOH solutions for pH adjustment, with the initial drug concentration fixed at 33.0 mg L^{-1}.

As Fig. 6 shows, the percentage of adsorption decreases by increasing the pH. Therefore, pH 3.0 was selected for further experiments. At pH 3.0, neutral form of OXM shows its predominant form in the solution. Its interaction with hydrophobic moieties of SDS is also maximized. At higher pHs, the decrease in the positive charge of adsorbent surface sites can cause a decrease in the adsorption of SDS.

The effect of contact time on the adsorption of OXM was studied to determine the time taken by SDSMNPs to remove OXM from a 33.0 mg L^{-1} solution at pH 3.0. A 0.05 g of SDSMNPs was added into a 25.0 mL of 33.0 mg L^{-1} drug solution. Absorbance of the solution at related wavelength of drug with time was determined to monitor the drug concentration. It can be seen that after about 30 min, almost all the drug became adsorbed. Agitation time of 30 min was then selected for further works.

3.6. Reusability and desorption solvent

The reusability and stability of SDSMNPs for the extraction of OXM was assessed by performing five consecutive separations/desorption cycles under the optimized conditions. Desorption of OXM from the adsorbent was performed with 2.0 mL of pure acetonitrile as described in Section 2.4. There was no significant change in the performance of the adsorbent during these cycles, indicating that the fabricated SDSMNPs is a reusable and stable solid phase sorbent for the extraction of OXM.

3.7. 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 15.0–3300.0 ng mL^{-1} for a sample volume of 25.0 mL. The calibration equation is

$$A = 4.0 \times 10^{-5} C + 0.007$$

with a correlation coefficient of 0.9948 ($n=10$), where A is the absorbance change of the Fe^{3+}–OXM complex at 530 nm and C is the concentration of OXM in the sample solution in ng mL^{-1}. The limit of detection, defined as LOD$=3S_b/m$, was obtained as 4.0 ng mL^{-1} of OXM; where LOD, S_b and m are the limit of detection, standard deviation of the blank and the slope of the calibration graph, respectively. The relative standard deviation (R.S.D.) for 1.0 and 2.5 mg L^{-1} of OXM was 1.65% ($n=3$) and 0.77% ($n=3$), respectively. As the amount of OXM in 25.0 mL of the solution was concentrated to 2.0 mL of acetonitrile, a preconcentration factor of 12.5 was achieved in this method. In order to evaluate the analytical applicability of the proposed method, it was applied to the determination of OXM, in the absence and presence of MSL, in human urine sample. The urine sample was analyzed after spiking by different amounts of OXM and MSL to it. The results are given in Table 1 that show good recoveries were obtained from the procedure. Moreover, presence of MSL has no considerable effect on the determination of OXM. The obtained recoveries were in ranges of 97.0–106.1%.

Table 1
Assay of OXM in human urine samples by means of the proposed method.

Spiked value of OXM (ng mL^{-1})	Spiked value of MSL (ng mL^{-1})	Found (ng mL^{-1})	Recovery percent of OXM
166.0	–	162.3	97.8
166.0	100.0	161.1	97.0
250.0	–	245.7	98.3
250.0	150.0	243.6	97.4
266.0	–	274.0	103.0
266.0	200.0	262.1	98.5
1000.0	–	1060.6	106.1

4. Conclusions

A simple, sensitive and selective method was developed for the spectrophotometric determination of OXM in the presence of its main metabolite after preconcentration using SDS coated maghemite nanoparticles. To the best of our knowledge, this is the first report on the application of modified nanoparticles to the determination of oxymetholone. The present method has following advantages over reported methods. Synthesized adsorbent is distinct in terms of sensitivity and selectivity towards the investigated drug. In addition, these magnetic nanoparticles carrying the target drug could be easily separated from the aqueous solution simply by applying an external magnetic field; no filtration or centrifugation was necessary. Furthermore, the proposed method gives an efficient and cost effective method with very low detection limits and good relative standard deviation; and can be applied to the determination of traces of OXM in human urine samples.

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