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Removal of codeine phosphate from water and artificial wastewater using sand modified with amine and carboxylic acid groups

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ABSTRACT

Pharmaceutical active compounds are known as emerging contaminants and their amounts are increasing in the environment. This study is focused on removing codeine phosphate (CPh) from water. In this respect, removing CPh by sand and two different types of modified sand were analyzed. The first silica sand modification was carried out by (3-Amino propyl) trimethoxysilane, and silica particles were coated by amine groups (S-A). With the second modification, the carboxylic acid group was bound with silica particles (3-Amino propyl) trimethoxysilane. Characterization was conducted by Fourier transform infrared spectroscopy, elemental analysis, thermogravimetric analysis, X-Ray Diffraction, and scanning electron microscopy. Effects of pH, contact time, and temperature of two modified silica sand were investigated. The results showed that silica sand does not have any effect on removing CPh; however, the removal percentages of S-A and S-C were 55% and 69%, respectively. Adsorption isotherm and kinetic were studied for both adsorbents. The results of the experiments show that the adsorbents follow Langmuir and pseudo-second-order rate. Maximum adsorption capacity (q_{max}) of the S-A and S-C was 3.3 and 4.14 (mg/g) respectively. These adsorbents could be regenerated easily and used for more than 10 times. The speed of desorption was very fast. This study proposes that these adsorbents could be utilized for CPh removal from wastewater: the results show that removal percentages of CPh from wastewater for S-A and S-C adsorbents are 30% and 37%, respectively.

Keywords: Silica sand; Modified sand; Pharmaceutical active compounds; Codeine phosphate; Removal; Water treatment

1. Introduction

Pharmaceutical active compounds (PhACs), personal care products (PCPs), and endocrine disrupting compounds (EDCs) have raised concerns due to their increasing existence in the water environments: they are known as Emerging Contaminants (ECs) in the environmental waters context [1–3]. Likewise, they have received significant attention over the past decade [4] on account of their adverse effect on the human health and other parts of the ecosystem, including unusual sexual differentiation, development of the nervous, immune systems, and other organs [5–7]. Production and use of PhACs have increased over the years [8–11]. PhACs are introduced into the environment via different ways, like improper disposal of unused drugs, agricultural runoff, pharmaceutical effluents, and wastewater effluent discharge [9,12,13]. PhACs are released into wastewater treatment plants (WWTPs), though WWTPs are not suitable environments for the removal of PhACs [2,14,15]. Some studies have demonstrated that some PhACs are removed within WWTPs but some of them are persistent and WWTP technologies are not effective. Thus, their concentrations are from low ng L^{-1} to low μg l^{-1} [2,16]. These emerging compounds (ECs) and some of their metabolites can affect humans' life and ecosystem through both drinking water

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and the food chain [2,17]. Risk of water consumption for several years with low concentration of ECs has remained unanswered [1,18].

This study focuses on the removal of codeine phosphate (CPh), which is a narcotic drug used to treat pain and cough [19,20] in the aquatic environment. CPh is one the PhACs and its importance is related to its high consumption: 361,000 kilograms of codeine were produced in 2013 and 249,000 kilograms were utilized by people [21]. Some studies conclude that CPh has been observed in drinking water with an amount close to 30 ng/L [1,22]. Other studies show that degradation of codeine produces the maximum metabolite of this material, which are known as 6-acetylcodeine [23]. Some of these found that codeine amounts in influent and effluent were the same, being 26 and 67 ng/L, in two WWTPs in Taipei and Taiwan: the absence of 6-acetylcodeine in these effluents was taken as evidence for no codeine degradation.

There are a large number of inorganic materials, but a lot of attention has been paid to silica for water and wastewater treatment because its structure is stable and porosity of silica can be controlled. Their surface also has reactivity, and this kind of material has low degree of swelling [24]. A lot of research has been conducted on the functionalization of silica particles. For instance, Skandari et al. investigated silica coated with carbon nano tube for removing hydrophobic NOM (hydrophobic natural organic matter) [25]. Majewski et al. also researched surface engineered silica coated with 3-(2-aminoethyl) aminopropyltrimethoxysilane for eliminating pathogenes from water [26]. Moreover, Girginova et al. worked on silica coated magnetic paricles for removing Hg^+ from water [27].

In this study, two modifications were conducted on sand: the first modification was carried out by the amine group, while the second modification was done by the acidic group. These two modifications were chosen because they have stability in water and, in addition, can adsorb CPh by hydrogen boding. CPh removal possibility by non-modified sand was experimented in the next step. The aim of this study is to investigate removal of CPh from water and artificial wastewater by modified-sand particles and regeneration of these adsorbents.

2. Material and methods

2.1. Instruments

Infrared spectra were recorded on a Fourier transform infrared spectrometer (FTIR 410; Jasco, Japan) using KBr pellets. Total nitrogen, carbon, and sulfur were determined using a CHNS analyzer, model NA 1500 from Carlo Erba Instruments. Thermogravimetric analysis (TGA) was done by using a TGA 50–H (Shimadzu, Japan). X-Ray Diffraction analysis was done to investigate the structure of crystals and chemical structure by XRD machine (X'Pert PRO MPD, PANalytical Company). Scanning electron microscopy (SEM) images were obtained on an EM 208 (Philips, Netherlands). The dose of the materials in water was measured by spectrophotometer DR5000 Hach and high-performance liquid chromatography (Agilent HPLC, 1200 series). pH values were measured by pH meter metrohm 827.

2.2. Reagents and solutions

(3-Amino propyl) trimethoxysilane, toluene anhydrous, methanol, hydrochloric acid, tribromoacetic acid, and sodium bicarbonate were purchased from Merck Chemicals. Codeine phosphate was received from the Behansar Company. A stock of 500 mg/L was prepared and stored at 4°C for further usage. In this study, magic buffer was used. An aqueous solution which consisted of 0.24 g of boric acid, 2.3 mL of acetic acid, and 2.7 mL of phosphoric acid were diluted with distilled water to reach 1000 mL in a flask. The pH values from 3 to 8 were adjusted by using sodium hydroxide 4 M.

2.3. HPLC method

Quantification of the codeine phosphate was carried out by high-performance liquid chromatography (Agilent HPLC, 1200 series). The detector of the system was uv/vis and the separation was carried out by c18 column (10 cm–4.6 mm, with 5 µm particle size). The mobile phase was the mixture of methanol, ammonium acetate buffer (pH = 6.9), and acetonitrile (80:10:10) with a flow rate of 1.5 mL/min. The detection wavelength was 254 nm. The injection volume of the codeine phosphate was 10 µL.

2.4. Modification of sand with (3-amino propyl) trimethoxysilane

Initially, 5 g sand was added to 100 mL hydrochloric acid 0.1 M. This solution remained for 12 h. Then the sand was separated from the aqueous solution. The sand was washed with water until pH of the solution reached 7 and it dried afterwards. Next, that sand was crushed by a pestle in a mortar and was sieved with mesh numbers of 100 and 200. Then a solution of 47.5 mL of toluene anhydrous and 2.5 mL of (3-amino propyl) trimethoxysilane was prepared before adding the sand from the previous step to the prepared solution. Next, the mixture was stirred at 70°C for 24 h. Thereafter, solid phase was separated from aqueous phase by filter paper: the solid phase was washed with 40 mL toluene. In the next step, sand was washed with 20 mL methanol. Finally, the product was placed in an ambient temperature to dry out. The schematic modification of this process is shown in Fig. 1a.

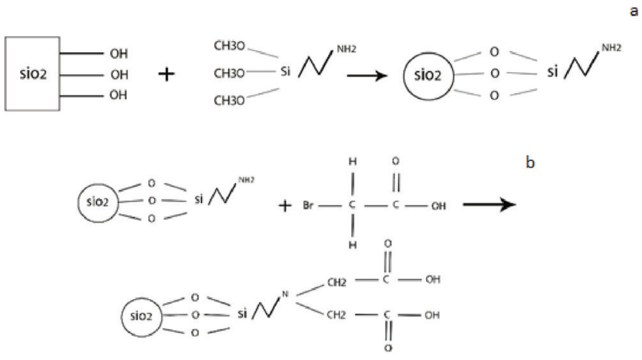

Fig. 1. Schematic presentation of grafting NH_2 and COOH on SiO_2.

2.5. Modification with tribromoacetic acid

A solution of 0.1 M sodium bicarbonate in a 100 mL volumetric flask was prepared. Then, 2 g of tribromoacetic acid were added to the solution. Next, 5g of S-A was added to the aqueous solution and it was stirred for 8 h in an ambient temperature. After that, the solid phase was separated by filter paper and washed with 50 mL of 0.1 M sodium bicarbonate. Then, that was washed with 100 mL of distilled water and separated by filter paper. Finally, it was placed in an ambient temperature to dry out. The schematic presentation of grafting COOH on SiO_2 can be seen in Fig. 1b.

2.6. Analysis of the sand and modified adsorbents

2.6.1. Optimum pH

Aqueous solutions of CPh with the concentration 20 mg/L were prepared at different pH levels by magic buffer. Then for this experiment, 0.1 g sand or modified sand was added to 100 mL solution of 20 mg/L CPh and the solution was stirred on magnetic stirrer for 30 min. Next, the solution was filtered. Finally, the concentration of drug in the filtered solution was determined by HPLC.

2.6.2. Adsorption isotherm

First, aqueous solutions with different CPh concentrations from 50 to 100 mg/L at optimum pH level were prepared. For this purpose, 20 mL of the solutions were poured into a beaker as a sample and 0.05 g of modified sand was added to each solution. Then, sample solutions were stirred on magnetic stirrer for 1 h. After that, the stirred solution was filtered. Finally, the same process as above was followed.

2.6.3. Application of method

Artificial codeine phosphate wastewater was prepared by adding 0.001 g of the CPh powder to 1 L of treated wastewater which contained 0.09 g lime, 7 mg toluene, 0.09 g sodium carbonate, 0.02 g acetic acid, 0.05 g sulfuric acid, 5 mg ammonia (25%), and 5 mg butanol with COD of 50 mg/L [28]. Then, 20 mL of the solution was poured into two beakers and 0.1 g of S-A and S-C adsorbents were added to the solutions: the solutions were put on a magnetic stirrer and left there for 5 min. Finally, solutions were filtered and the drug in the solutions was determined by HPLC.

3. Results and discussion

3.1. Characterization

3.1.1. FTIR

For the first modification, FTIR shown in Fig. 2 (b) indicates that the sand has been coated with amine and the modification carried out successfully. In the

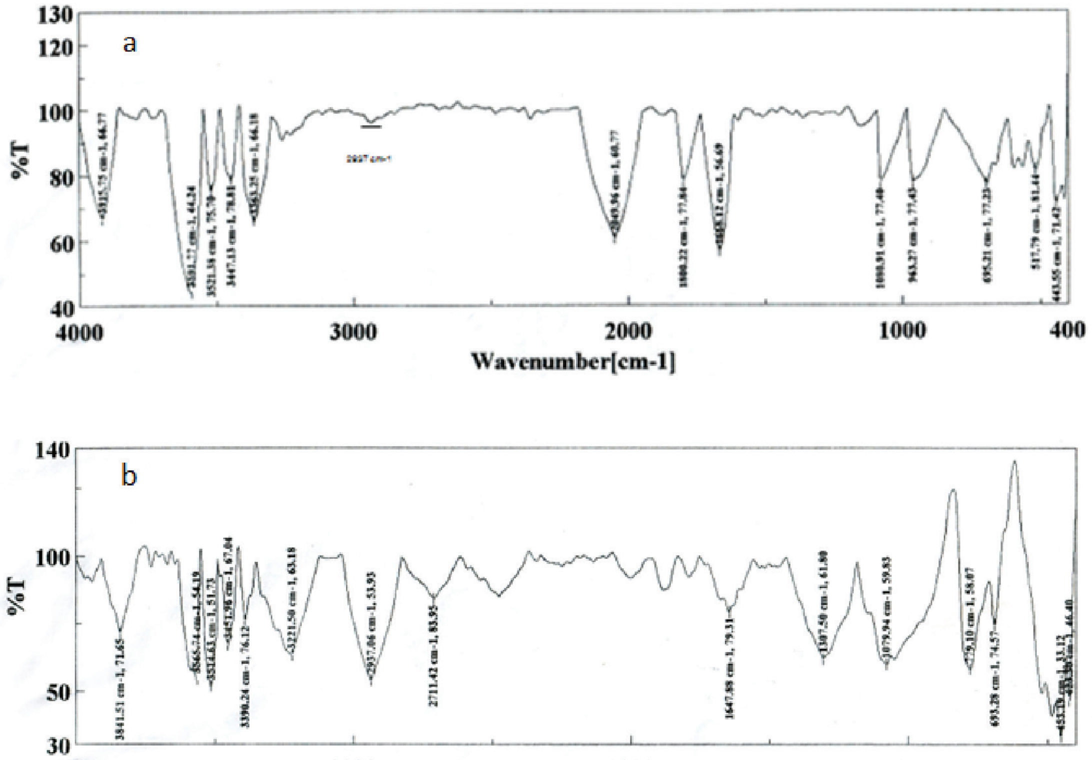

Fig. 2. (a) FTIR of S-c; (b) FTIR of S-A.

FT-IR spectrum of S-A, the bands at 1079, 1647, 2937, and 3451 cm^{-1} can be assigned to the Si–O stretching, C=O stretching, C–H stretching, and OH stretching respectively. FTIR of S-C shown in Fig. 2 (a) indicates that sand has been coated with carboxylic acid and the modification carried out successfully. In S-C FT-IR spectrum, the bands at 1080, 1800, 2937, and 3447 cm^{-1} can be assigned to the Si–O & C–O, O–C=O, C–H, and OH stretching respectively.

3.1.2. CHNS

In CHNS analysis of S-A, existence of 2.23% nitrogen, 5.63% carbon, and 0.43% hydrogen proves that modification was carried out correctly. This is so because existence of nitrogen is a reason that sand particles get coated by a mine groups successfully. Similarly, existence of 1.5% nitrogen, 13.98% carbon, and 0.72% hydrogen in S-C CHNS analysis establish that modification was carried out successfully because these are the proof of existence of COOH on the sand particles.

3.1.3. TGA

The TGA analysis shown in Fig. 3 indicates that weight loss (5.63%) of the particles at 600°C is due to decomposition of coated organic matters on sand. This process started and continued to 200°C, and from that point remained constant till 600°C.

3.1.4. SEM

SEM of the particles is shown in Fig. 4, which explored the morphology of the particles.

SEM shows that the shape of the particles is hunk, their surfaces are smooth, and the adsorbent bulk has micro metric pores. Dimensions of the adsorbent are in the range of 20–180 µm.

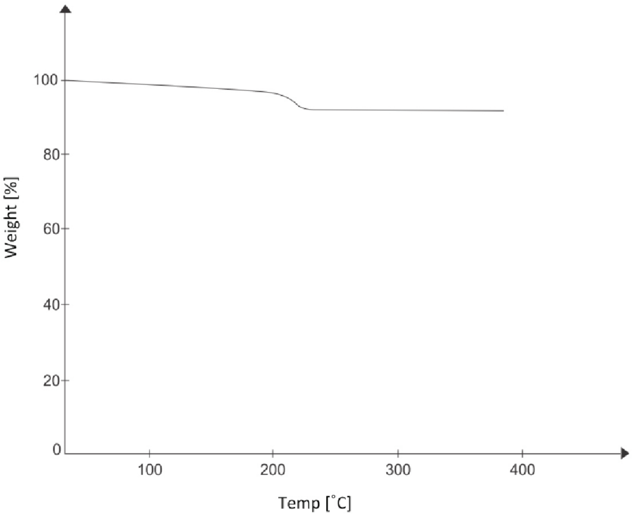

Fig. 3. TGA plot of S-C.

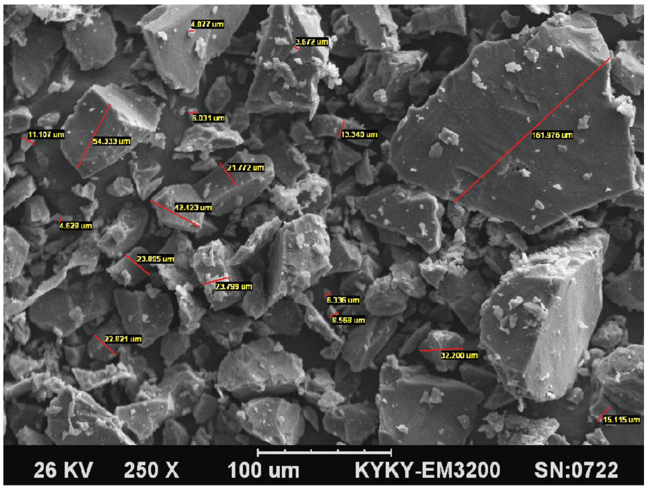

Fig. 4. SEM of particles.

3.1.5. XRD

The characteristic peaks at 20.9880, 26.7864, 36.6823, 39.588, 40.426, 42.577, 50.2874, and 60.0836 in Fig. 5a show that the material is silica sand [29,30]. In Fig. 5b, it can be seen that the characteristic peak at 26.7864 in Fig. 5a has shifted 0.18% and is at 26.7377. Crystalline structure also has not changed in the presence of amine group.

3.2. Result of analysis of the sand and modified sand

3.2.1. Sand

According to the results of the chromatography conducted as part of the experiment, CPh removal with sand was insignificant and the sand failed to remove the existing codeine in the water. This is because codeine phosphate is hydrophilic and log K_{ow} of codeine phosphate is 1.14: removal efficiency of this micro pollutant is low because these compounds are not easily adsorbed by sand [31].

3.2.2. Optimum pH

According to Fig. 6, the optimum pH values of S-A and S-C were 6 and 4 respectively, and the CPh chemical was neutral. Zeta potential analysis was carried out: graphs are shown in Fig. 7. With regard to these graphs, the pH_{ZPC} of S-A and S-C adsorbents were 7.6 and 7.8 respectively (the pH of zero point of charge corresponds to the pH value where the surface electric charge of the adsorbents is zero). In both adsorbents in pH < pH_{zpc}, NH_2 groups in S-A and COOH groups in S-C are protonated, and adsorbents surfaces were positively charged, it strengthens the hydrogen bonds between adsorbents and CPh. At acidic pH values of about 3 or 4, carboxylic acid groups (–COOH) in S-C become neutral and CPh can be adsorbed by hydrogen bonds. By increasing the pH value, carboxylic acid groups (–COOH) are ionized and turn to (–COO$^-$) so that electrostatic repulsion prevents more CPh adsorption. On the other hand, acidic pH values for S-A cause amine groups (–NH_2) to turn to (–NH_3^+): electrostatic repulsion also prevents CPh adsorption. By

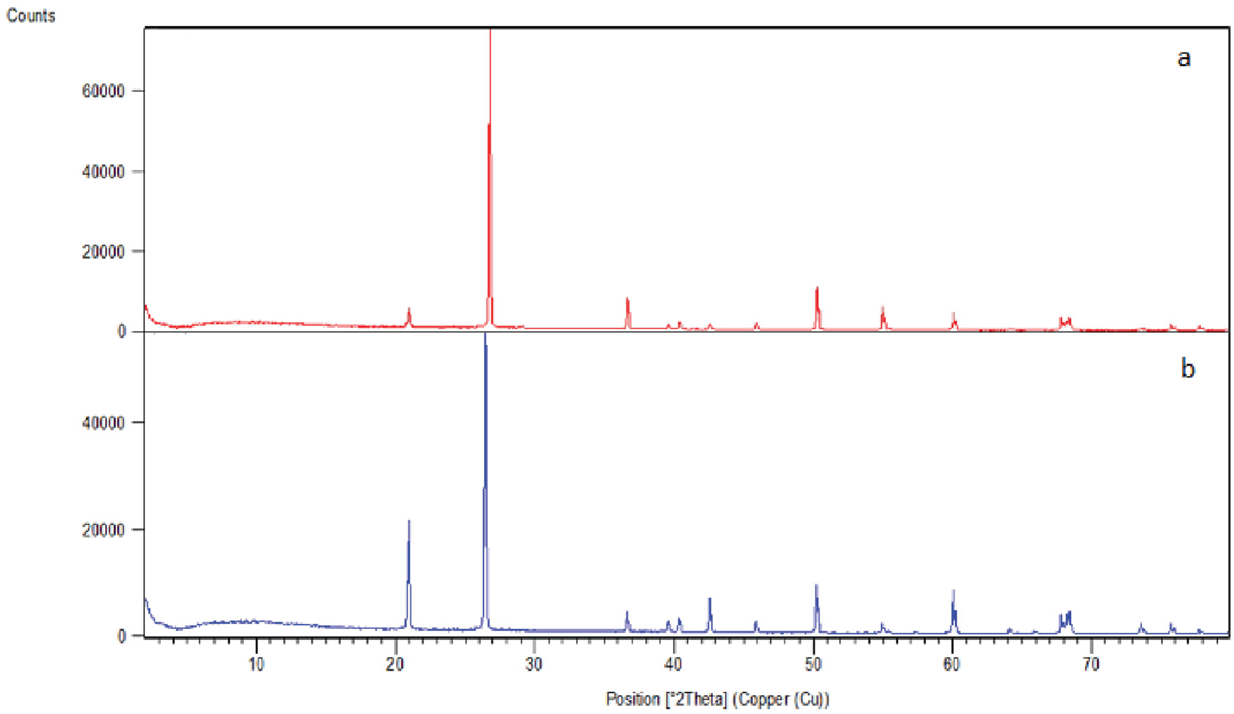

Fig. 5. (a) XRD pattern of sand; (b) XRD pattern of S-A.

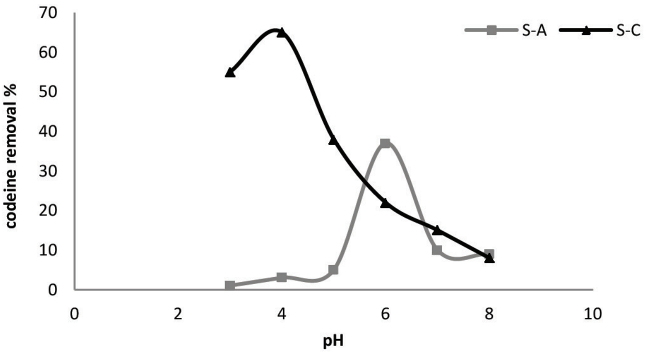

Fig. 6. Variations of CPh removal by changing pH on S-A and S-C adsorbents.

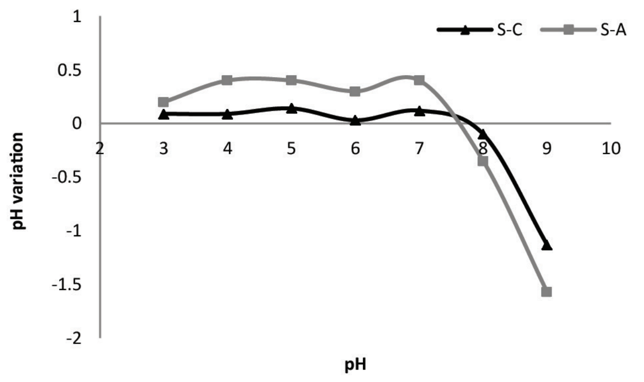

Fig. 7. Point of zero charge graph of S-A and S-C adsorbents.

increasing pH value and getting close to neutral pH values, the amount of adsorption increases because of its zeta potential. The maximum removal of CPh by S-A and S-C at optimum pH levels was 37% and 65%, respectively.

3.2.3. Adsorption isotherm

Adsorption isotherm experiments present the relationship between per unit of adsorbate which is adsorbed by the amount of adsorbent (q_e mg/g) and the concentration of adsorbate at the end of the adsorption process (C_e mg/g) [32–34]. In this study, Langmuir, Freundlich, and Temkin adsorption isotherm models were utilized. These adsorption isotherms were used for determination of the mechanism of the adsorbate adsorption [32]. Additionally, equilibrium concentration of adsorbate (mg/L) was measured by using this method: the nature of the sorption process can be evaluated in this fashion [35,36] .

Langmuir adsorption isotherm: this model represents adsorption of mono layer of adsorbate on the surface of the adsorbent [37]. The Langmuir equation is:

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} k_l \cdot C_e} \tag{1}$$

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{C_e}{q_{\max} \cdot k_l} \tag{2}$$

where q_e is the amount of adsorbate which adsorbs per unit weight of adsorbent (mg/g) and C_e is the equilibrium concentration of adsorbate (mg/L). In addition, q_{max} and K_L

are defined as maximum adsorption capacity (mg/g) and Langmuir isotherm constant (L/mg) respectively.

Freundlich adsorption isotherm: this model is used for representing the type of adsorption for heterogeneous surfaces. Freundlich equation is:

$$In\ q_e = InK + \frac{1}{n} In\ C_e \tag{3}$$

where K and n are defined as Freundlich isotherm constant (mg/g) and adsorption intensity respectively. Additionally, q_e is the amount that adsorbs per unit weight of adsorbent (mg/g) and C_e is the equilibrium concentration of adsorbate (mg/L).

Temkin adsorption isotherm: this model describes the interaction between the adsorbate and adsorbent. This model is valid for medium concentrations and describes the decreasing temperature of the layer with regard to the interaction because of the covering [38]. Temkin equation is:

$$q_e = \frac{RT}{b} \cdot In\left(AC_e\right) \tag{4}$$

$$q_e = B\ In\,A + B\ In\,C_e \tag{5}$$

where $B = \frac{RT}{b}$, A is the Temkin isotherm constant (L/g), b is the constant related to heat of sorption (J/mol), R is universal gas constant (8.314 J/mol·K), and T is the absolute temperature (K). Moreover, q_e is the amount of adsorbate which adsorbs per unit weight of the adsorbent (mg/g) and C_e is the equilibrium concentration of adsorbate (mg/L).

Both data of the adsorbents followed Langmuir adsorption isotherm: the amounts of three adsorption isotherm constants are shown in Table 1. The results of Langmuir adsorption isotherm shows that q_m for S-C is greater than S-A, so this adsorbent can adsorb more CPh. In addition, $\frac{1}{n}$ in Freundlich adsorption isotherm is a factor that shows adsorption intensity. The slope $\left(\frac{1}{n}\right)$ is between 0 and 1. When the slope is more than 1, adsorption process is cooperative. If $\left(\frac{1}{n}\right)$ is closer to 0, adsorption process is more heterogeneous. The slope $\left(\frac{1}{n}\right)$ of S-A is 0.114, and this value for S-C is 0.075. It is obvious that the adsorption process of S-C is more heterogeneous than S-A [39,40]. In Temkin adsorption isotherm, the parameter of b shows sorption heat: the adsorption reaction is exothermic because b for both adsorbents is positive. The value of B for S-C is smaller than this value for S-A: this shows that temperature of S-C adsorption process is less than the temperature of S-A adsorption process [41]. The assumption of the Langmuir adsorption isotherm is that the surface of the adsorbent is homogeneous and the adsorption is mono layer and chemical.

Table 1
Isotherm parameters for adsorption of codeine onto S-A and S-C

		S-A	S-C
Langmuir	q_m (mg/ g)	3.30	4.14
	k_l (L/mg)	0.50	0.36
	R^2	0.996	0.998
Freundlich	n	8.75	13.36
	k_f (mg/g)	2.38	2.88
	R^2	0.984	0.979
Temkin	B	0.428	0.274
	b (J/mol)	5791.43	9035.63
	A (L/g)	122.73	26790.43
	R^2	0.985	0.971

3.2.4. Contact time

The contact time changed from 15 s to 90 m; effects of contact time on removal of CPh by adsorbents were investigated. Fig. 8(a) shows that removal of CPh by S-A occurred in the first 2 min, and that S-A adsorbed 55% of the amount of drug in solution in that time. Also, Fig. 8 (b) establishes that S-A saturated within 2 min and the adsorbent became 50% saturated within 15 s. Results reveal that the pace of interaction between CPh and S-A was fast. Fig. 8 (a) shows that maximum adsorption of drug by S-C was 68% in 5 min, while Fig. 8 (b) shows that saturation for this adsorbent occurred in 5 min and that S-C was 50% saturated in less than 15 s. The adsorption process of S-C was as fast as the adsorption process of S-A.

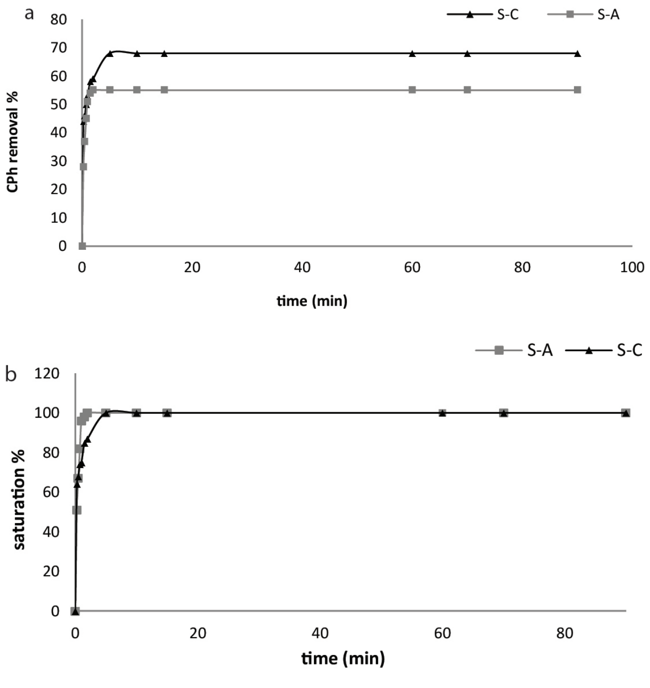

Fig. 8. (a) Effect of contact time on codeine phosphate removal %. (b) Effect of contact time on saturation percentage of adsorbents.

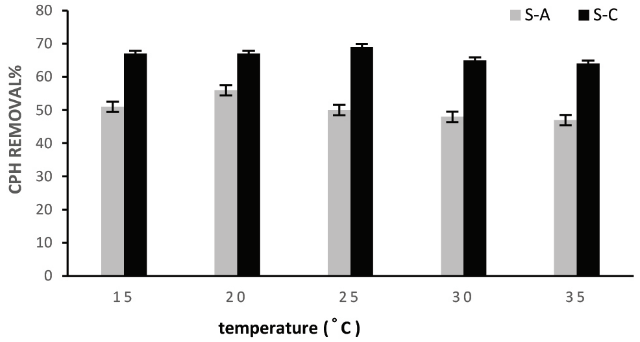

Fig. 9. Effect of temperature on codeine phosphate removal by S-A adsorbent and S-C adsorbent.

3.2.5. Temperature

Analysis results related to temperature variation show that temperature was more effective on sorption of S-A than S-C adsorbent. However, the results revealed that both adsorbents were hardly sensitive to temperature. As seen in the plot of Fig. 9, sorption percentage decreased to some extent with increase in the temperature. Maximum removal occurred at 20 and 25°C for S-A and S-C adsorbents at 56% and 69%, respectively.

3.2.6. Regeneration

The regeneration experiments of S-A were carried out after adsorption by methanol: their results are shown in plot of Fig. 10. Accordingly, at first, high sorption with percentage of 82% was done. Then the removal percentage was almost constant with a percentage of 77%: after the 17th regeneration, the removal percentage was 66%. These experiments were conducted for S-C adsorbent, and as can be seen in Fig. 10, the highest removal percentage of CPh was 95% at first: after this, the removal percentage was constant at 92% upon decreasing the adsorption. After the 17th regeneration, the removal percentage reached 78%. Regeneration efficiency by methanol was more than 94% for S-A and was 97% for S-C for each process of adsorption and desorption.

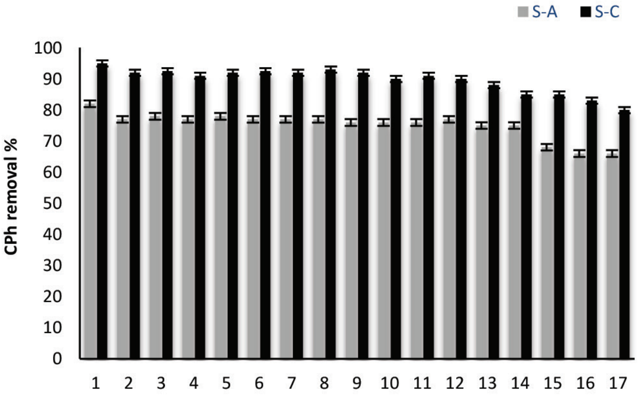

Fig. 10. Effect of regeneration on codeine phosphate removal% for S-A adsorbent and S-C adsorbent.

3.2.7. Adsorption kinetic

Kinetic studies are important because they describe what is going on in the sorption process. In this study, pseudo-first-order rate equation, pseudo-second-order rate equation, and Morris-Webber model were used. Criterion for choosing a model was based on the amounts of correlation coefficients of the models (R^2): if the correlation coefficient of a model was proximately 1, that model was seen as corresponding to the experimental data.

The pseudo-first-order rate equation is a linear form of this model represented by Lagergren [42]:

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1 \times t}{2.303} \tag{6}$$

In this equation, q_e and q_t are defined as the amount of adsorbate which adsorbes the adsorbent (mg/g) at equilibrium and time. K_1 is the sorption rate constant (min^{-1}) and t is time (min). In recent years, scientists have consistently used this equation for description of adsorption of pollutants.

For studying kinetic adsorption, pseudo-second-order rate equation was used: this equation was represented by Lagergren as [42]:

$$\frac{t}{q_t} = \frac{1}{K_2 {q_e}^2} + \frac{1}{q_e} t \tag{7}$$

where t is time (min), K_2, q_e, and q_t are the sorption rate constants (g·mg^{-1}·min^{-1}), and the amount of adsorbate which adsorbes the adsorbent (mg/g) at equilibrium, and time respectively.

Morris and Webber found that sorption changes with $t^{0.5}$ not t in adsorption. The equation of the Morris-Webber model is [43] :

$$q_t = K_{in} t^{0.5} \tag{8}$$

where K_{in} is the intra-particle diffusion rate constant. Moreover, q_t is amount of adsorbate which adsorbs the adsorbent (mg/g) at time. A sorption process consists of mass transfer, film diffusion, and intra particle diffusion. Mass transfer step is very fast, so the reaction rate cannot be controlled by this step. If the plot corresponds to experimental data, and the plot starts from the origin, it means that the intra-particle diffusion is the sole rate-limiting step. If the graph of this model consists of two parts, two models of the intra-particle diffusion and film diffusion control the sorption rate [42,44].

According to the plots of Fig. 11, the adsorption kinetic data of S-A and S-C adsorbents corresponded to pseudo-second-order rate equations and the correlation coefficient was equal to 1 for both of them.

Furthermore, the adsorption kinetic data of both adsorbents also corresponded to the pseudo-first-order rate equation because correlation coefficient is more than 0.9. The q_e (mg/g) and k_2 (g/mg·min) parameters are shown in Table 2.

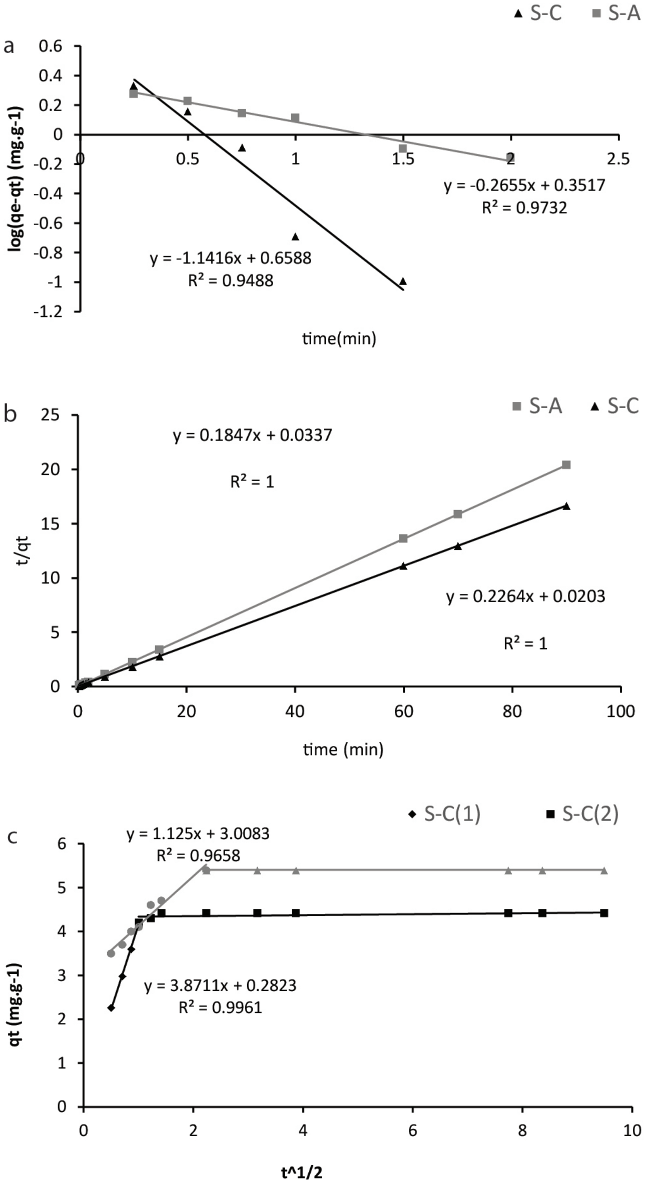

Fig. 11. Adsorption kinetics of S-A and S-C adsorbents. a) The pseudo-first-order b) pseudo-second-order c) Morris and Webber.

Table 2
Rate constants and correlation coefficients of the pseudo second-order kinetic models

		S-A	S-C
q_e (mg/ g)		4.60	2.28
k_1 (min^{-1})	Pseudo-first-order rate	2.63	0.62
R^2		0.948	0.973
q_e (mg/g)		4.40	5.41
k_2 (g/mg·min)	Pseudo-second-order rate	2.83	1.38
R^2		1	1

Morris and Webber graphs for both adsorbents include two parts: this means that the two models of intra-particle diffusion and film diffusion control the sorption rate.

3.2.8. Application of method

This stage of the experiment was conducted with artificial wastewater. Volume of the samples was 20 mL and the amount of adsobents was 0.1 g. This experiment was repeated three times. pH of the solution was almost 8 and the maximum adsorption of two adsorbents after 5 min was 31% and 37% for S-A and S-C adsorbents respectively. HPLC results of one of the experiments are shown in Fig. 12.

S-A adsorbent's results were 28%, 30%, and 31%; S-C adsorbent's results were 36%, 37%, and 37%. For better representation of the results, they were reported statistically. CPh removal percentage of S-A was 29.66% ± 5.16%. CPh removal percentage of S-A was 36.66% ± 1.58%.

4. Conclusion

These two methods of modification of silica particles were easier and cheaper than other methods. The size of particles was not nanometeric: this made these adsorbents cheaper than nanometric adsorbents. All the results of this study are shown in Table 3. With regard to these results, we

Table 3
Total results of the experiments

Adsorbent	Parameters					
	pH	Temperature	Adsorption isotherm	Adsorption kinetic	Regeneration efficiency %	Contact time
S-A	6	Low sensitivity	Langmuir (q_m = 3.3 mg/g)	Pseudo-second-order rate (q_e = 4.4 mg/g)	More than 94%	2 min 55%
S-C	4	Low sensitivity	Langmuir (q_m = 4.14 mg/g)	Pseudo-second-order rate (q_e = 5.4 mg/g)	More than 97%	5 min 69%

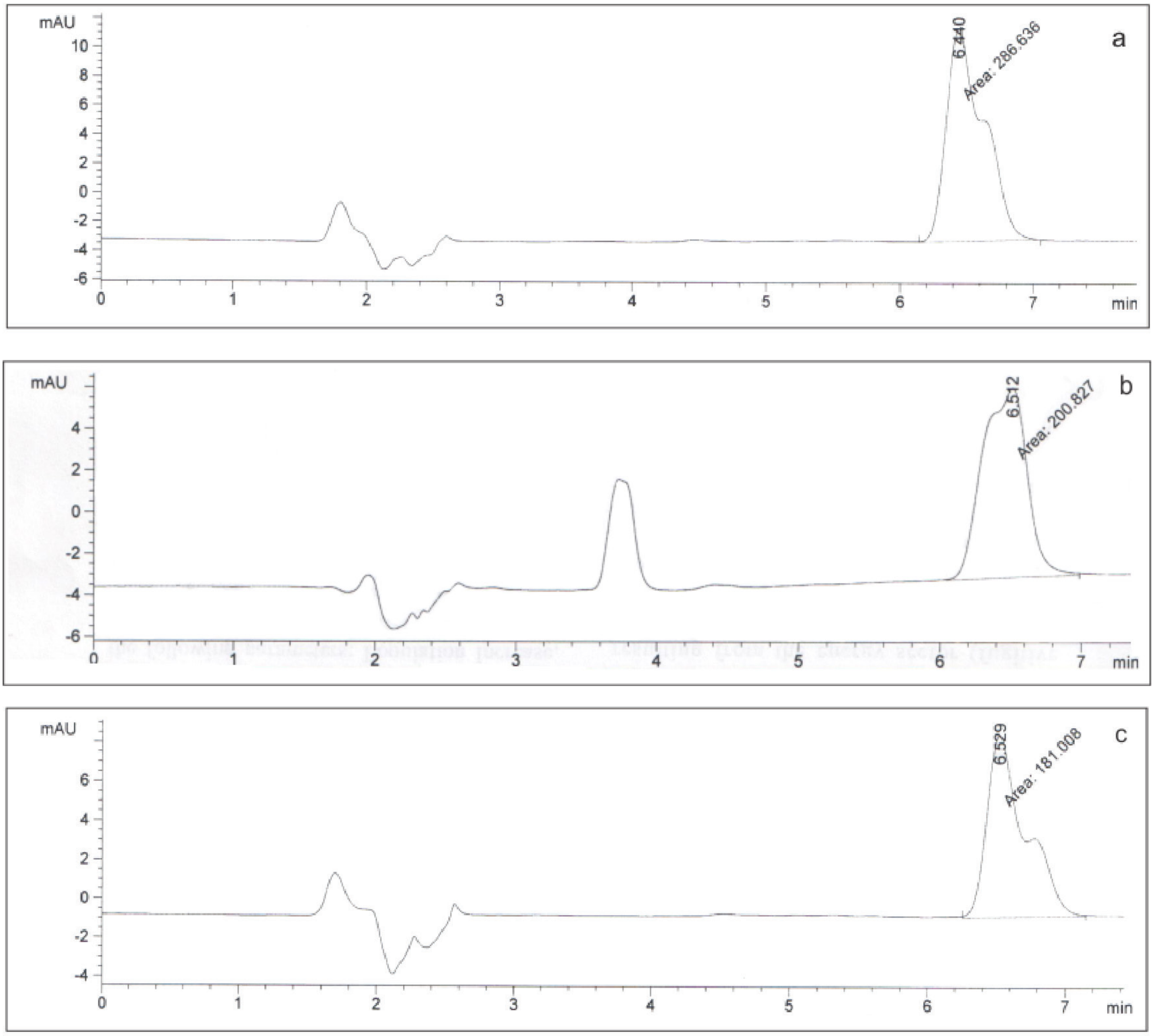

Fig. 12. HPLC results of method application. (a) Amount of CPh in artificial wastewater; (b) amount of CPh after using S-A; (c) amount of CPh after using S-C.

can say that S-C is more efficient than S-A in CPh removal from water and that silica particles do not have enough efficiency for this issue. The advantages of these adsorbents were fast adsorption and low temperature sensivity. These adsobents could be regenerated by methanol easily: their regeneration efficiencies are high, and utilizing them can decrease the operation costs of water treatment. In all, conventional Water Treatment Plants (WTP)are not effective in removing Emerging Contaminants (EC). Thus, it is a good idea to use novel methods which can be used in coventional WTPs. As noted earlier, Skandari et al. could remove a large quantity of hydrophobic NOM from water with silica coated with carbon nanotubes (q_{max}= 81.96 mg/g CNT) [25]. Mjewski et al. were also able to eliminate between 10^2 and 10^4 cfu/mL pathogens with 10 g/L surface engineered silica coated with 3-(2-aminoethyl) aminopropyltrimethoxysilane [26]. Some researches have been conducted to investigate CPh removal through different ways, for example Szymonik et al. reported that CPh was adsorbed on activated sludge by 33% . It is obvious that S-A and S-C can be used quicker and easier than activated sludge, and their removal percentage is higher. Including the techniques used in this research, there are a lot of methods which can equip WTPs to handle ECs.

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Symbols

A — The Temkin isotherm constant (L/g)
b — The constant related to heat of sorption (J/mol)
C_e — The equilibrium concentration of adsorbate (mg/L)
K — Freundlich isotherm constant (mg/g)
K_{in} — The intra-particle diffusion rate constant
K_1 — The sorption rate constant (min^{-1})
K_2 — The sorption rate constant ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$)
K_L — Langmuir isotherm constant (L/mg)
N — Adsorption intensity
q_e — The amount of adsorbate which adsorbs per unit weight of adsorbent (mg/g)
q_{max} — Maximum adsorption capacity (mg/g)
q_t — Amount of adsorbate adsorbes the adsorbent at time (mg/g)
R — Universal gas constant (8.314 J/mol·K)
t — Time (min)
T — The absolute temperature (K)

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