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RESEARCH ARTICLE - CHEMISTRY

Removal of Selected Pharmaceuticals from Aqueous Solutions Using Natural Jordanian Zeolite

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Abstract

In this study, the removal of selected pharmaceuticals including ibuprofen, diclofenac sodium, indomethacin, chlorpheniramine maleate, and paracetamol from water using natural Jordanian zeolite was studied. The influence of pH, contact time, adsorbent dosage, and initial pharmaceutical concentration on the adsorption process was investigated using batch and column methods. The optimal pH for the removal of all selected pharmaceuticals was found to be 2 except for diclofenac sodium where the optimal pH was 6. The optimum adsorption time was found to be 80 min. The percentage removal increased as the initial concentration of the pharmaceuticals increased from 10.0 to 50.0 mg/L except for indomethacin where the removal decreased as the initial concentration increased. After optimization, the highest removal was found to be 88.3, 30.1, 59.0, 85.8, and 12.7% for ibuprofen, diclofenac sodium, indomethacin, chlorpheniraminemaleate, and paracetamol, respectively. Langmuir and Freundlich isotherm models were used to evaluate the adsorption efficiencies of the investigated pharmaceuticals. The results demonstrated that Langmuir isotherm fits the experimental data for diclofenac sodium, indomethacin and paracetamol with adsorption capacity (Q_{max}) of 4.8, 26.6, and 55.6 mg/g, respectively, whereas Freundlich isotherm fits the experimental data for both ibuprofen and chlorpheniramine maleate. Continues flow experiment was performed on ibuprofen under constant influent concentration and fixed flow rate. Equal eluted fractions of 100 mL were collected and analyzed for ibuprofen content. The results indicated that percentage removal of ibuprofen on zeolite was found to be the highest after fraction 9 with 78% removal.

Keywords Jordanian zeolite · Pharmaceutical removal · Adsorption · Wastewater treatment · Langmuir isotherm

1 Introduction

Water has a broad impact on all aspects of human life including but not limited to health, food, energy, and economy [1]. Water resources in Palestine are mainly the Jordan River, surface water, and groundwater [2]. Water quality in Palestine is considered to be acceptable in general with no serious indications of pollutants in the deep aquifers. However, there is contamination of water in the shallow aquifer wells and springs. The expected increase in the Palestinian population and development in social, economical, and industrial sec-

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tors will increase the pressure on the already scarce water resources [3].

Pharmaceuticals and day care products are considered to be new emerging pollutants due to the increase in their usage and as such can enter the water body through many pathways. Palestine is no exception, and hence, there are many concerns that this will result in an increase in the concentrations of these compounds in the waterbody after passing through different wastewater treatment facilities. Worldwide, traces of pharmaceuticals, typically at levels of nanograms to micrograms per liter range, have been reported in the water cycle, including surface waters, wastewater, groundwater, and to a lesser extent, drinking water [4].

The occurrence of pharmaceuticals in the environment and the water cycle at trace levels has been widely discussed and published in the literature during the past decade [4]. The observed development of the detection of these pollutants at trace levels is largely attributable to the advancement of the analytical techniques and instrumentation employed [4].

In practice, there are various conventional methods available for the removal of pharmaceuticals such as reverse osmosis, precipitation, chemical reduction, but these methods require high experimental setup, more expensive, and also less effective. Removal of pharmaceuticals by adsorption is one of the most promising techniques which are considered to be low cost, more effective, and eco-friendly [5]. Acidic pharmaceuticals, for example, ibuprofen, diclofenac sodium, and indomethacin, with pK_a values varying from 4.1 to 4.9 occur as anions at neutral pH. Therefore, this class of drugs is not readily removed by sludge during sludge treatment and hence remains in the aqueous phase as potential pollutants [6].

Zeolite is a hydrated alumino-silicate material having cage-like structures with internal and external surface areas of up to several hundred square meters per gram and cation exchange capacities of up to several milliequivalents per kg [7]. Both natural and synthetic zeolite are used in the industry as adsorbents, soil modifiers, ion exchanger, and molecular sieves [7–9].

Natural zeolite has been utilized for the removal of pharmaceuticals and antibiotics from contaminated water with good results [10–12]. Behera et.al [13] studied the sorption of ibuprofen, a nonsteroidal anti-inflammatory drug, onto various soil minerals, viz. kaolinite, montmorillonite, goethite, and activated carbon through batch experiments. Their results showed that the sorption of ibuprofen onto all sorbent was pH dependent with optimum value at pH = 3. Furthermore, it was shown that activated carbon showed the highest adsorption capacity among all adsorbents used (28.5 mg/g).

In this study, we report on the removal of selected pharmaceuticals from water using the natural Jordanian zeolite (Intermediate silica) as an adsorbent. The effect of pH, contact time, adsorbent dosage, and initial concentration of these pharmaceuticals on the adsorption process is investigated in both batch and continuous flow modes. The adsorption kinetics and adsorption isotherms are also analyzed for further characterization and optimization.

2 Experimental

2.1 Materials and Instruments

Pure standards of ibuprofen (> 99%), diclofenac sodium (> 99%), indomethacin (> 99%), chlorpheniramine maleate (> 99%), and paracetamol (> 99%) were obtained from local pharmaceutical company. Methanol (> 99%) was obtained from Sigma-Aldrich (Munich, Germany). Natural Jordanian zeolite samples were brought from University of Jordan. The zeolite used in this study is intermediate silica with Si/Al ratio equal 4.142 [14]. The samples were provided from area located 65 km S-SE of Ma'an in the southern part of Jordan and covered a surface of about 875 km^2. Successive layers of shale and siltstone were reported for the Paleozoic rocks of southern Jordan. The pH was measured using pH meter (TOA electronics™, model, Japan). The samples were agitated on an electronic shaker (Big bill shaker, Banstaed, Themolyne, USA). The concentrations of drugs in aqueous samples were determined spectrophotometrically (UV-spectrophotometer, Model: UV-1601, Shimadzu, Japan).

2.2 Methods

2.2.1 Calibration Curves

(a) Stock solutions: 1000 mg/L stock solution of each pharmaceutical was prepared by dissolving separately ibuprofen, diclofenac sodium, indomethacin, and chlorpheniramine maleate and paracetamol in 1000 mL of 1:1 methanol–water mixture by volume.
(b) Calibration curves: The following diluted solutions were prepared from each stock solution of the above pharmaceuticals (10.0, 20.0, 40.0, and 50.0 mg/L), and absorbance at λ_{max} for each drug (Table 1) was read for each solution against 1:1 methanol–water mixture by volume as a blank. The recorded absorbance was then plotted vs. concentration for each pharmaceutical (in mg/L) and the regression equation, and R^2 was determined using linear least square algorithm.

2.3 Batch Adsorption Isotherms

Equilibrium relationships between adsorption capacity (q) for each adsorbate (ibuprofen, diclofenac sodium, indomethacin, chlorpheniramine maleate and paracetamol)

Table 1 λ_{max} and pK_a for the selected pharmaceuticals employed in this work

Pharmaceutical Name	λ_{max} (nm)	pKa
Ibuprofen	224	5.2
Diclofenac sodium	276	4.0
Indomethacin	225	3.8
Chlorpheniramine Maleate	261	9.3
Paracetamol	243	9.5

and their concentration at fixed adsorbent dosage (Natural Jordanian Zeolite) and constant temperature are described by adsorption isotherms. Analysis of these isotherms provides information about the effectiveness of the adsorbent toward the removal of each respected adsorbates. These experiments were conducted at the optimum pH, contact time, and adsorbent dosage.

2.3.1 Effect of pH

For each studied pharmaceutical, 50.0 mg of zeolite was transferred to several 250.0-mL erlenmeyer flasks. To each flask, 50 mL of 50.0 mg/L of the spiked solutions with the selected pharmaceutical was added after adjusting its pH to the required values between 2 and 8 using either 0.20 M HCl or 1.0 M NaOH solutions. The solutions were then allowed to agitate for 2 h at 25 °C. The solutions were then filtered using a 0.45-μm Millipore syringe filters, and the absorbance was recorded at λ_{max} of each pharmaceutical.

2.3.2 Effect of Contact Time

50 mg of zeolite was transferred to several 250.0-mL erlenmeyer flasks. 50 mL of 50.0 mg/L of each spiked solution with the selected pharmaceutical was added to each flask after adjusting its pH to the optimum value. The solutions were allowed to agitate for different time intervals (10, 20, 40, 60, 80, and 120 min) at 25 °C. At the selected time for each flask, the sample was filtered using a 0.45-μm Millipore syringe filter and the absorbance at λ_{max} was recorded.

2.3.3 Effect of Adsorbent Dosage

0.5, 1.0, 1.5, and 2.0 g of adsorbent were transferred to separate four 50-mL erlenmeyer flasks, and 50 mL of 50 mg/L of the spiked solutions of each pharmaceutical at the optimum pH was added to each flask. Solutions were left to agitate for 80 min and filtered using a 0.45-μm Millipore syringe filter, and the absorbance was recorded at λ_{max}.

2.3.4 Effect of Initial Absorbent Concentration

50.0 mL of 10.0, 20.0, 40.0, and 50.0 mg/L of the spiked solutions at the optimum pH was added to 50.0-mL Erlenmeyer flask containing 1.0 g of zeolite. The solutions were allowed to stir for 80 min at 25 °C and then filtered using a 0.45-μm Millipore syringe filter, and the absorbance was measured at λ_{max}.

All experiments described above were conducted in triplicates, and results were taken as average of three measurements.

2.4 Column Experiment

Column filter experiments were performed with 9/1 (w/w) mixtures of sand and zeolite (20 cm layer) in a column of 25 cm length and 3.5 cm diameter prepared by mixing 10 g of zeolite and 90 g of sand. Quartz sand was thoroughly washed by distilled water and dried at 105°C for 24 h prior its use. Glass wool layer of 2 cm was placed at the bottom of the column to prevent clogging. 1000 mL of 50 mg/L adsorbate solutions was passed through the column at a fixed flow rate of 2 mL min^{-1}. Fractions of 100 mL (each) were collected, and the concentration of the selected pharmaceutical was determined spectrophotometrically.

2.5 Mathematical Treatment

In the adoption isotherm and adsorption kinetics studies, the adsorption capacity at equilibrium or at any time t, (Q_e (mg/g), and Q_t (mg/g), respectively) was evaluated using Eqs. 1 and 2.

$$Q_e = \frac{(C_0 - C_e)\,V}{W} \tag{1}$$

$$Q_t = \frac{(C_0 - C_t)V}{W} \tag{2}$$

where C_0 represents the initial adsorbate concentration (mg/L), C_e and C_t are the final concentration after 2 h or at the time t, respectively, V is the volume of solution in liters, and W is the mass of zeolite in grams.

The applicability of Langmuir and Freundlich equilibrium isotherm models was assessed for the adsorption capacity for each pharmaceutical used. This was achieved by testing their linearized from as given by Eqs. 2 and 3, respectively.

$$\frac{C_e}{Q_e} = \frac{1}{K\,Q_m} + \frac{C_e}{Q_m} \tag{3}$$

$$\ln Q_e = \ln k_f + \frac{1}{n}\ln C_e \tag{4}$$

where Q_e, C_e, Q_m, and k_f represent the amount of each pharmaceutical being adsorbed at equilibrium per gram of zeolite (mg/g), equilibrium concentration (mg/L), maximum adsorption capacity (mg/g), and Freundlich capacity parameter ($mg^{(1-1/n)}L^{1/n}/g$), respectively; K and n are the adsorption constants for Langmuir and Freundlich isotherms, related to energy of adsorption and adsorption intensity, respectively.

3 Results and Discussion

The removal of the studied pharmaceuticals by the Jordanian zeolite was investigated and optimized with respect to pH, contact time, adsorbent dosage, and initial concentration. The following sections discuss the effect of each parameter on the percent removal of the selected pharmaceutical in light of their chemical structure and physical properties.

3.1 Effect of pH

Figure 1 displays the effect of pH on the percent removal of the studies pharmaceuticals by zeolite in the pH range of 2–8. Inspection of this figure reveals that the percent removal decreases with increasing pH for all studied pharmaceuticals except for diclofenac sodium. The optimum pH for all the studied pharmaceutical is 2 except for diclofenac sodium which shows an optimum pH of 6. Furthermore, the percent removal these pharmaceuticals at the pH 2 increases in the order of paracetamol < indomethacin < ibuprofen < diclofenac sodium < chlorpheniramine maleate. In order to explain these observations, Scheme 1 displays the chemical structure of these pharmaceutical which demonstrates that paracetamol, indomethacin, ibuprofen, and diclofenac sodium have a carboxylic acidic group with pKa less than 6 (Table 1), whereas chlorpheniramine maleate has a pyridine group with pKa 9.3. Furthermore, zeolites contain aluminum, silicon, and oxygen in their framework, whereas cations and

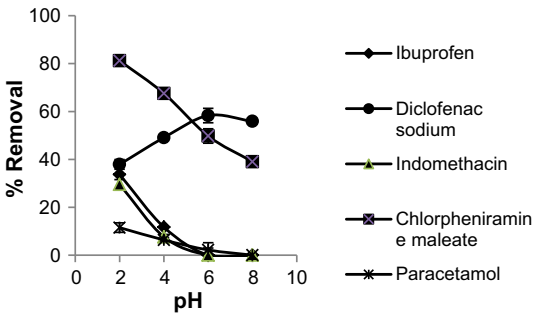
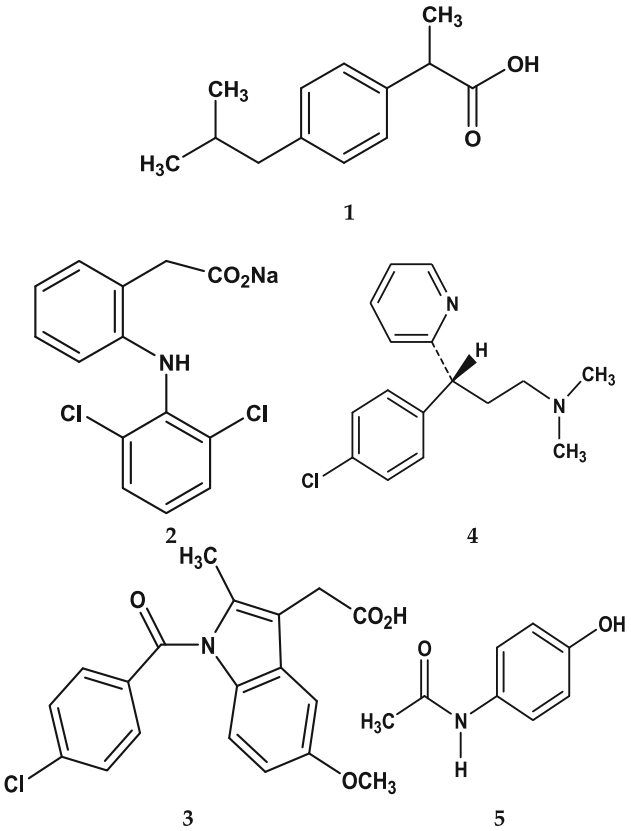


Fig. 1 Percent removal of studied pharmaceuticals as a function of pH at $T = 25\,°C$, contact time = 120 min, initial conc. = 50 mg/L, adsorbent dosage = 0.5 g/L, and shaking speed of 250 rpm



Scheme 1 Chemical structures of investigated pharmaceuticals: **a** ibuprofen, **b** diclofenac sodium, **c** indomethacin, **d** chlorpheniramine maleate, **e** paracetamol

water are placed in the pores. The tetrahedral coordination of the silicon and aluminum atoms in zeolites is affordable via shared oxygen atoms. Similarly to clays, zeolites have a rigid, 3D crystalline structure consisting of a network of interconnected tunnels and cages. The pore and channel sizes are nearly uniform, allowing the zeolites crystal to act as a molecular sieve. This unique structure makes the zeolite an excellent host to water molecules and positively charged ions with an appropriate molecular size to fit into the pores. Examples for such ions are potassium, sodium, and calcium. Based on the chemical structure of zeolites, it is expected that at low pH such as pH 2 the three NSAIDS will interact strongly with the zeolite molecules through a relatively strong interactions of the free carboxylic group proton and the zeolite oxygen atoms connected to the silicon and aluminum elements. On the other hand, at a pH higher than their pKa's such as pH 6, it is quite understood that the interactions between those NSAIDs and the zeolite molecules will be minimal due to the repulsion between the negatively charged carboxylate group (the dominant form of the NSAID at pH 6) and the zeolite oxygen atoms (electron rich). An exception of this rule is diclofenac sodium, where at pH 6 the NSAID might participate in strong interactions with the zeolite molecules via

the following suggested mechanism; the sodium cation of diclofenac can penetrate the zeolite pores and can serve as a good host to diclofenac via electrostatic interactions between the cation and the relatively electronic rich amine group of diclofenac. In the other two NSAIDs, paracetamol and indomethacin, this kind of interactions cannot be afforded due to a lack of a heteroatom or a function rich in electrons. Further, as shown in Fig. 1, the removal of diclofenac sodium by the zeolite increases with an increase in the pH (up to 6). This might be due to the fact that at higher pH values (2–6) the concentration of proton (H+) is decreased such that its competition with sodium cation for binding with diclofenac is minimal, thus leading to stronger interactions between the drug and the zeolite (the drug's amine and sodium cation placed within the zeolite's pores).

On the one hand, the behavior of the percent removal of chlorpheniraminemaleate could be explained on the bases that at low pH and since the drug has pKa of 9.13, all the molecules bear positive charges leading to larger attraction with the negatively charged surface and the observed highest percent removal . As the pH increases, the drug undergoes deprotonation forming to neutral molecules with lower attraction to the surface and to the observed decrease in its percent removal.

3.2 Effect of Contact Time

Figure 2 displays the effect of contact time on the percent removal of the studies pharmaceuticals on Jordanian zeolite. For all pharmaceutical, the maximum percent removal was reached in less than 10 min indicating fast kinetics. This short time for the adsorption kinetics did not allow for the analysis of the adsorption kinetic model within the limited data for each studied pharmaceutical. However, and for all studies pharmaceutical, the optimum contact time was set at 80 min to insure that equilibrium state is reached.

3.3 Effect of Adsorbent Dosage

Figure 3 illustrates the impact of zeolite dosages on the percent removal of pharmaceuticals from spiked solutions. Inspection of Fig. 3 reveals that as the adsorbent dosage increases, the percent removal of all studied pharmaceutical increases reaching maximum value at adsorbent dosage of 1.0 g/L for ibuprofen, 2.0 g/L for diclofenac sodium and indomethacin, and 1.5 g/L for chlorpheniramine maleate and paracetamol. These values were selected as the optimum dosage for further studies.

3.4 Effect of Initial Concentration

The effect of the initial concentrations on removal capacity of the selected pharmaceuticals at the optimum pH, contact time, and adsorbent dosage was studied in the range 10–50 mg/L (Fig. 4). Inspection of Fig. 4 reveals that when the initial concentration increases from 10 to 50 mg/L, the removal capacity of all pharmaceuticals increases from 0.04 to 2.0 mg/g. This effect can be attributed as follows: higher initial concentrations increase the driving force in order to overcome the mass transfer resistance of pharmaceutical molecules between the aqueous and solid phases. Moreover, the increase in the uptake capacity with increasing initial concentration may also be as the result of more intensity interaction between natural zeolite and soluble molecules.

3.5 Adsorption Isotherms

For ibuprofen, a plot of C_e Q_e versus C_e gave nonlinear relation which indicates that Langmuir isotherm do not fit the experimental data, whereas a plot of log Q_e versus log C_e gave a linear relation with $R^2 = 0.9997$, indicating that

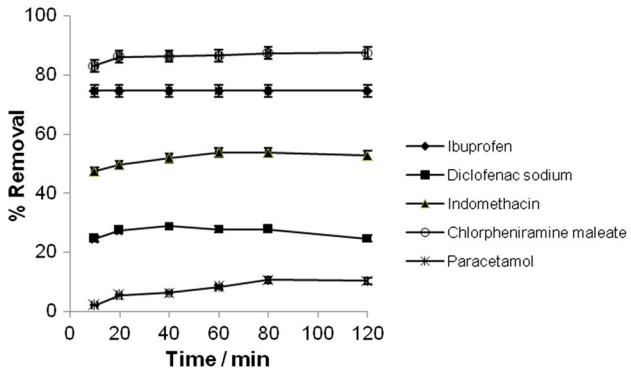


Fig. 2 Percent removal of studied pharmaceuticals as a function of contact time at $T = 25\,^{\circ}\mathrm{C}$, pH = 2 for ibuprofen, indomethacin, chlorpheniramine maleate, and paracetamol, pH 6 for diclofenac sodium, initial conc.= 50 mg/L, adsorbent dosage = 1.0 g/L, and shaking speed 250 rpm

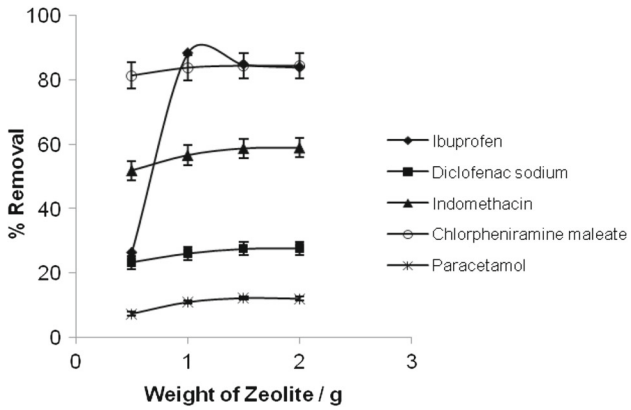


Fig. 3 Percent removal of studies pharmaceuticals as a function of adsorbent dosage at $T = 25\,^{\circ}\mathrm{C}$, pH = 2 for …… and 6 for diclofenac sodium, initial conc. = 50 mg/L, contact time = 80 min, and shaking speed 250 rpm

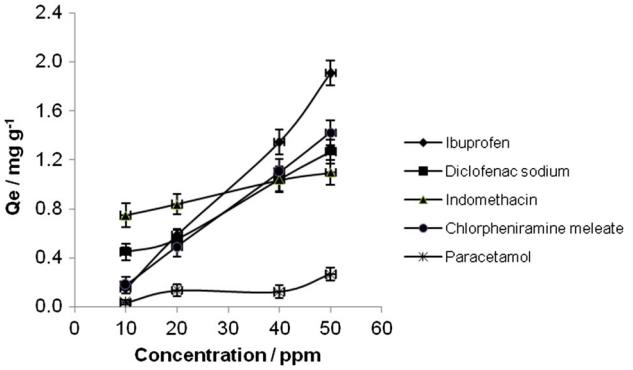


Fig. 4 Removal capacity of pharmaceuticals as a function of initial concentrations at $T = 25\,^{\circ}\mathrm{C}$, pH = 2 and 6, adsorbent dosage = 1.0 g, contact time = 80 min

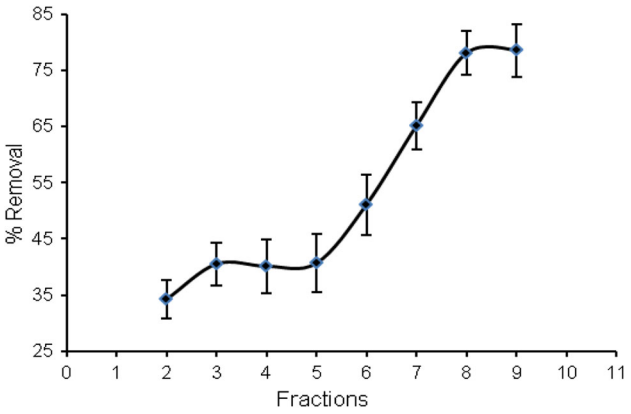


Fig. 5 Percentage removal of Ibuprofen on zeolite as a function of different fractions at $T = 25\,^{\circ}\mathrm{C}$, pH = 2, and initial conc. = 50 mg/L

Table 2 Langmuir and Freundlich isotherms constants at 25 °C for the studied pharmaceuticals at the optimum conditions

Adsorbate	Langmuir model		
	Q_{max} (mg/g)	K_L (L/mg)	R^2
Diclofenac sodium	4.75	0.047	0.992
Indomethacin	26.60	1.14	0.992
Paracetamol	55.6	0.44	0.992
Adsorbate	Freundlich model		
	n (mg/g)	K_L (L/mg)	R^2
Diclofenac sodium	1.2	8.38	0.991
Indomethacin	1.7	2.10	0.947
Paracetamol	0.797	137	0.933

Freundlich isotherm model is a better model to describe the removal ibuprofen by zeolite. The Freundlich constants k_f (related to adsorption capacity) and $1/n$ (related to removal intensity) were determined to be 1.23 mg/g and 0.717, respectively (Table 2).The same behavior was also followed for the removal of Chlorpheniramine maleate on zeolite with k_f and n of 2.11 mg/g and 3.57, respectively (Table 2). On other hand, Langmuir isotherm model was found to be the best to model to describe the removal of diclofenac sodium, indomethacin, and paracetamol indicating ideal adsorption processes for these pharmaceuticals on the surface of zeolite. The Langmuir isotherm constant for each pharmaceutical was evaluated from the regression equations and is listed in Table 2.

3.6 Continuous Flow Mode

Column experiments were conducted on the removal of ibuprofen by zeolite as described in Sect. 2.4. Figure 5 shows the percent removal as function of collected fraction. The results showed that the highest percent removal of ibuprofen on zeolite was found to be for the eluted fraction number 9 which is about 78% as shown in Fig. 5. The increasing percentage removal as function of fractions of column experiment is due to more intensity interaction between natural zeolite and soluble molecules. Similar performances were registered with the rest of studied pharmaceuticals.

4 Conclusions

Natural Jordanian zeolite is effective for removal of ibuprofen, indomethacin, diclofenac sodium, and chlorpheniramine maleate from aqueous solution. Natural Jordanian zeolite is characterized by large surface area, microporous nature, high adsorption capacity, and easy availability. Nevertheless, it was found not much effective for removal of paracetamol.

The effect of pH, contact time, adsorbent dosage, and initial concentration of pharmaceuticals on the removal process was studied. The optimum pH for all pharmaceuticals was found to be 2 except for diclofenac sodium where its optimum pH was 6. The optimum adsorbent dosage was 1.0 g for ibuprofen, 2.0 g for diclofenac sodium, and indomethacin, whereas 1.5 g for chlorpheniramine maleate and paracetamol. The optimum initial concentration of pharmaceuticals on the adsorption process was 50 mg/L. Diclofenac sodium, indomethacin, and paracetamol have a good fit with Langmuir isotherm model with adsorption capacity 4.8, 26.6, and 55.6 mg/g, respectively. Ibuprofen and chlorpheniramine maleate were found to fit with Freundlich isotherm with adsorption capacity of 1.23 and 2.11 mg/g, respectively. The difference in percentage removal of batch and column experiments was accepted with not more than 10%, indicating that both methods could be used as successful tool for elimination of pharmaceutical molecules.

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