Removal of Diclofenac from Aqueous Solutions Using Modified Pumice with Magnesium Chloride

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Abstract

Background: Diclofenac is one of the drug compounds that is known as an emerging contaminant in aqueous solutions. Studies have shown that biological treatment is not sufficient to treat these compounds and new methods such as adsorption should be used to prevent contamination of aquatic environments. One of the native absorbers in this regard is the pumice. This study aimed to investigate the removal of diclofenac from aqueous solutions using magnesium chloride modified pumice.

Methods: In this experimental study, with a practical approach, the required adsorbent was prepared from pumice. Magnesium chloride was used for pumice modification. The experiments were performed in a closed system at laboratory temperature. In this study, the effect of variables, adsorbent dose, contact time, and pH on diclofenac removal was investigated. Diclofenac was analyzed by KNAUER model HPLC at a wavelength of 254 nm.

Results: Modified pumice by magnesium chloride was able to remove 95.83% of diclofenac (20 mg/l) at a concentration=1 g/l for 15 minutes at pH=5. Comparison of modified and natural pumice performance in 5, 10, 15, 30, 40 minutes with an average of 89.52% of modified pumice removal, compared to 48.15% of natural pumice removal, which was 1.86 times more efficient.

Conclusion: Pumice can be used as a cheap, available, and highly effective adsorbent for the removal of diclofenac from aqueous solutions.

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Introduction

Iran is one of the top twenty countries in the world in terms of drug consumption and terms of drug per capita, After China, Iran is the second country which uses the druge excessively in Asia.[1] Drug contamination in aquatic environments is a global issue that affects aquatic animals, microorganisms, and human health.[2] Conventional treatment plants are not very efficient in removing these compounds, because the concentration of most drugs in the effluent is close to their concentration in inlet sewage.[3] High solubility and stability in the environment are the distinctive features of these pollutants that do not decompose under normal conditions and require special reactions to decompose under special conditions.[4] Various used drugs in medicine and veterinary are the main source of emerging pollutants.[5]

Some studies have shown the presence of 60 drug compounds in water resources by 2002.[4] Some of these compounds include drugs and personal care products that have been observed in effluents in the range of ng/l to µg/l.[6] About 5 to 90% of the drugs used are not absorbed by the body and after their toxicity disappears in the liver in the form of glucuronide, it is discharged through the urine and feces into the sewage network and aqueous solutions.[7] Because there is no serious monitoring of drug control and routine tests such as BOD and COD are not responsive,[8] as a result, contaminants enter the aquatic environment along with the effluent.[9]

Therefore, effluent from wastewater treatment plants is one of the main reasons for concern about emerging pollutants, which has caused destructive and unknown effects on the environment and public health.[10] Although concentrations of drugs in the environment are low or less effective, and direct and short-term tests cannot show the biological effects of these drugs, but target and non-target organs are exposed to these drugs. Over time, they accumulate in tissues and endanger the environment and human health.[4]

Diclofenac is a potent non-steroidal anti-inflammatory drug (NSAID) with analgesic and antipyretic effects. The drug is extensively metabolized in phenol compounds in humans and animals and excreted as glucuronide or sulfate.[11, 12] The molecular structure of diclofenac is shown in Figure 1.[13]

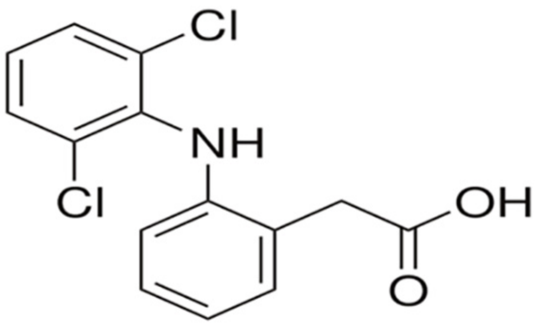

Figure 1: Diclofenac molecular structure

Diclofenac has been identified in many freshwaters around the world. More than 100 publications have reported its presence in surface and groundwater. The drug is analyzed in freshwater at environmental toxicology levels.[13]

The global average concentration of diclofenac in aqueous solutions has been reported 0.032 and a maximum of 18.72 µg/L. The average of this drug in several inlets and outlets of wastewater treatment plants in 2012 was observed to be 1.00 and 0.8 µg/L, respectively, which shows the low efficiency (elimination of 20% and less) of conventional treatment processes.[14]

Various processes such as reverse osmosis, adsorption on activated carbon, ozonation, advanced oxidation systems such as Fenton or Photofenton, ultrasonic, pre-oxidation with an ultraviolet lamp, and optical catalyst with titanium dioxide nanoparticles are used to remove drug compounds from water.[15] pumice is one of the cheap adsorbents that has been considered in recent years in various treatment technologies to remove contaminants.[16] The original and modified version has been developed to remove contaminants with high efficiency.[9]

Modification of pumice with magnesium chloride increases the specific adsorption level from 2.34 to 41.63 m^2/g compared to natural pumice by increasing the percentage of magnesium oxide and chloride.[17] Liquid chromatography-mass spectrometry (HPLC/ MS/MS) has been used to measure medicinal compounds in water according to the US Environmental Protection Agency 1694 guidelines.[18] Equation (1) was used to determine the adsorption capacity.[19]

$$\text{Removal rate (\%)} = \frac{\text{Initial concentration} - \text{Concentration after adsorption}}{\text{Initial concentration}} \times 100 \quad \text{(1)Eq.}$$

The average concentration of diclofenac in Karaj river water and its effluents was 0.034 µg/l. Also, in treatment plants and effluents entering the river, the concentrations of diclofenac were 082.0 and 064.0 µg/l.[20]

In the study of phenol uptake from wastewater by pumice modified with magnesium/copper bimetallic particles, the best phenol removal performance (97.3%) at a dose of 2 mg/l, pH=8, and contact time of 30 minutes was reported.[21] In this study, "removal of diclofenac from aqueous solutions using pumice modified with magnesium chloride" was investigated.

Methods

This study was an experimental research with an applied approach. The experiments were performed on a laboratory scale and in batch mode. Diclofenac was measured by HPLC connected to an LC-6AD pump equipped with an absorption detection lamp and fluorescence emission. The characteristics of the column used were C18,4.6×250mm. 5 µm) with a mobile phase of 30% by volume of HPLC water and 70% by volume of acetonitrile. The analysis was performed at room temperature with the settings of the device isocratically. The diclofenac peak at 254 nm was obtained in the second minute.

Preparation of Natural Pumice

The pumice used in this study was obtained from the mines of the Qorveh region of Kurdistan. To prepare pumice samples as adsorbent, pumice stone was first crushed by a mill and granulated using a 16 mesh (1.190 mm). The granulated particles were washed several times with tap water and then several times with distilled water. They were then immersed in concentrated hydrochloric acid for 24 hours (to remove particle color and reduce turbidity and make porosity). After immersion in distilled water, it was washed and placed in an oven at 150 °C for 24 hours. Natural pumice was used after drying.

Preparation of Modified Pumice with Magnesium Chloride

To prepare the modified pumice, 200 ml of magnesium chloride solution (2mol/l) was added to 10 g of the previous stage pumice and placed in a mixer at 300 rpm for one hour. The pumice was then washed with water and placed in an oven at 150 °C for 48 hours. Modified pumice by magnesium chloride was then available. Pumice properties were determined before and after shaving with magnesium chloride by using infrared analysis (FTIR). Also, the characteristics of a sample of pumice after adsorption of diclofenac sodium were determined using electron microscopy (SEM) imaging.

After determining the adsorbent properties was optimized by changing the variables as diclofenac concentration, pumice concentration, duration, and pH using the classical method, One Factor at a Time.

Analysis Method

Characteristics of natural and modified magnesium chloride pumice with infrared (FTIR) and natural and modified pumice with magnesium chloride after diclofenac absorption were determined using electron microscopy (SEM).

Results

FT-IR Test Analysis

To investigate the functional groups in the pumice structure before and after structural modification, the FT-IR test was used and the results are shown in Figure 2 (a and b).

The spectra shown in Figure 1 are similar to the pumice spectra in similar articles.[22-24] In the FT-IR spectrum of unmodified pumice, the absorption peaks at wavelengths cm-11411 and cm-11010 were related to asymmetric and symmetrical tensile vibrations of Si-O-Si bonds in the SiO42- groups.[24] Also, the flexural vibration of Si-O-Si bonds at the wavenumbers of 1712 cm and 1424 cm has shown the absorption peak.

The peak at wavelength 1631 cm is also related to the vibration of reducing carbon bonds in the crystal lattice.[25] After modification of the pumice structure by magnesium chloride, it caused a wide peak in the wavenumber=13347 cm and also an absorption peak in the wavenumber=11612 cm, which was related to the tensile and flexural vibration of the O-H bonds related to surface adsorption water, respectively.[26] It is known that with the modification of pumice by magnesium chloride, the water absorption of the sample has increased, which can be proof of the successful modification of pumice by this material. Another difference between the two spectra was the formation of a new small peak at 11524 cm, which was related to the tensile vibration of Mg-Cl bonds in magnesium chloride.[27] The displacement peak of the tensile vibration of the Si-O-Si bonds from 110-cm10 in the spectrum of the unmodified sample to the 1997-cm wave number could be another confirmation of the presence of magnesium chloride in the silicon oxide structure in the pumice.

Analysis of FE-SEM Test Results

FE-SEM test was used for microscopic examination of pumice structure before and after correction. The resulting micrographs are shown in Figure 3 to Figure 5.

According to Figure 3, in the natural pumice micrograph, particles with an average size of 2.8 micrometers and in the image with a magnification of 15,000 times the cavities with an average size of 2.2 micrometers can be seen. Figure 4 shows a spherical particle with an average diameter of about 8 micrometers in a micrograph of magnesium chloride modified pumice. Also, in the pumice sample modified with magnesium chloride, the number and size of cavities are much less than the natural pumice sample and their average size has reached about 0.4 µm. In the micrograph of the magnesium chloride-modified pumice sample after adsorption of diclofenac sodium (Figure 5), although in the low magnification image (Figure 5 (a)) the sample appears porous. But carefully in the high-magnification images, it is clear that these porosities are shallow, and in fact, are only low and high in the sample structure. According to Figure 5 (d), it is clear that unlike the two samples of natural pumice and pumice modified with magnesium chloride, no porosity can be observed at a magnification of 15,000 times. Also in the sample of pumice modified with magnesium chloride after adsorption of diclofenac sodium (c) cubic particles with an average size of about 28.4 micrometers can be seen.

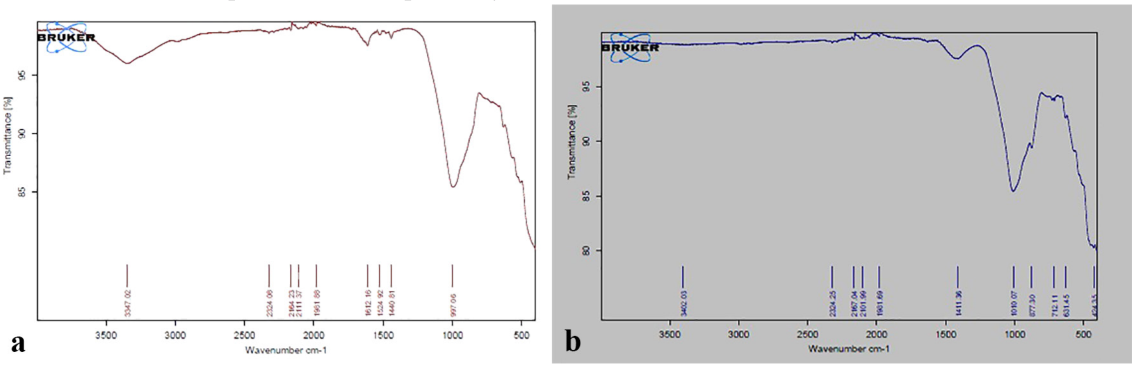

Figure 2: Results of FT-IR pumice test (a) before and (b) after correction by magnesium chloride

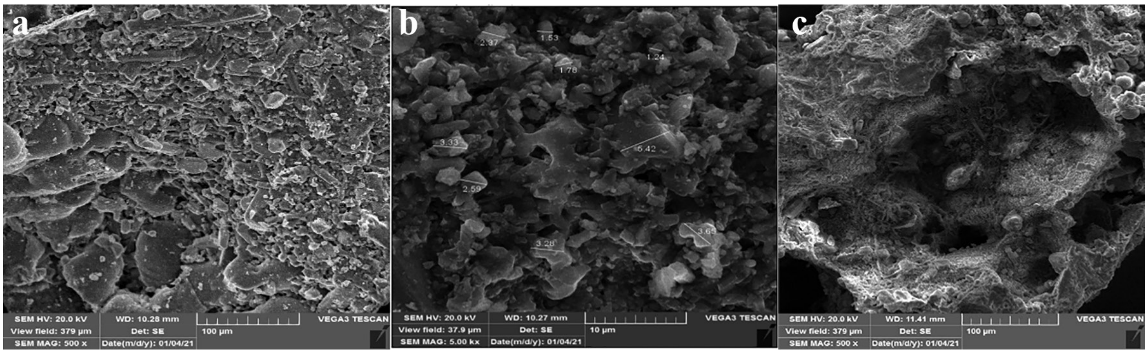

Figure 3: Micrographs of natural pumice at three magnifications (a) 500, (b) 5000, and (c) 15,000 times

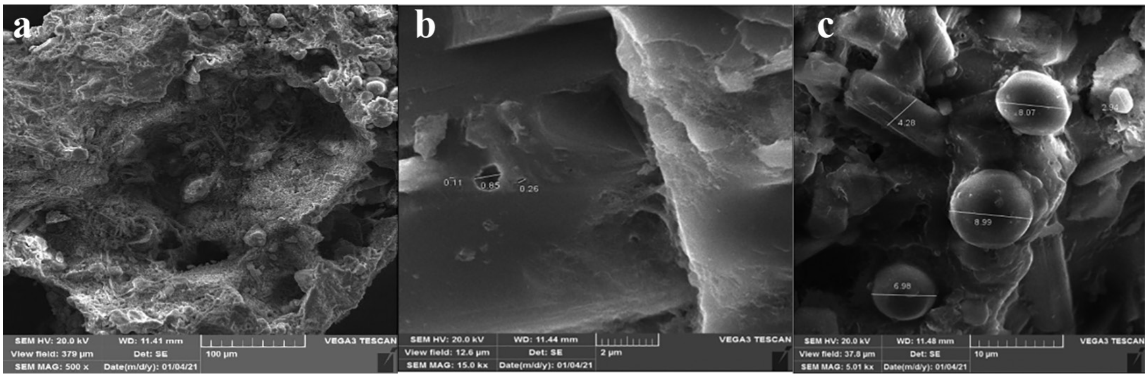

Figure 4: Micrographs of magnesium chloride modified pumice sample at three magnifications (a) 500, (b) 5000 and (c) 15,000 times

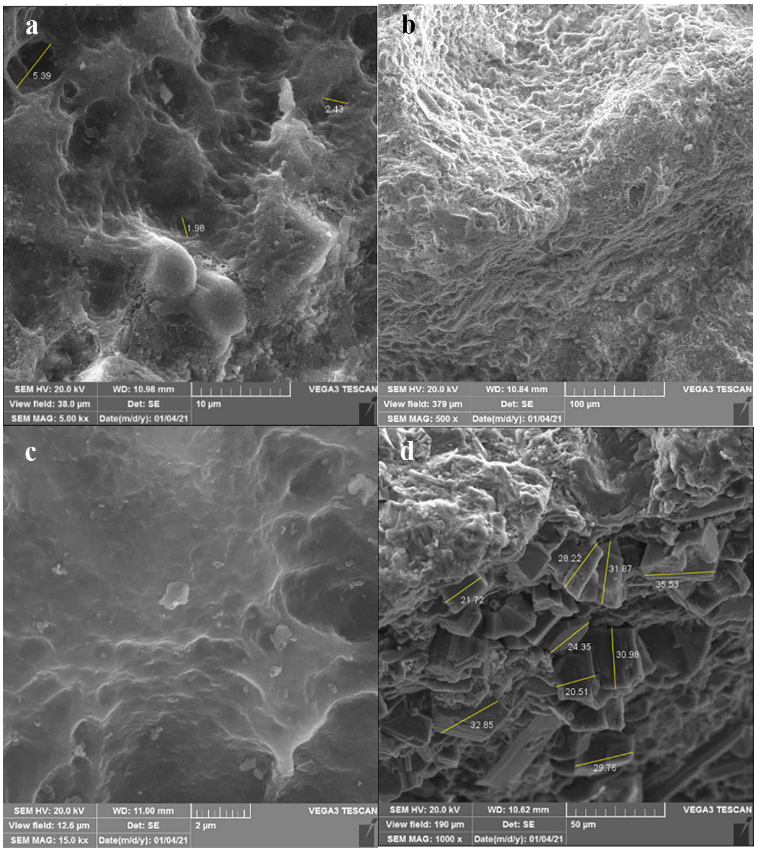

Figure 5: Micrographs of the pumice sample modified with magnesium chloride after adsorption of diclofenac sodium at three magnifications (a) 500, (b) 1000, (c) 5000 and (d) 15000 times

Effect of Natural Pumice Concentration on Diclofenac Removal

A solution of 20 ppm diclofenac was prepared for the experiments. To determine the optimal amount of pumice, 10 g of natural pumice was added to the weight of 250 ml of diclofenac and placed in a mixer at 200 rpm, and analyzed at intervals of 15, 30, and 60. The results are shown in Figure 6. Due to the high rate

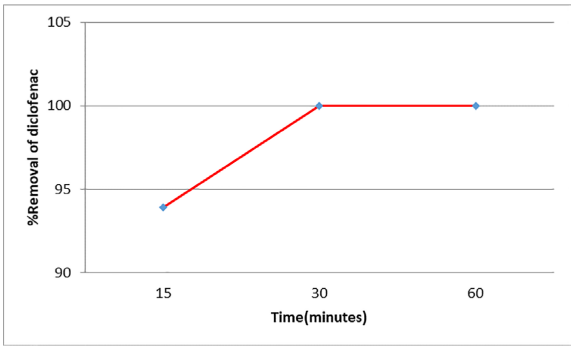

Figure 6: diclofenac sodium removal with 10 g of natural pumice and contact time (minutes)

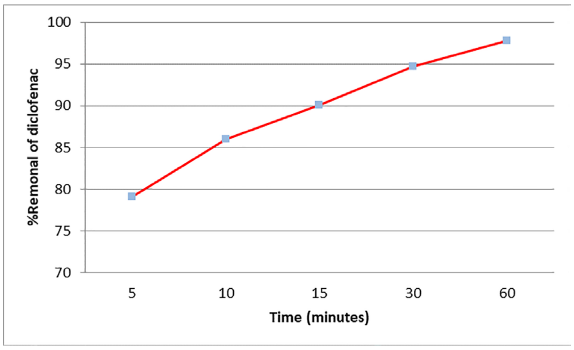

Figure 7: Elimination of diclofenac sodium with a concentration of 20 rpm and 1 g of natural pumice and contact time (minutes)

of removal to determine the optimal concentration in the next step with natural pumice one gram per liter will be tested.

Experiments were performed with 1 gram of natural pumice for 5, 10, 15, 30, and 60 minutes. The results of the analysis shown in Figure 7 increased with increasing removal time.

Effect of Magnesium Chloride Modified Pumice Concentration on Diclofenac Removal

Experiments were performed at 0.5 and 1 g/l magnesium chloride modified pumice for 5, 10, 15, 30, and 60 minutes. According to Figure 8, with increasing the duration and concentration of the modified pumice, the removal efficiency increased and 0.5 g of the modified per liter pumice was selected as the optimal concentration and the duration of 15 minutes was selected as the optimal time.

PH Effect

To determine the effect of pH of solution on diclofenac adsorption by pumice modified with magnesium chloride, 15-minute experiments carried out in the pH range of 3, 5, 7, 9 and 11 with a concentration of 0.5 g / l, and pumice modified with magnesium chloride and a concentration of 20 mg / l diclofenac. The results are shown in Figure 9. The highest removal efficiency was shown at pH=5 equal

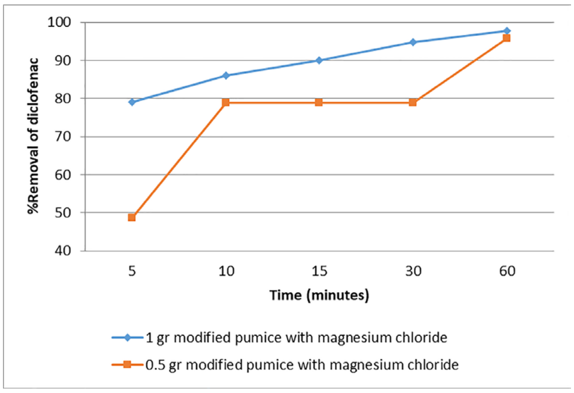

Figure 8: Removal of diclofenac sodium with 0.5 and 1 g of modified pumice with magnesium chloride and contact time (minutes)

to 95.83 which was selected as the optimal pH.

According to the results, the concentration of 20 ppm diclofenac sodium, 0.5 g of pumice modified with magnesium chloride, 15 minutes of exposure to pumice, pH 5 were selected as the optimal factors. Also, the mass load in 250 ml Samples were obtained to remove diclofenac sodium as the optimal volume.

Discussion

The results of this study showed that pumice modified with magnesium chloride has a high capacity and speed in adsorption of diclofenac sodium. In the FT-IR

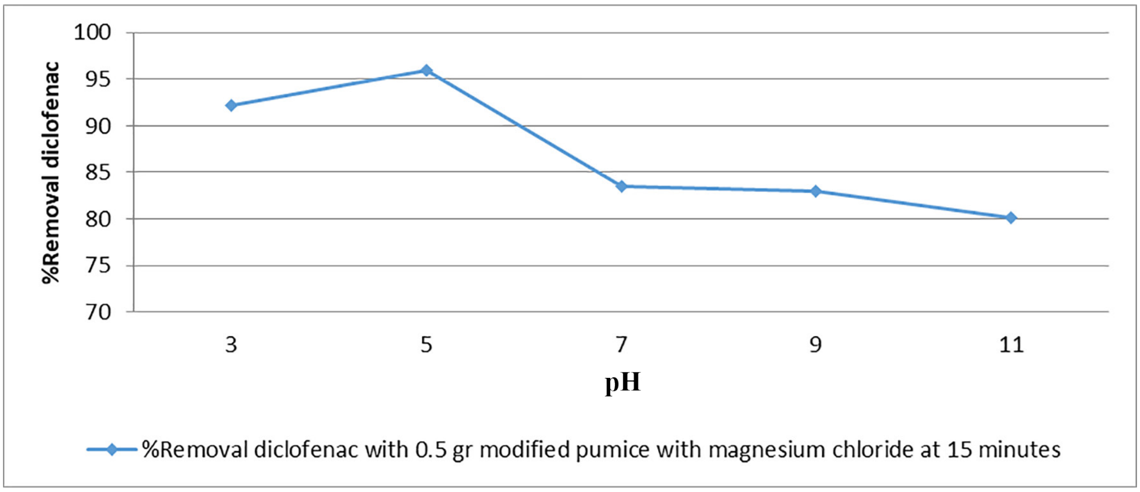

Figure 9: Removal of diclofenac sodium with 0.5 and 1 g modified pumice with magnesium chloride and contact time (minutes)

spectrum of unmodified pumice, the adsorption peaks appeared to be Si-O-Si bonds in the SiO42- groups.[24] On the other hand, the absorption peak located in the wavenumber 1631 cm was also related to the vibration of reducing carbon bonds in the crystal lattice.[25]

After modification of the pumice structure by magnesium chloride, it caused an absorption peak in the wavenumber 11612 cm, which is related to the O-H bonds related to adsorption water.[26] It is known that with the modification of pumice by magnesium chloride, the water absorption of the sample has increased, which can be evidence of the successful modification of pumice by this substance.[27]

The displacement of the peak associated with the Si-O-Si bonds from the unmodified sample range to the 1997 cm-wave number could be further evidence of the placement of magnesium chloride in the silicon oxide structure of the pumice. Determining the appearance and composition of the structure of an adsorbent is one of the most important points in the adsorption process. SEM images for natural pumice and pumice after correction with magnesium chloride and after adsorption of diclofenac sodium showed that in natural pumice particles with an average size of 2.8 µm and in the image with 15000 times magnification cavities with an average size of 2.2 µm can be seen. Spherical particles with an average diameter of about 8 µm were observed in the pumice-modified images of magnesium chloride. Also, in the pumice sample modified with magnesium chloride, the number and size of cavities are much less than the natural pumice sample and their average size has reached about 0.4 µm. Sample appears to be porous in the images of the magnesium chloride-modified pumice sample after adsorption of diclofenac sodium at low magnification. However, a closer look at the high-magnification images reveals that these porosities were shallow, and were only low and high in the sample structure. According to the pictures, it is clear that unlike the two samples of natural pumice and pumice modified with magnesium chloride, no porosity can be seen at 15000 times magnification.

Also, in the pumice sample modified with magnesium chloride, after adsorption of diclofenac sodium, cubic particles with an average size of about 28.4 µm can be seen. Based on the test results, the comparison of modified and natural pumice performance in 5.10, 15, 30, 40 minutes with an average of 89.52% of modified pumice removal (48.15%) was more efficient than natural pumice removal (1.86 times). The optimal dose of 0.5 g/l pumice modified with magnesium chloride was selected as the adsorbent concentration. Due to the increase in adsorbent concentration and contact time, it was found that by decreasing the pumice concentration (natural and modified with magnesium chloride), the removal efficiency of diclofenac also decreased.

This may be due to the availability of adsorption sites, where adsorption sites in magnesium chloride-modified pumice were much larger and deeper than in natural pumice. These results were consistent with studies by other researchers. Haji Bagher Tehrani et al. In 2017, in a study on the removal of cephalexin with pumice, reported that the removal efficiency increased with increasing the adsorbent dose up to 5 g/l. In other words, the removal efficiency was negligible with increasing the dose from 5 to 10 g/l. Probably due to the density of available binding sites on the adsorbent and the lack of access to active sites in the adsorbent and the balance between diclofenac molecule on the adsorbent and in the aqueous medium.[28]

According to the results obtained from experiments at pH=5, the highest removal efficiency of diclofenac was obtained. The reason for the decrease in efficiency at high and low pH can be attributed to the competition between diclofenac and hydrogen ions and hydroxyl ions. Studies show that at high pH the dominant surface electric charge is negatively charged at the surface of the adsorbents. Finally, since the surface charge of the modified pumice was negative, the number of negative charges increased with increasing pH. On the other hand, due to the anionic nature and proton loss, the electrostatic attraction between the adsorbent and the pollutant decreases and affects the adsorption efficiency.[9, 29] These results are consistent with studies by other researchers. Khodayari et al. Reported in 2018 that the maximum removal of the antibiotic metronidazole was achieved with carbonated pumice in a fixed bed at a pH=5.[9]

Torabi Hakmabadi et al. reported in 2016 that the maximum removal of diclofenac from aqueous solutions was achieved by ammonium chloride-activated carbon at pH 5.[30] In the present study, the removal efficiency increased up to 60 minutes by increasing the contact time using natural pumice modified with magnesium chloride. Due to the economic aspect, the highest removal efficiency was obtained up to 10 minutes with a steep slope. From 10 to 60 minutes, the slope of the removal line increased smoothly and evenly.

These results are consistent with studies conducted by other researchers in terms of the removal process. For example, in 2017, in a study on the removal of cephalexin with pumice, Haji Baqer Tehrani et al. Reported that the equilibrium time for the adsorbent used was within 60 minutes. However, since the removal efficiency was not optimal at this time, the contact time of 150 minutes at which the highest adsorption took place was used in other experiments. With an increasing time of more than 150 minutes, the rate of increase of removal percentage was very small, so for the economical operation of the absorption operation, the optimal time of 150 minutes was considered. The removal efficiency of the antibiotic was initially continued with a steep slope and then the slope of the removal line became almost flat. The reason for this is that when the active adsorption sites were filled, the adsorption rate was controlled and antibiotics were transferred from the outside of the adsorbent to the inner sites of the adsorbent particles.[28] Torabi Hakmabadi et al. Reported in 2016 that the removal time of diclofenac from aqueous solutions by ammonium chloride activated carbon increased from 62.5 to 100%, respectively, by increasing the contact time from 10 to 40 minutes.[30]

Conclusion

In this study, the removal of diclofenac from aqueous solutions was investigated using magnesium chloride modified pumice. According to the results, modification of pumice with magnesium chloride increased the specific surface area and adsorbent capacity. This indicates that at the same initial concentration of diclofenac less adsorbent dose is required than normal pumice, with increasing adsorbent concentration and contact time the removal efficiency increased, and with increasing pH, the removal efficiency decreased. Pumice can be used as an inexpensive, widely available natural adsorbent to remove diclofenac from aqueous solutions.

Conflicts of interest*:* None declared.

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