Extraction and preconcentration of diclofenac through adsolubilisation process using magnetic nanoparticles adsorbent prior to its spectrophotometric determination

Sohrab Ershad[1], Akbar Razmara[1], Kamyar Pourghazi[2], Mitra Amoli-Diva[1,2]

[1]*Department of Chemistry, Faculty of Science, Payam Noor University, P.O. Box 19395-3697, Tehran, Iran*
[2]*Faculty of Chemistry, Kharazmi (Tarbiat Moallem) University, Tehran, Iran*
E-mail: Sohrabsd@yahoo.com

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A novel, fast and sensitive method based on cetyltrimethyl ammonium bromide-coated Fe_3O_4 nanoparticles as an efficient adsorbent was developed for solid-phase extraction of diclofenac. The unique properties of magnetic nanoparticles (MNPs) including high surface area and superparamagnetism give the method the advantages of high extraction capacity, fast separation and low consumption of the adsorbent. The main parameters affecting extraction and desorption efficiency, such as the amount of surfactant, pH of the sample solution, desorption conditions, breakthrough volume, amount of MNPs, extraction and desorption times, and ionic strength, were investigated and optimised. Under optimum conditions, the method was successfully applied to determine the analyte and good linearity in the range of 50–1400 ng mL^{-1} ($r^2 = 0.9998$) was achieved with a low detection limit of 15 ng mL^{-1}. The relative standard deviations of 2.76 and 1.73% (for a concentration of 50 and 500 ng mL^{-1}, respectively) and a high enrichment factor of 98 were obtained. The method was successfully applied for the determination of diclofenac from spiked human plasma and urine samples and good recoveries in the range of 96–101% were obtained.

1. Introduction: Diclofenac (2-[2-(2,6-dichlorophenyl) aminophenyl] ethanoic acid) (Fig. 1) is one of the most widely used non-steroidal anti-inflammatory drugs (NSAIDs) with analgesic, antipyretic and anti-inflammatory effects [1] and it is usually found as sodium or potassium salt [2]. As an analgesic, it has fast onset and long duration of action [3]. Compared with the other NSAIDs, it is well tolerated and rarely produces gastrointestinal ulceration or other serious side effects. Thus, it can be considered as one of the few NSAIDs of 'first choice' in the treatment of chronic painful and inflammatory conditions [4].

The extensive clinical use of diclofenac triggered our interest in the determination of this drug by a sensitive, simple and rapid technique. Several methods have been reported for the determination of diclofenac in pharmaceutical preparations or biological fluids, such as high-performance liquid chromatography (HPLC) [5–8], spectrophotometry [9], high-performance thin layer chromatography [10], capillary zone electrophoresis [11] and electrochemical detections [12–14]. Most of the reported methods suffer from disadvantages, such as being laborious, time-consuming, having a long response time, the requirement of expensive instruments and low detection capability. On the other hand, a sample pretreatment procedure is usually needed when traces of the drug must be determined in complex matrices, such as biological fluids.

In the past few years, a new solid phase extraction (SPE) method based on the adsorption of surfactant at the solid–liquid interface was developed [15]. Surfactant molecules form bilayer aggregates named mixed hemimicelles (hemimicelles and admicelles) under certain conditions which are similar to Langmuir-Blodgett films; but these aggregates are stable equilibrium structures that are easily formed on a wide variety of surfaces, even porous or heterogeneous materials [16]. Adsolubilisation is a phenomenon by which species at low concentrations in an aqueous solution dissolve within the organic interior of admicelles. Since the outer surface of hemimicelles is hydrophobic whereas that of admicelles is ionic, they can provide two-fold mechanisms for the retention of analytes [17, 18]. This technique has many advantages, such as high extraction efficiency, easy elution of analytes, high breakthrough volume and no clean-up steps [19–21].

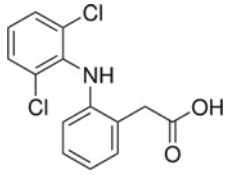

Figure 1 *Structure of diclofenac*

Recently, magnetic nanoparticles (MNPs) have been recognised as new adsorbents with large surface areas and small diffusion resistance [22]. These nanostructured materials possess a high surface area and superparamagnetic properties, which can provide higher capacity, rapid extraction and ease of separation for large volume samples by applying a strong external magnet [23]. So far, only a few SPE procedures based on surfactant-coated Fe_3O_4 nanoparticles have been reported in the analysis of drugs in different matrices [23–25] and, to the best of our knowledge, neither magnetic separation nor the mixed hemimicelles SPE method has yet been applied for the determination of diclofenac in biological samples.

In the work reported in this Letter, we established a mixed hemimicelles SPE procedure based on the adsorption of cetyltrimethyl ammonium bromide onto the surface of Fe_3O_4 MNPs. The adsorbent possesses the advantages of both mixed hemimicelles and MNPs and was used for the determination of diclofenac from biological fluids. The predominant factors affecting the extraction efficiency were studied and the method was successfully applied to the extraction and preconcentration of diclofenac from plasma and urine samples.

2. Experimental

2.1. Chemicals and reagents: All reagents were of analytical grade and used as supplied. Ferrous chloride tetra hydrate ($FeCl_2{\cdot}4H_2O$), ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), sodium chloride, cetyltrimethyl ammonium bromide and glycerol were purchased from Merck (Darmstadt, Germany). Diclofenac standard was obtained from the Center of Quality Control of Drugs, Tehran, Iran. A stock standard solution of the drug (20 µg mL^{-1}) was prepared by dissolving appropriate amounts of diclofenac in deionised water. This solution was replaced every week to

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prevent decomposition of the drug. The working standard solutions were prepared daily by appropriately diluting the stock solution with deionised water.

2.2. Instrumentation: The UV–Vis spectra of the solutions were carried out using a UV-240 Shimadzu (Tokyo, Japan) UV–Vis spectrophotometer equipped with 0.5 × 1 cm quartz cell. Spectra recording was carried out in absorbance mode in the absorption wavelength of 280 nm. A Metrohm 827 pH meter (Herisau, Switzerland) with a combined glass electrode was used for the pH measurements. The liquid chromatographic system was carried out using an Acme 9000 (Young Lin, Anyang, Korea) equipped with a Young Lin SP930D pump and a UV–Vis 730D detector. An L1-ODS-1 column (5 µm, 250 × 4.6 mm) was utilised with the injection volume set to 20 µL. The mobile phase consisted of methanol–water containing 0.1% glacial acetic acid (50:30 v/v) at a flow rate of 2 mL min^{-1} with the isocratic elution. The UV detection of diclofenac was performed at 280 nm. A CM30 transmission electron microscope (TEM) (Phillips, Amsterdam, The Netherlands) was used to characterise the particle size and morphology of the nanoparticles. Phase characterisation of MNPs was performed by an APD-2000 X-ray diffractometer (XRD) (Riva Del Garda, Italy) using a Cu Kα radiation source ($\lambda = 1.54059$ Å). The Fourier transform infrared spectroscopy (FTIR) spectrum of the prepared MNPs was carried out by a WQF-510A FTIR spectrometer (Rayleigh, Beijing, China) in the range of 400–4000 cm^{-1} for samples dispersed in KBr. Size distribution of CTAB-coated MNPs was performed on a hydrosol nanoparticle size analyser and a zeta potential analyser (Malvern, UK) which is based on the dynamic light scattering (DLS) technique.

2.3. Synthesis of MNPs: MNPs were synthesised according to the procedure described previously [26]. Briefly, 11.68 g of $FeCl_3 \cdot 6H_2O$ and 4.30 g of $FeCl_2 \cdot 4H_2O$ were transferred into a 250 mL round bottom flask and dissolved in 200 mL of deionised water under nitrogen atmosphere at 85°C. Then, 45 mL of 25% (w/w) ammonia solution was added. The orange colour of the solution turned to black immediately. After cooling down to room temperature, the suspension was collected at the bottom of the flask using an external magnate and rinsed sequentially with deionised water (3 × 200 mL), 0.02 M NaCl (2 × 100 mL) and again with deionised water (2 × 200 mL). The prepared magnetic suspension was then stored at a concentration of 20 mg mL^{-1} at 4°C until use.

2.4. Recommended SPE procedure: The mixed hemimicelles SPE procedure was carried out in a batch mode as follows: 200 mL of sample solution containing 100 µg of diclofenac was placed in a 250 mL beaker and the pH was adjusted to about 10 with 1.0 M NaOH solution. To prepare CTAB-coated MNPs assemblies, 2.5 mL of MNPs (20 mg mL^{-1}) was added to 5 mL of 5 mg mL^{-1} CTAB solution. The mixture was stirred for 2 min and added into the sample solution. The suspension was diluted to 200 mL and stirred for 5 min to facilitate the adsorption of the target analyte. Then, the adsorbent was isolated by applying an external supermagnet on the bottom of the beaker and the supernatant was poured out. The adsorbed analyte was eluted with 2 × 1 mL of methanol. The concentration of diclofenac was determined using the UV absorbance of the eluate at 280 nm. A blank solution was also run under the same conditions without adding the drug.

2.5. Sample preparation: Human plasma from seven healthy male volunteers aged between 28 and 32 years were obtained from the Iranian Blood Transfusion Organisation. The urine samples were collected from five healthy male volunteers aged between 24 and 32 years and stored at −18°C. For the analysis, the samples were placed in an oven at 37°C for 3 h and then centrifuged at 3000 rpm for 10 min. A measure of 20 mL of each sample was spiked with appropriate amounts of diclofenac stock solution and diluted to 200 mL after adjusting the pH. Then, the proposed mixed hemimicelles SPE procedure was performed under optimum conditions.

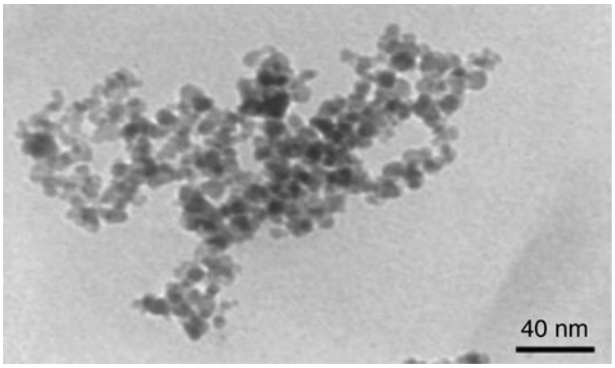

Figure 2 *TEM image of the prepared MNPs adsorbent*

3. Results and discussion

3.1. Characterisation of Fe_3O_4 nanoparticles: Fig. 2 shows the TEM image of the prepared Fe_3O_4 nanoparticles and indicates the particles are relatively uniform with a mean diameter of 7.4 ± 1.6 nm. The XRD pattern of MNPs is represented in Fig. 3. As can be seen, the pattern displays reflection peaks in peak positions (2θ) of 30.4, 35.7, 43.4, 53.5, 57.3 and 62.7 which were related to the diffraction planes of 220, 311, 400, 422, 511 and 440, respectively. This pattern does match well with those from the Joint Committee on Powder Diffraction Standards (JCPDS Card, File No. 19-0629) for magnetite. The specific surface area was determined using the Brunauer-Emmett-Teller (BET) equation applied to the adsorption data on nitrogen adsorption/desorption experiments. The results of the BET method have shown that the average specific surface area of magnetite nanoparticles was 64.1 $m^2 g^{-1}$. It can be concluded from these values that this type of adsorbent is nanoparticles with relatively large specific surface area. Furthermore, the size and size distribution of CTAB-coated MNPs were estimated by the DLS technique. Fig. 4 shows the scattering intensity distribution of CTAB-coated MNPs dispersed in ultrapure water at room temperature. The pH of this solution was 10. As can be seen, the average hydrodynamic size determined from the DLS data was about 50 nm. The hydrodynamic diameters were larger than those obtained from TEM images, which is due to the partial agglomeration of MNPs in an aqueous solution.

3.2. Mixed hemimicelle-based SPE

3.2.1 Effect of the amount of surfactant: The surfaces of Fe_3O_4 nanoparticles are generally covered with hydroxyl groups which vary in form at different pHs. Magnetite nanoparticles are negatively charged when the pH is higher than the pH of the point of zero

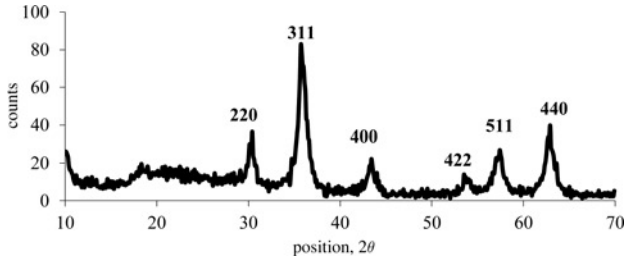

Figure 3 *XRD pattern of the prepared MNPs adsorbent*

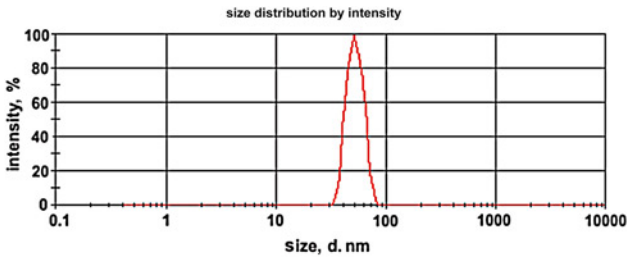

Figure 4 *Particle size distribution of CTAB-coated MNPs measured by DLS*

charge (pH_{pzc}), which is reported to be 6.05 previously [23, 25, 27] for Fe_3O_4 MNPs. Therefore, the adsorption of diclofenac ions onto the adsorbent surface does not occur. On the other hand, cationic surfactants such as CTAB will adsorb onto the surface of MNPs through the positive ammonium moiety in this pH and make the surface of the adsorbent hydrophobic. Further addition of CTAB can form mixed hemimicelle aggregates and causes the adsorption of the analyte. So the effect of the amount of surfactant on the adsolubilisation of diclofenac was studied in batch mode. As can be seen from Fig. 5*a*, the adsolubilisation of the analyte was increased remarkably with increase in the amount of CTAB in the range of 15 mg and then it increased gradually till 25 mg. When the added amount of CTAB exceeded 25 mg, adsolubilisation decreased gradually. This can be explained by the gradual formation of micelles which causes the analyte to redistribute in the bulk solution. Therefore the amount of 25 mg of CTAB was used for the next experiments.

3.2.2 Effect of solution pH: The surface charge of Fe_3O_4 nanoparticles is pH dependent. Hence, pH is one of the important influencing factors on the adsolubilisation behaviour of a mixed hemimicelle system. In this work the effect of pH was studied by varying the pH in the range of 4–12. As can be seen from Fig. 5*b*, the CTAB-coated MNPs do not exhibit obvious adsorption when the pH value is below 6. This may be explained by the fact that the MNPs have a positive charge below the pH_{pzc} and efficient interaction does not occur between the MNPs and CTAB molecules. When the pH value reaches above the pH_{pzc}, the adsorption efficiency of the analyte increased dramatically and reached maximum at pH 10. Therefore, a pH value of 10 was chosen as an optimum value for subsequent experiments.

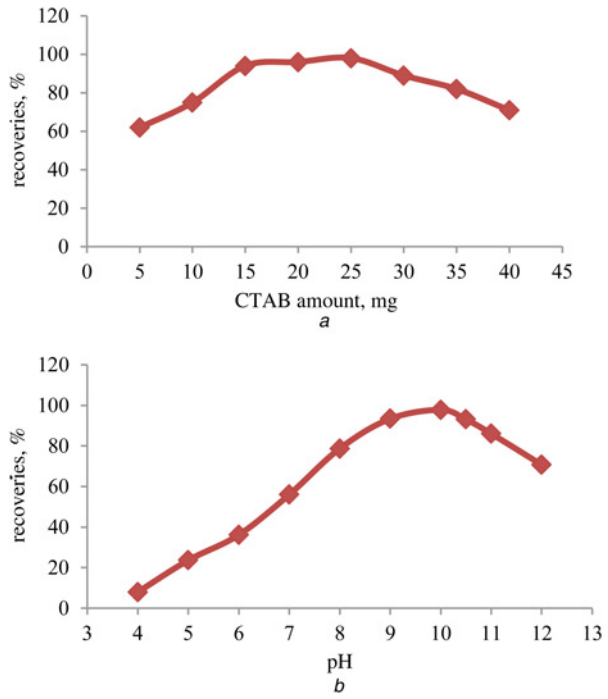

Figure 5 *Effect of the amount of CTAB and pH on the recovery of the analyte*
a CTAB
b pH
Sample volume; 200 mL, diclofenac concentration; 500 ng mL^{-1} and amount of the MNPs; 50 mg

3.2.3 Desorption conditions: Organic solvents are known to disrupt the surfactant aggregates (such as mixed hemimicelle systems). Thus, the desorption of diclofenac was investigated using different solvents including methanol, acetonitrile, acetone and 1.0 M HNO_3. Experimental results have revealed that 1.0 M HNO_3 oxidised the Fe_3O_4 nanoparticles and lost magnetisation. On the other hand, CTAB-coated MNPs exhibited a relatively low degree of dispersion in acetone causing less analyte desorption. Satisfactory recoveries (98%) were obtained using 2 × 1 mL of methanol as a desorbing solvent and higher volumes of acetonitrile (about 8.0 mL) was required for desorbing the analyte with the same recoveries. Thus, 2 mL of methanol was selected for subsequent experiments.

3.2.4 Sample volume: Breakthrough volume is a key parameter in any SPE procedure. The breakthrough volume for diclofenac was determined using a series of different volumes (50–300 mL) of aqueous solution containing 100 µg of the analyte. A measure of 50 mg Fe_3O_4 nanoparticles and 25 mg CTAB were added to each sample. The results indicate that the quantitative recoveries were obtained with sample volumes of up to 200 mL and above this amount it was decreased because the higher sample volumes cause the analyte loss from the adsorbent surface. Thus, a sample volume of 200 mL was selected as the optimum volume for the next studies.

3.2.5 Extraction and desorption time: The extraction and desorption time profiles were investigated by varying the mixing time of the magnetic adsorbent with sample solution/desorbing solvent in the range of 1–20 min. The experimental results reveal that 5 min was sufficient for satisfactory extraction and 3 min was enough for complete desorption of the analyte. The high surface area of MNPs, rapid dynamic process and homogeneous distribution of nanoadsorbent throughout the sample can be the possible reasons for obtaining such a fast SPE procedure. In a word, a complete SPE process can be performed in <30 min.

3.2.6 Effect of the MNPs amount: The required amount of MNPs for the complete separation and recovery of diclofenac in 200 mL of solution containing 100 µg of the analyte at pH 10 was studied in the range of 10–100 mg. Experimental results indicated that maximum recoveries were obtained when the amount of MNPs was 50 mg. This lower amount of adsorbent compared with the traditional SPE sorbents is because of the high surface area of nanoparticles and MNPs amount of 50 mg was used for subsequent experiments.

3.2.7 Effect of ionic strength: The ionic strength of the working solution was studied by varying the NaCl concentration in the range of 0–0.02 M. The results indicate that the extracted amount of diclofenac decreased with an increase in the ionic strength of the solution. This observation indicates that electrostatic interaction has an important role in the adsorption process and competition of sodium ions with CTAB cations for the negative surface of MNPs can cause abatement of the formation of mixed hemimicelle aggregates on the surface of MNPs. Therefore, the recommended procedure was followed without salt addition.

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Table 1 Determination of diclofenac in human plasma and urine samples ($n = 5$, ±%RSD)

Sample	Amount added, ng mL^{-1}	Amount found, ng mL^{-1}	Recovery, %
plasma	0	–	–
	50	48.24 ± 2.2	96.4
	500	487.5 ± 6.55	97.5
	1000	979.46 ± 9.89	97.9
urine	0		–
	50	49.04 ± 1.94	98.1
	500	504.72 ± 5.94	100.9
	1000	998.42 ± 9.57	99.8

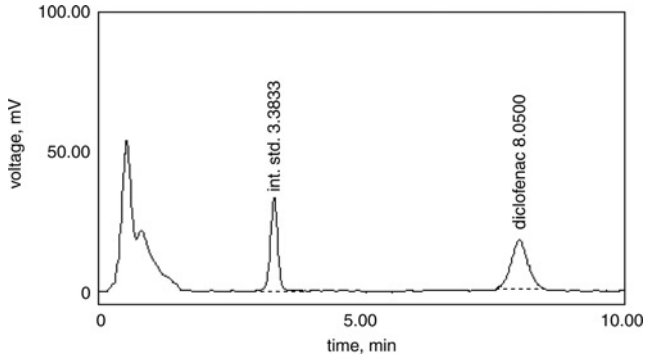

Figure 6 *Representative chromatogram of urine sample spiked with 100 ng mL^{-1} of diclofenac*

3.3. Analytical performance: Quantitative parameters, such as linear range, limit of detection (LOD), precision (as relative standard deviation (%RSD)) and enrichment factor (EF) were evaluated. The calibration curve was constructed by diluting the diclofenac stock solution to 200 mL with deionised water. The developed method exhibits good linearity in the range of 50–1400 ng mL^{-1} with a correlation coefficient r^2 of 0.9998. The LOD, which is defined as LOD = $3S_b/m$, where S_b and m are the standard deviation of the blank and the slope of the calibration curve, respectively, was obtained to be 15 ng mL^{-1}. The precision of the method was calculated using five replicate experiments using 200 mL of aqueous sample solution containing 50 and 500 ng mL^{-1} of diclofenac, and the %RSD of 2.76 and 1.73% was obtained, respectively. The EF, defined as EF = $V_s/V_e \times R\%$, where V_s is the sample volume, V_e is the elution volume and $R\%$ is the per cent recovery, was obtained as 98. As the results reveal, the proposed method exhibits good linearity, a low LOD and a high EF for the determination of the analyte.

3.4. Application of the method: The proposed mixed hemimicelle SPE method was applied for the determination of diclofenac in biological fluids including spiked human plasma and urine samples prepared as mentioned in Section 2.5. The results are given in Table 1. As can be seen, good recoveries in the range of 96–101% were obtained, which indicate that the complex matrices of biological fluids do not interfere with the analysis of diclofenac and the method has potential application to complex matrices without any pretreatment steps. The accuracy of the method was evaluated by an analysis of urine sample spiked with 100 ng mL^{-1} of diclofenac using an HPLC method. Fig. 6 shows the representative chromatogram of the sample. As can be seen, no interferences from the sample matrix were observed. The results indicate that the proposed SPE procedure can eliminate sample matrix effects and the precision of measurements was acceptable.

4. Conclusion: In this Letter, CTAB-coated Fe_3O_4 nanoparticles as an efficient adsorbent were synthesised and successfully applied to provide convenient, fast and efficient extraction and preconcentration of diclofenac from human plasma and urine samples. The method combines the advantages of mixed hemimicelles and MNPs and possesses several interesting characteristics such as simplicity, low cost and a high EF, especially when more sophisticated techniques such as HPLC or spectroflourimetry are not available. The good recoveries and precision of the method indicate that the proposed method has analytical potential for extraction and preconcentration of other drugs from biological fluids.

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