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INVESTIGATION OF DICLOFENAC REMOVAL FROM DRINKING WATER BY COAGULATION METHOD

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ABSTRACT

In this study, the removal of diclofenac from drinking water was investigated by using four different coagulants ($FeCl_3.6H_2O$, $MgCl_2.6H_2O$, $Al_2(SO_4)_3.18H_2O$, $FeSO_4.7H_2O$). All of the coagulation experiments were performed by using jar test. After the determination of optimum coagulant dosage and pH, coagulation experiments were performed at four different temperatures to determine the effect of temperature. The highest removal efficiency of diclofenac was obtained as 57.6% with $FeSO_4.7H_2O$ at pH5. It was determined that the removal efficiency increased with increasing temperature for all coagulation experiments.

Keywords: diclofenac, coagulation, drinking water

INTRODUCTION

Contaminants that are found in drinking water have emerged as a problem for many years. It is a basic right for every person to reach clean and healthy drinking water. There have been many studies conducted on this topic in the world of science. Solution methods have been investigated for contaminated water. Today, as human and veterinary use of pharmaceuticals becomes increasingly widespread, they have entered among the contaminant groups for which important and urgent measures must be taken. Pharmaceutically Active Compounds (PhACs) are produced in order to diagnose, treat and improve several diseases, impairments, abnormal physical conditions or their symptoms that can be seen in humans and animals and which can contain one or more active ingredients (1).

Pharmaceutical pollution first appeared in 1970s (2). In 1980s, analyses began to be made to measure pharmaceutical residues in surface waters (3). However, technologies were developed in the 1990s to detect the concentrations of pharmaceutical residues at μg/L and ng/L levels in aquatic media (4).

The most common route for transferring pharmaceuticals into aquatic environments is human consumption. As a result of that, they are thrown into the sewage system by the body, and from there, they reach the wastewater treatment plants and finally surface waters. After the disposal of PhACs, these chemical substances or their metabolite products formed in the body can leak into the water environment through urine and feces. Therefore, PhACs are detected in soil, surface waters, bottom muds, domestic wastewaters, sewage muds, and underground waters (5).

Coagulation is a widely-used process because it is an effective method for eliminating natural organic substances and turbidity in drinking water (6). The results of some studies in the literature have showed that the efficacy of drug removal by coagulation method in drinking waters was generally low (7, 8, 9). This is most likely due to the low hydrophobicity of the drugs and the lack of a mechanism to be adsorbed into the flock (7).

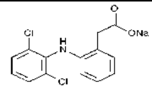
Most analgesics (painkillers) have anti-inflammatory and antipyretic properties. Many painkillers are used in large quantities in many countries and are sold without prescription.

In this study, the removal of diclofenac (an analgesic drug) from drinking water by coagulation method was examined, and the effect of temperature on this method was investigated. In recent years, drug residues in drinking waters and superficial waters have been detected all over the world and in our country. For this purpose, it is important to examine the removal methods of drug substances. From this point of view, it is considered that our study will contribute to the literature.

MATERIALS AND METHODS

Diclofenac, which is a common non-steroidal anti-inflammatory drug, was used in the study. The active drug substance was obtained from Merck. Diclofenac is a non-steroidal anti-inflammatory drug used in order to reduce inflammation and relieve pain in arthritis and acute injuries in humans and animals. Some properties of diclofenac are given in Table 1. Diclofenac was found to be about 2 ng/L in well water (10) and at a maximum level of 380 ng/L in groundwater (11). It is estimated that the global consumption of diclofenac is 940 tons per year (12).

Table.1. Some properties of diclofenac

DICLOFENAC	
Chemical formula	
Molecular formula	$C_{14}H_{11}Cl_2NO_2$
CAS No	15307-86-5
Molecular weight	296.14 g/mol
Log K_{ow}	4.51
pK_a	4.15
Other names	o-)2-6-Dichloroanilino) phenylacetic acis, sodium salt
Melting point	284°C (543.2°F)
Toxicity	LD_{50}: 95 mg/kg (mouse)

Coagulants, which are widely used in both industrial wastewater treatment and drinking water treatment, have been selected in this study. The coagulants used and some features of them are shown in Table 2.

Table.2. Coagulants used in this study and their properties

Coagulants	Chemical formula	Molecular weight (g/mol)	Density	Melting point
Aluminum sulfate	$Al_2(SO_4)_3.18H_2O$	666.42	2.67 g/cm^3	770 °C
Iron III Chloride	$FeCl_3.6H_2O$	270.33	2.9 g/cm^3	306 °C
Iron III Chloride	$FeSO_4.7H_2O$	278.02	1.895 g/cm^3	60-64 °C
Magnesium Chloride	$MgCl_2.6H_2O$	203.30	1.569 g/cm^3	117 °C

The jar test experiments were carried out on 6-station jar testing apparatus. In the jar test experiments, the optimum working conditions for each coagulant, which was used for the removal of active drug substances, were determined. In all jar test experiments, rapid stirring was performed at 100 rpm for 1 min, slow stirring was performed at 30 rpm for 30 min, and precipitation process was performed for 30 min, respectively. In the first phase of the study, the optimum pH value for each coagulant used in the study was determined. At this stage, drug and coagulant dosages were kept constant at 5 mg/L and at 100 mg/L, respectively; and drug removal was studied at different pH values (3, 4, 5, 6, 7, 8, 9, 10, 11, 12). In the second phase of the study, the experiment was carried out at optimum pH values determined separately for each drug and coagulant in order to determine the optimal dosage of the coagulant. At this stage, drug concentrations were kept constant at 5 mg/L, and different coagulant dosages (10, 25, 50, 75, 100, 125, 150, 175 mg/L) were tested.

In the last stage of the study, different temperature values (10, 15, 20 and 25°C) were studied at optimal coagulant dosages, and pH values for an average steady-state plasma drug concentration of 5 mg/L were measured in order to investigate the effect of temperature on drug removal. Temperature adjustment was provided with water jacket.

In the study, the active drug substances were measured using HPLC with a UV detector (high-performance liquid chromatography) (brand name: Perkin Elmer).

Solid Phase Extraction Technique

Sample preparation steps were performed using solid phase extraction technique before HPLC analysis. The reason why we used solid phase extraction technique is that samples are removed from the undesired compounds and are then concentrated. With the cleaning process, it is possible to remove impurities which can cause failure in analyses, prevent the detection of the substance being sought or contaminate the analysis device. The condensation process in the samples is due to the low levels of drug concentrations in the water that would not allow direct detection in the HPLC/UV system.

Solid Phase Extraction (SPE) technique is preferred because it can be applied in a shorter time and has a higher recovery rate compared to Liquid-Liquid Extraction (LLE) technique. The samples are extracted using the Oasis HLB 3 cc/60 mg SPE cartridge before HPLC analysis. Thus, it is purified from other organic compounds that will interfere with the analysis and inorganic ions that can block the column. The samples were adjusted to pH = 2 with 1 N Hydrochloric Acid (HCl). Since the selected pharmaceutical compounds are acidic, lowering the pH of wastewater samples allows these materials to hold on the extraction cartridge and thus increases the recycling rate. In studies conducted, the best recovery for acidic drugs in solid phase extraction was achieved at pH = 2.

RESULTS AND DISCUSSION

Investigation of Diclofenac Removal with FeSO4.7H2O Coagulation

Determination of Optimum pH

To examine the removal of diclofenac, the jar test experiments were carried out at 100 mg/L coagulant dosage and 5 mg/L drug dosage at 10 different pH values (3, 4, 5, 6, 7, 8, 9, 10, 11, 12) using FeSO4.7H2O as coagulant. The optimum percent of diclofenac removal was 57.6% at pH 5. The percentage removal rates obtained at all pH values are shown in Figure 1.

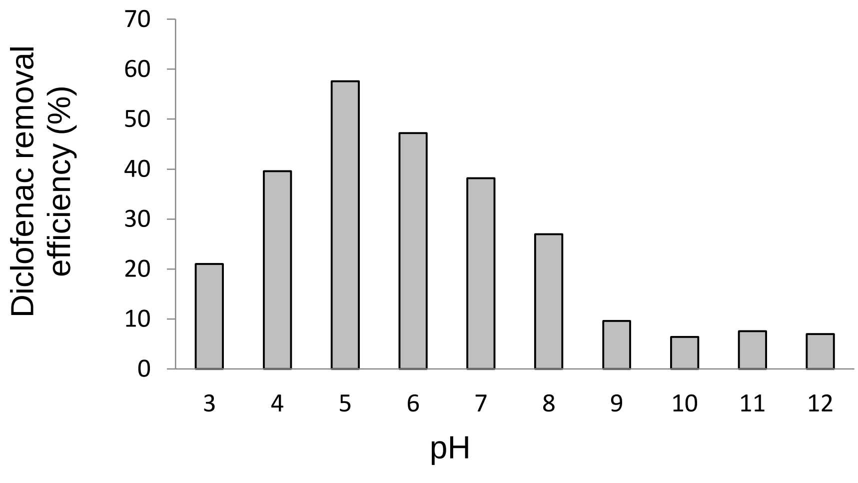


Figure 1. Removal efficiencies of diclofenac by $FeSO_4.7H_2O$ with coagulation at different pH values.

Determination of Optimum Coagulant Dosage

7 different FeSO4.7H2O coagulant dosages (10, 25, 50, 75, 100, 125, 150 mg/L) were tested at the determined optimum pH value (5), at 5 mg/L drug dosage and at 20°C. As a result of the study, 125 mg/L was selected as the optimum coagulant dosage. The removal percent of diclofenac at 125 mg/L coagulant dosage was calculated to be 57.6%. The applied coagulant dosages and the percentage removal rates are shown in Figure 2.

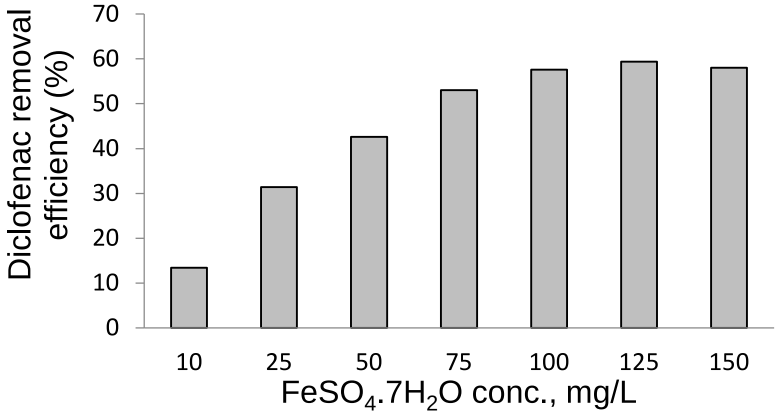


Figure 2. Removal efficiencies of diclofenac at different $FeSO_4.7H_2O$ concentrations.

Effect of Temperature on Diclofenac Removal with FeSO4.7H2O Coagulation

For diclofenac removal, 4 different temperatures (10, 15, 20, 25°C) were studied at the optimum pH and coagulant dosage in order to demonstrate the effect of temperature in FeSO4.7H2O coagulation. It was observed that the percent removal efficiency increased with the increasing temperature. The percent removal efficiencies corresponding to the temperature values are shown in Figure 3.

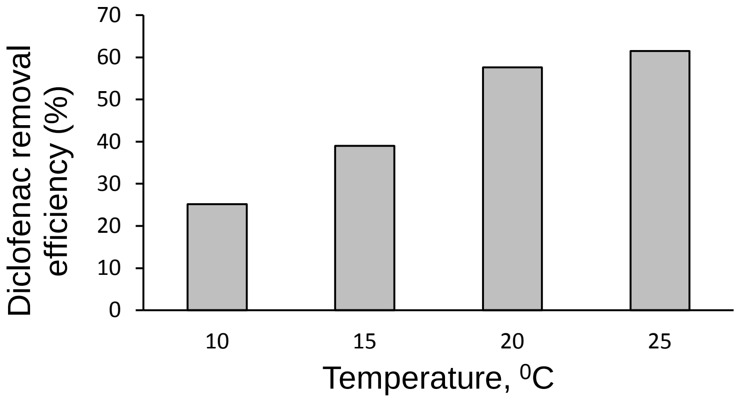


Figure 3. Removal efficiencies of diclofenac with $FeSO_4.7H_2O$ coagulation at different temperatures.

Investigation of Diclofenac Removal with $FeCl_3.6H_2O$ Coagulation

Determination of Optimum pH

To examine the removal of diclofenac, the jar test experiments were carried out at 100 mg/L coagulant dosage and 5 mg/L drug dosage at 10 different pH values (3, 4, 5, 6, 7, 8, 9, 10, 11, 12) by using $FeCl_3.6H_2O$ as coagulant. The optimum percent of diclofenac removal was 34.2% at pH 10. The removal rates obtained at all pH values are shown in Figure 4.

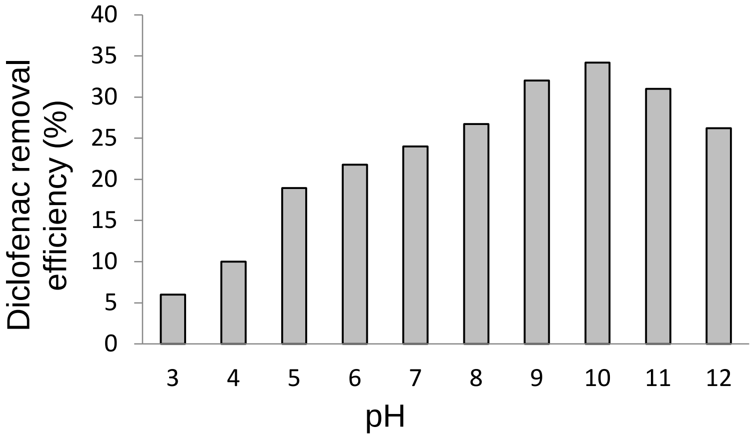


Figure 4. Removal efficiencies of diclofenac with $FeCl_3.6H_2O$ coagulation at different pH values.

Determination of Optimum Coagulant Dosage

7 different $FeCl_3.6H_2O$ coagulant dosages (10, 25, 50, 75, 100, 125, 150 mg/L) were tested at the optimum pH value (10), at 5 mg/L drug dosage and at 20°C. As a result of the study, 100 mg/L was selected as the optimum coagulant dosage. The removal percent of diclofenac at 100 mg/L coagulant dosage was calculated to be 34.2%. The applied coagulant dosages and the removal rates are shown in Figure 5.

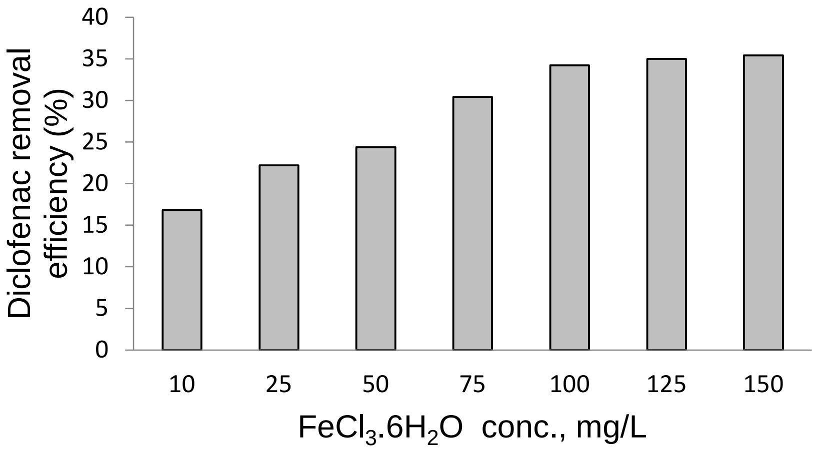


Figure 5. Removal efficiencies of diclofenac with coagulation at different $FeCl_3.6H_2O$ concentrations.

Effect of Temperature on Diclofenac Removal with $FeCl_3.6H_2O$ Coagulation

For diclofenac removal, 4 different temperatures (10, 15, 20, 25°C) were studied at the optimum pH and coagulant dosage in order to demonstrate the effect of temperature in $FeCl_3.6H_2O$ coagulation. It was observed that the removal efficiency increased with the increasing temperature. The removal efficiencies corresponding to the temperature values are shown in Figure 6.

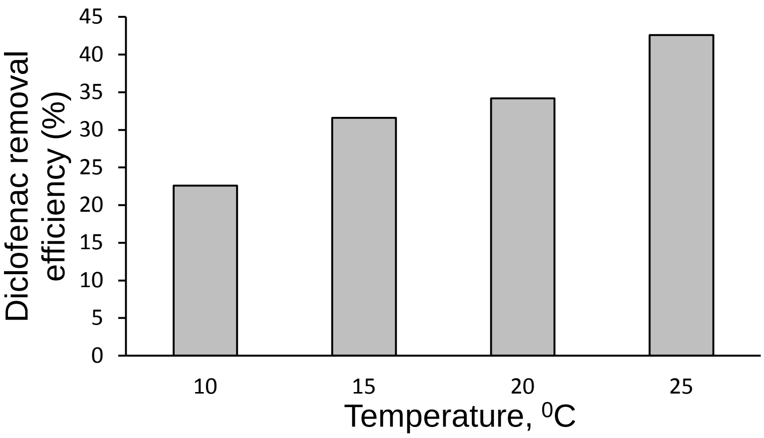


Figure 6. Removal efficiencies of diclofenac with $FeCl_3.6H_2O$ coagulation at different temperatures.

Investigation of Diclofenac Removal with $Al_2(SO_4)_3.18H_2O$ Coagulation

Determination of Optimum pH

To examine the removal of diclofenac, the jar test experiments were carried out at 100 mg/L coagulant dosage and 5 mg/L drug dosage at 10 different pH values (3, 4, 5, 6, 7, 8, 9, 10, 11, 12) by using $Al_2(SO_4)_3.18H_2O$ as coagulant. The optimum percent of diclofenac removal was 30% at pH 6. The removal rates obtained at all pH values are shown in Figure 7.

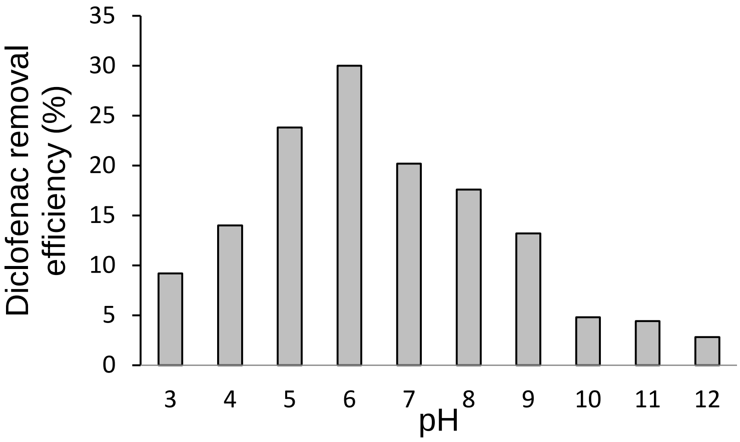


Figure 7. Removal efficiencies of diclofenac with $Al_2(SO_4)_3.18H_2O$ coagulation at different pH values.

Determination of Optimum Coagulant Dosage

7 different $Al_2(SO_4)_3.18H_2O$ coagulant dosages (10, 25, 50, 75, 100, 125, 150 mg/L) were tested at the optimum pH value (6), at 5 mg/L drug dosage and at 20°C. As a result of the study, 100 mg/L was selected as the optimum coagulant dosage. The percent removal of diclofenac at 100 mg/L coagulant dosage was calculated to be 30%. The applied coagulant dosages and the percentage removal rates are shown in Figure 8.

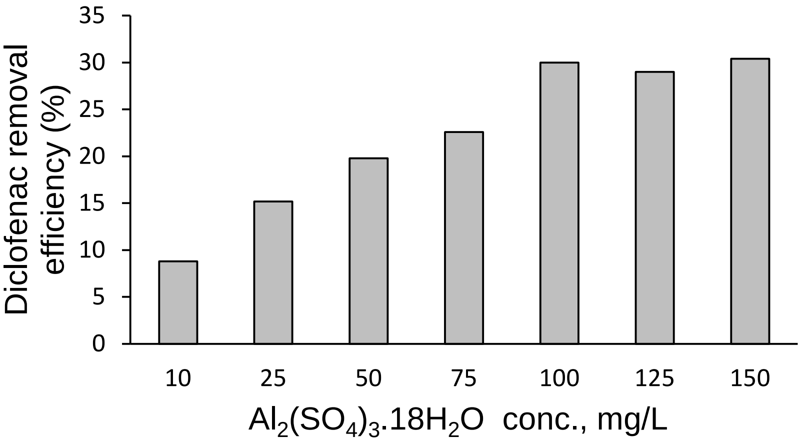


Figure 8. Removal efficiencies of diclofenac with coagulation at different $Al_2(SO_4)_3.18H_2O$ concentrations.

Effect of Temperature on Diclofenac Removal with $Al_2(SO_4)_3.18H_2O$ Coagulation

For diclofenac removal, 4 different temperatures (10, 15, 20, 25°C) were studied at the optimum pH and coagulant dosage in order to demonstrate the effect of temperature in $Al_2(SO_4)_3.18H_2O$ coagulation. It was observed that the percent removal efficiency increased with the increasing temperature. The removal efficiencies corresponding to the temperature values are shown in Figure 9.

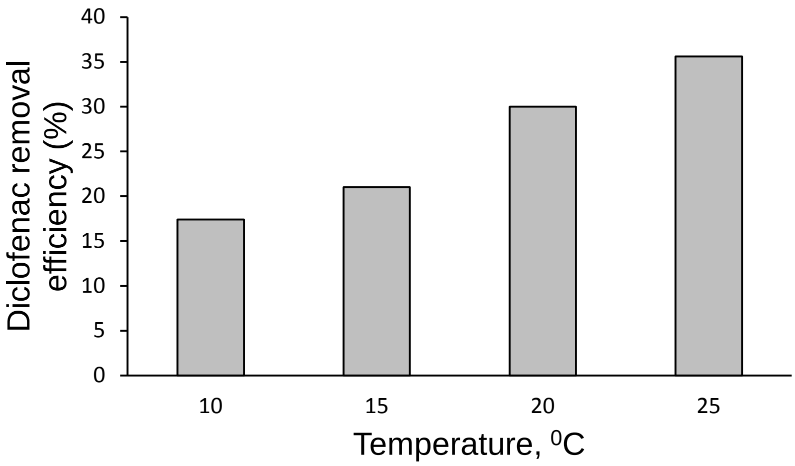


Figure 9. Removal efficiencies of diclofenac with $Al_2(SO_4)_3.18H_2O$ coagulation at different temperatures.

Investigation of Diclofenac Removal with $MgCl_2.6H_2O$ Coagulation

Determination of Optimum pH

To examine the removal of diclofenac, the jar test experiments were carried out at 100 mg/L coagulant dosage and 5 mg/L drug dosage at 10 different pH values (3, 4, 5, 6, 7, 8, 9, 10, 11, 12) by using $MgCl_2.6H_2O$ as coagulant. The optimum percent of diclofenac removal was 39.8% at pH 11. The percentage removal rates obtained at all pH values are shown in Figure 10.

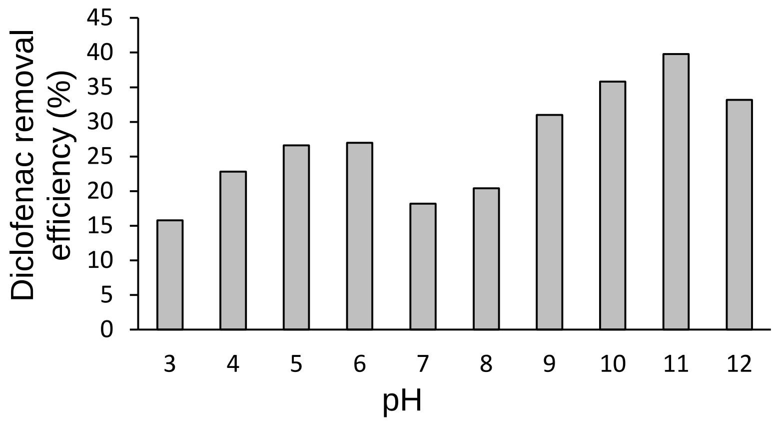


Figure 10. Removal efficiencies of diclofenac with $MgCl_2.6H_2O$ coagulation at different pH values.

Determination of Optimum Coagulant Dosage

7 different $MgCl_2.6H_2O$ coagulant dosages (10, 25, 50, 75, 100, 125, 150 mg/L) were tested at the optimum pH value (6), at 5 mg/L drug dosage and at 20°C. As a result of the study, 100 mg/L was selected as the optimum coagulant dosage. The removal percent of diclofenac at 100 mg/L coagulant dosage was calculated to be 39.8%. The applied coagulant dosages and the percentage removal rates are shown in Figure 11.

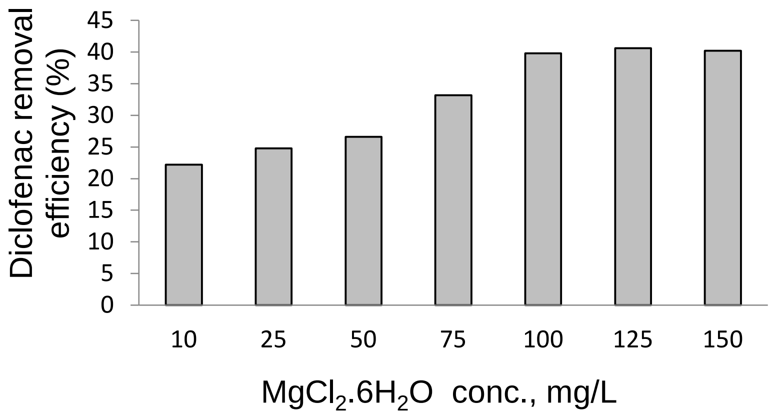


Figure 11. Removal efficiencies of diclofenac with coagulation at different $MgCl_2.6H_2O$ concentrations.

Effect of Temperature on Diclofenac Removal with $MgCl_2.6H_2O$ Coagulation

For diclofenac removal, 4 different temperatures (10, 15, 20, 25°C) were studied at the optimum pH and coagulant dosage in order to demonstrate the effect of temperature in $MgCl_2.6H_2O$ coagulation. It was observed that the percent removal efficiency increased with the increasing temperature. The percent removal efficiencies corresponding to the temperature values are shown in Figure 12.

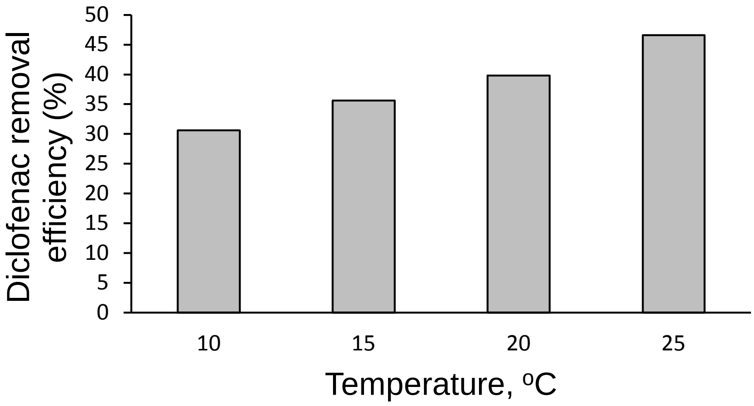


Figure 12. Removal efficiencies of diclofenac with $MgCl_2.6H_2O$ coagulation at different temperatures.

The optimum pH and dosages of diclofenac for 4 different coagulants were determined. The coagulant agent-based values were graphically displayed in order to compare the results obtained. The removal efficiencies at the optimum pH and dosages of diclofenac obtained for 4 different coagulants are shown in Figure 13.

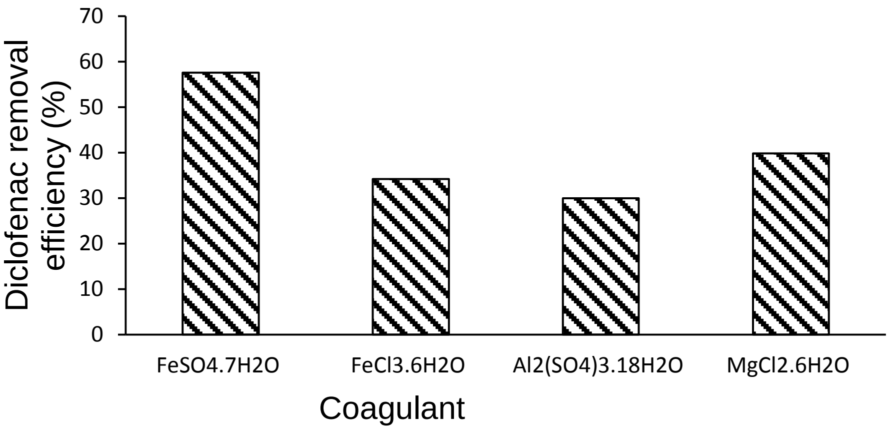


Figure 13. Removal efficiencies of diclofenac with coagulation by four coagulants at optimum conditions.

CONCLUSIONS

The highest removal efficiency for diclofenac was found to be 57.6% at pH 5 and 20°C with FeSO4.7H2O coagulation. It is thought that this result occurred because pH was close to pKa and diclofenac was less ionized at this pH. As pH increases and moves away from pKa, this refers that adsorption tendency decreases depending on the aqueous solubility of diclofenac (13).

In the study investigating the removal of diclofenac by coagulation method, the removal efficiencies at four different temperature values for four different coagulants were examined, and it was observed that the removal efficiency increased with the increasing temperature. Xiao et al. reported that low temperature had a negative effect on flocculation rate (14). Moreover, Guan et al. showed that temperature elevation increased the removal of turbidity (15). It was seen in the experiments that the precipitation rate and removal efficiency increased with the increasing temperature at which coagulation occurs and that larger flocks occurred with increasing temperature (16). In this study, it is thought that the percent removal efficiency for diclofenac increased with the increasing temperature because flocculation structure increased and grew, and thus, more drugs were held in flocks.

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