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Evaluation of the Removal Efficiency of Diclofenac in the Aquatic Environment by Combined Coagulation and Adsorption Processes

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Abstract: In decades, the presence of anti-inflammatory drugs diclofenac (DCF) in water resources has become an extremely threatening factor in terms of environmental protection and pollution. In this study, the removal efficiencies of DCF in aqueous sources were studied by adsorption, conventional coagulation, and combined coagulation methods using carbon nanotubes (CNTs). Experimental studies were carried out by adding certain doses of 1 g/L stock DCF solution prepared in the laboratory to water samples. In order to determine the adsorbing capacity of DCF, three different adsorbents as single-walled CNT (SWCNT), multi-walled CNT (MWCNT), and powdered activated carbon (PAC) were used as a function of pH and ionic strength. As a result of batch adsorption experiments performed in both ULW and UDWTP samples, the highest DCF sorption capacity was observed in SWCNT at pH =3 as 4.82 $mg.g^{-1}$ and 3.82 $mg.g^{-1}$, respectively, and also DCF adsorption capacity increased when the ionic strength was increased from 6.0×10^{-1} to 1.0 M. Furthermore, the experimental results showed that the Freundlich equation about correlation coefficient (R^2=0.99) is the best isotherm model to describe the adsorption process in all water sources. On the other hand, results in coagulation experiments demonstrated that the maximum removal percentages of DCF in ULW (94.81%) and UDWTP (91.97%) occurred with combined SWCNT with Alum compared to only Alum coagulation. Experimental data obtained in this study reveal that combined coagulation with CNTs is more appropriate to minimize the pollution caused by DCF, especially in the aquatic environment, rather than adsorption and coagulation processes.

Keywords: Diclofenac, environmental protection, adsorption, combined coagulation.

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INTRODUCTION

The scarcity of natural water resources potential and water pollution are among the leading global problems that should be emphasized (1). Wastewater discharged from various sources to the environment constitutes an important part of water pollution. Further, the structure and composition of the pollutants in the water vary depending on the result of houses, agricultural areas, hospitals, human activities, and different industrial processes (2). These new generation pollutants, called micropollutants, which are found in water from nanograms to micrograms, are resistant compounds that are difficult to remove with conventional treatment methods. (3). They can also occur as perfluorinated compounds, dioxins, aromatic hydrocarbons, and by-products of primary pollutants, as well as carbon-based compounds as solvents, pesticides, industrial chemicals, and by-products in the environmental environment (4). Micropollutants cause short and long-term toxicological effects such as antibiotic resistance and hormonal disorders in terms of human health (5). Currently, there is no regulated standard for important micropollutants such as pharmaceutical compounds, EDC, and PPCPs. In our country, "Environmental Quality Standard" values have been determined for micropollutants in order to protect and improve the quality of water resources within the scope of the "Regulation on Surface Water Quality" (6).

Pharmaceutical compounds (Pharmaceuticals), personal care products (PPCPs), and endocrine disrupting chemicals (EDCs) are among the most common types of micropollutants in aquatic environments such as surface waters, groundwater, drinking water, and wastewater treatment plants (7).

DCF, 2-[(2,6-dichlorophenyl)amino]phenylacetic acid, is a water-soluble (polar) non-steroidal anti-inflammatory drug with a permanent structure (8). It is often used to treat inflammation and pain in pathologies such as rheumatoid arthritis (9). After DCF is taken into the body, it is excreted in the urine with the resulting metabolites and less than 1% unchanged molecule as a result of biotransformation (10). DCF is of great importance in terms of environmental risk, as it has the highest acute effect among chemicals with an anti-inflammatory nature. In the studies, the lowest effect concentration (LOEC) value was observed in fish; changes in the liver, kidney, and gill cells have been reported at a DCF concentration of 1 µg/L, and deterioration in the renal tissue and changes in gill structures at a LOEC of 5 µg/L (11). Depending on its common use, DCF residues have often been detected in surface water sources, rivers, and water treatment plants. Many studies in the literature have revealed that conventional treatment processes such as coagulation and filtration, and adsorption, especially used in drinking water treatment plants, are ineffective in the removal of DCF (12). There are many studies on the removal of diclofenac in the literature (13-15). Suarez et al. investigated the removal efficiencies of pharmaceuticals such as DCF, naproxen, ibuprofen, and carbamazepine with conventional treatment processes (coagulation-flocculation + filtration) in their study on hospital wastewater (16). As a result of conventional treatment, they observed that the removal efficiencies of DCF, naproxen, ibuprofen, and carbamazepine were 22%, 31%, 12%, and 6%, respectively. Marcela et al. observed that the removal efficiencies of DCF vary between 5% and 40% in their studies using conventional treatment processes (17). Kennedy et al. observed a removal efficiency between 20% and 50% in the adsorption studies of 30 drug-based micropollutants, including DCF, with granular activated carbon at a pilot scale in drinking water treatment plants (18). In adsorption experiments using laboratory-scale powdered activated carbon, it was determined that micropollutants were removed at a higher efficiency when the activated carbon dose was increased (19). In the literature research on DCF removal, when carried out with advanced oxidation processes such as UV+H_2O_2, Fenton process ($Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\bullet + OH^-$), ozonation, UV+ ozonation, ozonation + peroxane ($O_3 + H_2O_2$), ozonation +UV+H_2O_2 and photocatalytic processes, the removal efficiencies found to be higher (21). On the other hand, carbon nanotubes (CNTs) have large surface areas and they are extraordinary properties with their porous and layered structures, generally, single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) are used in water treatment (20). Due to their adjustable physical, chemical, and electrical structures, they are often used in water treatment technology as organic and inorganic substances, heavy metals, volatile organics, personal care products, pharmacological products, and endocrine disruptors. It is widely used as an effective adsorbent in the removal of micropollutants such as chemicals (21, 22). Further, since some of the CNTs are hydrophilic, they can easily remove most of the micropollutants thanks to their high solubility in water and high adsorption properties. In this study, considering these disadvantages of the treatment processes used to date for the removal of micropollutants, the use of carbon nanotube materials, which have become very attractive, as a coagulant material has been considered as an alternative. There is a few number of studies in the literature comparing the removal efficiency of DCF compounds using adsorption and combined coagulation processes. Therefore, the original value of this study is that it will be one of the first studies in which it is planned to remove micropollutants that cannot be removed by conventional treatment methods such as coagulation and adsorption in drinking water sources, using CNT materials as coagulants, with high efficiency by combined coagulation method.

EXPERIMENTAL

Water source and sampling

The water samples used in the experimental studies were taken from Ulutan Dam (ULW), which provides drinking water to Zonguldak in Turkey, and from the Ulutan drinking water treatment plant outlet (UDWTP). Water quality parameter values related to water samples are given in Table 1.

The samples were taken as single samples in 5 L glass containers and quickly delivered to the laboratory. The water samples were kept in the refrigerator at +4 ºC against any microbial activity until they were used in experimental studies.

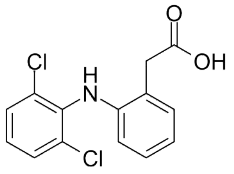
Chemicals and Reagents

DCF was supplied by Sigma Aldrich (Germany). Table 2 displays the chemical structure and physical properties of DCF. The stock solution of DCF was prepared by weighing 0.1 g with an analytical balance and dissolved completely in 1 L of distilled water.

Table 1: Physicochemical characteristics of water sources.

Parameters	**Unit**	**Ulutan Dam (ULW)**		**Ulutan Drinking Water Treatment Plant (UDWTP)**	
		Min-Max.	**Average**	**Min-Max.**	**Average**
pH	◌_	7.07-7.42	7.21	7.68-8.16	7.88
Turbidity	NTU	3.1-8.6	4.2	0.3-0.9	0.6
Conductivity	µS/cm	385-696	543	211-487	328
Alkalinity	mg/L $CaCO_3$	88-132	118	104-139	130
T. Hardness	mg/L $CaCO_3$	123-171	135	132-194	149
Chloride	mg/L	41-75	54	63-125	79
TOC	mg/L	4.15-6.27	5.47	3.81-6.32	4.85
UV_{254}	cm^{-1}	0.07-0.12	0.85	0.08-0.14	0.11
SUVA	L/mg.m	2.17-2.61	2.35	2.58-3.02	2.75

Table 2. Physical and chemical properties of DCF.

CAS Number	15307-86-5
Molecular formula	$C_{14}H_{11}Cl_2NO_2$
Molecular structure	
Molecular weight	296.16 g/mol
Log Kow	4.5
pKa	4.15
Solubility in water	2.37 mg/L (25 °C)

SWCNTs (1–2-nm diameter, 5–30-mm length) were obtained from Cheap Tubes, Inc. (Brattleboro, Vermont, USA). MWCNTs (50–80-nm diameter, 5–9-mm length) were purchased from Sigma Aldrich (St. Louis, Missouri, USA). Aluminum sulfate ($Al_2SO_4.18H_2O$) and iron(III) chloride ($FeCl_3$) were purchased from Fisher Scientific (Fair Lawn, New Jersey, USA). Stock solutions of 10 g/L for both coagulants were prepared by adding 10 g of each chemical to 1 L of ultrapure deionized water and stirring overnight. NaCl was used to make solutions of various ionic strengths. Powdered active carbon (PAC) was purchased from Norit.

Purified CNTs

We followed the previous procedure for the purification of CNTs (23).

Coagulation Experiments

We followed the previous procedure for Coagulation Experiments (23).

Batch Adsorption Experiments

Stock suspensions of the adsorbents (MWCNTs, SWCNTs, and PAC) were prepared by adding 1 g of the adsorbents to 200 mL of distilled water and stirring the solution with a magnetic stirrer at 600 rpm. All the experiments were performed in the dark in a thermostat-controlled shaker, maintained at 25 °C and 200 rpm. Based on the results from preliminary kinetic studies, a stirring time of 6 h was selected as the equilibrium time for activated carbon. The amount of adsorbed DCF was calculated according to the following Equation (1);

$$Q_e = (C_0 - C_e) \times V/M \qquad \text{(Eq. 1)}$$

where Q_e is the adsorption capacity (mg. g^{-1}), C_0 and Ce are the initial and equilibrium concentrations in the solution (mg L^{-1}), respectively, V is the volume of the solution (L) and M is the mass of adsorbents (g).

Analytical Methods

DCF analyses were performed using a UV spectrophotometer (UV-Shimadzu-1800) device at a wavelength of 276 nm. All water samples were analyzed based on the procedures described in the Standard Methods (24). Before analysis, water samples were passed through 0.45 µm membrane filter paper. TOC analysis (Shimadzu-5000A TOC analyzer) was conducted by the high-temperature combustion method (24).

RESULTS AND DISCUSSION

Impact of pH and Ionic strength on DCF Adsorption

Figure 1 presents the adsorption capacity values of DCF on SWCNT, MWCNT, and PAC adsorbents at different pH values are shown. As seen in Figure 1, in both water samples, the highest adsorption capacity of DCF (Q_e= 4.82 mg.g^{-1}) was observed in the adsorption processes performed with SWCNT at pH 3.

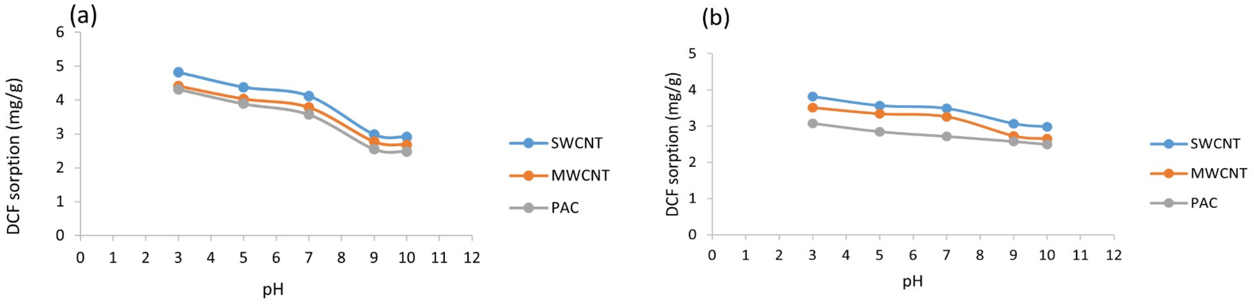


Figure 1: Effect of pH on DCF adsorption onto three adsorbents (a) ULW, and (b) UDWTP.

On the other hand, the sorption capacity of MWCNT and PAC was The DCF absorption capacities of MWNT and PAC at acidic pH values in Ulutan dam raw water samples varied between 4.40 and 3.90 mg.g^{-1}, respectively (Fig. 1a). It is between 3.5 and 2.85 mg.g^{-1} in the examples of the UDWPT (Fig. 1b). One of the important results obtained in this study is that the absorption capacity of DCF decreases significantly as the pH increases. As seen in Figure 1a, in DCF removal with SWNT, MWNT, and PAC adsorbents at pH 10, it was determined that the adsorption capacities decreased to 2.92, 2.68, and 2.48 mg.g^{-1}, respectively. Similarly, DCF removal performed with all three adsorbents in the water samples taken from UDWPT is between 70% and 90% at pH 3 and decreases to 20% at pH 10 (Fig. 1b). For example; the Q_e values of ULW samples were 4.41 and 4.03 mg.g^{-1} in adsorption with MWNT at pH 3 and pH 5, they decreased to 2.77 and 2.68 mg.g^{-1} at pH 10, respectively. Similar results have been obtained in studies on the subject in the literature (25, 26). In other words, the increase in pH will cause the dispersion of positively charged functional groups on the surface and the formation of new negatively charged groups. At high pH (pH = 10), due to deprotonation of the phenolic groups presented on the sorbent surface, the adsorption capacity is greatly reduced as the repulsion between the adsorbate and adsorbent negative charges increases. Moreover, electrostatic interactions are extremely important for the sorption mechanisms (11). Adsorption studies with SWCNT showed higher DCF removal compared to MWCNT and PAC. This result is probably related to the larger surface area and smaller diameter of SWCNT compared to others (27, 28). Figure 2 shows the effect of ionic strength on DCF adsorption in samples from both sources. In this study, to demonstrate the effect of ionic strength, NaCl was used to adjust the ionic strength, and five different concentrations of 0.2, 0.4, 0.6, 0.8, and 1.0 mol/L were applied to adjust the ionic strength.

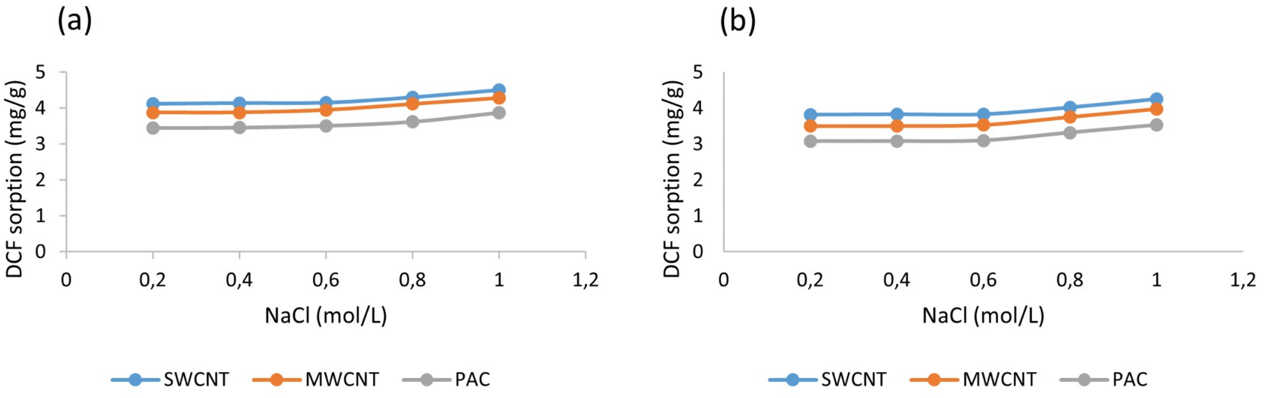


Figure 2: Effect of ionic strength on DCF adsorption onto three adsorbents (a) ULW and (b) UDWTP.

No significant change occurs in the adsorption of DCF on SWCNT, MWCNT, and PAC up to an ionic strength of 0.6 M. When the ionic strength increased from 0.6 to 1 M, the adsorption of DCF also increased from 4.15 to 4.5 for SWCNT, from 3.95 to 4.29 $mg.g^{-1}$for MWCNT, and from 3.51 to 3.87 $mg.g^{-1}$ for PAC at ULW samples (Figure 2a). Similarly, in the samples taken from the treatment plant, the adsorption capacity increased from 3.82 to 4.25 $mg.g^{-1}$ for SWCNT, from 3.51 to 3.98 $mg.g^{-1}$ for MWCNT, and from 3.08 to 3.53 $mg.g^{-1}$ for PAC (Figure 2b). This situation can be explained that sorbent particles and DCF molecules are both surrounded by an electric double layer due to electrostatic interactions. Based on the Gouy–Chapman theory of the diffuse double layer, the thickness of the double layer is compressed by an increase in the ionic strength of the solution (29). Further, the increase in ionic strength could enhance the uptake of ionic compounds such as DCF by CNTs because of a screening effect of the surface charge produced by the added salt (30, 31).

Adsorption Isotherms

In this study, Langmuir and Freundlich isotherm models were used to determine the adsorption capacity of DCF in both the raw water samples of the ULW and UDWTP samples. The linearized Langmuir isotherm model is expressed by the following Equation (2);

$$1/ Q_e = (1/K_L*Q_o*1/C_e) + 1/Q_o \qquad \text{(Eq. 2)}$$

Where Qe ($mg.g^{-1}$) is the amount of DCF in equilibrium held on the adsorbent, Q_o ($mg.g^{-1}$) is the maximum amount of DCF adsorbed, Ce ($mg.L^{-1}$) is the liquid phase concentration at equilibrium, and K_L ($L.mg^{-1}$) is the relationship between DCF and adsorbent.

On the other hand, the linearized Freundlich isotherm expression is shown by Equation (3).

$$LogQe = LogK_F + 1/n(LogCe) \qquad \text{(Eq. 3)}$$

Where, K_F ($(mg/g)(L/mg)^{1/n}$) and n (dimensionless) are constants, including factors affecting the adsorption process such as adsorption capacity and intensity, Q_e ($mg.g^{-1}$) adsorption capacity, and Ce ($mg.L^{-1}$) showing the equilibrium concentration, respectively.

In Figures 3 and 4, the sorption capacity of DCF by SWCNT, MWCNT, and PAC adsorbents in both water sources, respectively, is illustrated by Langmuir and Freundlich isotherm plots.

The experimental Q_e versus C_e data have been fit to Langmuir and Freundlich models and the isotherm parameters were determined. As shown in Figures 3 and 4, the Freundlich model fits the best for the experimental data for three adsorbents according to the R^2 value (R^2 = 0.99), as compared to the Langmuir model (R^2=0.97). Also, the Freundlich model is applied to adsorption in heterogeneous systems. Isothermal points showed an increase in adsorption capacity with DCF concentration increasing. In other words, plots display that the sorption did not achieve a limit value or the adsorbent saturation, indicating a multilayer adsorption process (32) Langmuir and Freundlich isotherm parameters, constants, and correlation coefficient R^2 and values showing the sorption potential of DCF on three different adsorbents in both water sources are given in Table 3.

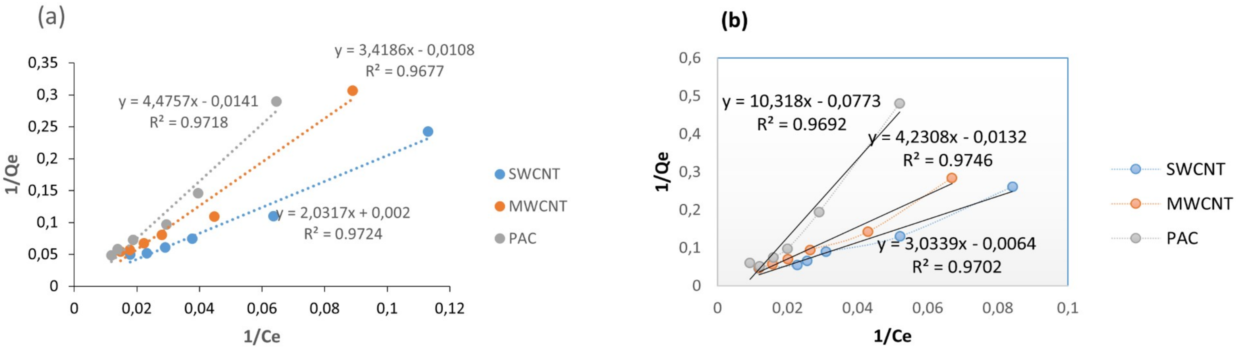


Figure 3. Langmuir isotherms of DCF sorption (a) ULW and (b) UDWTP.

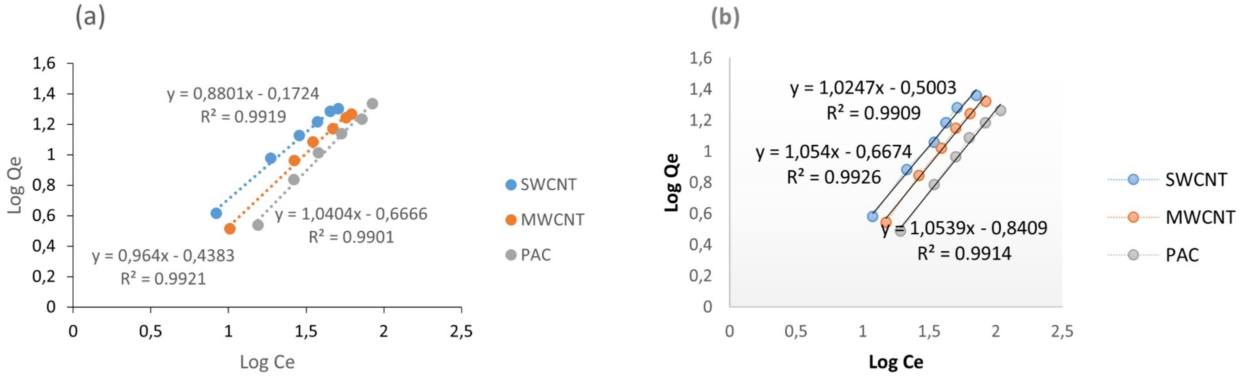


Figure 4. Freundlich isotherms of DCF sorption (a) ULW and (b) UDWTP.

Table 3. Isotherm parameters of Langmuir and Freundlich models for the sorption of DCF.

		Langmuir			Freundlich		
Source	**Adsorbents**	**Q_o (mg/g)**	**K_L (L/mg)**	**R^2**	**K_F**	**n**	**R^2**
ULW	SWCNT	500	0.0007	0.9718	1.668	1.498	0.9919
	MWCNT	92.59	0.0302	0.9677	0.999	1.9686	0.9921
	PAC	70.92	0.003	0.9724	0.725	2.213	0.9901
UDWT	SWCNT	156.25	0.002	0.9687	1.005	1.845	0.9909
	MWCNT	75.76	0.003	0.9635	1.003	2.15	0.9926
	PAC	12.94	0.008	0.9548	1.002	2.6272	0.9914

In the meantime, as a result of the DCF adsorption onto three adsorbents, the highest removals DCF (84.23% and 79.5%) was observed onto SWCNT in ULW and UDWTP, respectively, followed by MWCNT (77.25% and 71,56%) and PAC (68.4% and 61,27%). This result can probably be evaluated that the SWCNTs have a small diameter and large surface compared to MWCNTs and PAC (Figs. 3 and 4). On the other hand, the DCF percentage of DCF removal in ULW is slightly higher than in UDWTP. This finding shows that pH and ionic strength has an important impact on the adsorption process. In this study, while pH and conductivity values in ULW were 7.24 and 543 µS/cm respectively, these were measured as 7.88 and 384 µS/cm in UDWTP (Table 1). This can be also interpreted that two parameters can change the adsorbent surface charge and also pH may affect adsorbate solubility and dissociation of surface functional groups of adsorbent. Similar results were performed in some literature research (33-36).

DCF Removal by Conventional and Combined Coagulation

Figure 5 shows the percentages of DCF removal from water samples from ULW and UDWTP with only conventional coagulant and CNTs with Alum (combined coagulation) performed.

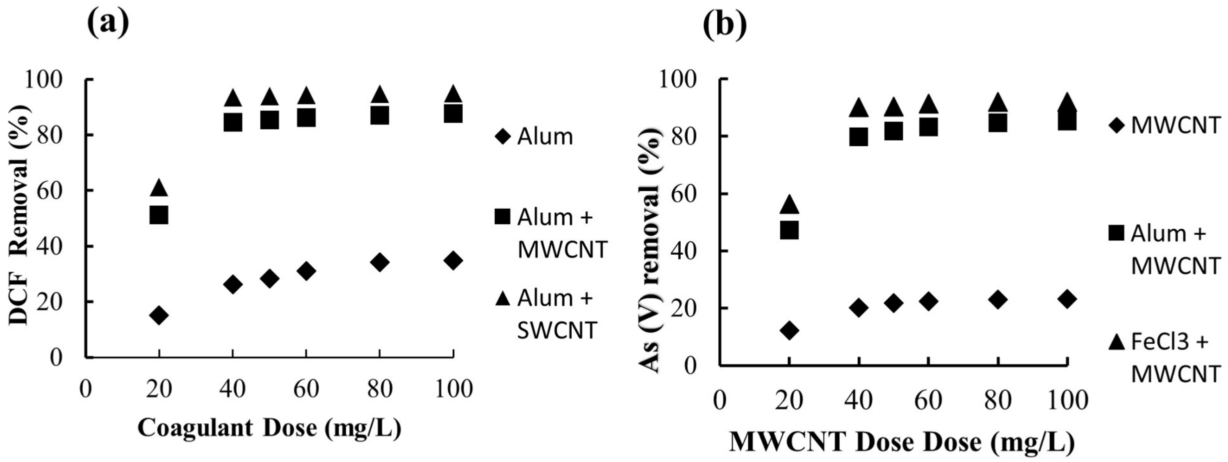


Figure 5: DCF removal with conventional and combined coagulation (a) ULW and (b) UDWTP.

The lowest DCF removal (12.3%) was observed as a result of coagulation with alum in UDWT. The maximum DCF removal in ULW detected when using only alum was recorded as 34.27%. The maximum removal percentages were achieved by combining coagulation with SWCNT+ Alum in ULW and UDWTP samples as 94.81% and 91.97%, respectively. On the other hand, the removal percentages of DCF were slightly lower in ULW (87.11%) and UDWT (84.6 %) samples using MWCNT+ Alum than using SWCNT + Alum. In this study, coagulation removal of DCF in ULW and UDWTP samples is also closely related to the nature of the natural organic matter in water resources and other inorganic and organic pollutants.

CONCLUSION

In this study, the removal efficiency of DCF in experimental studies carried out in the laboratory was investigated in batch adsorption, coagulation, and combined coagulation processes using CNTs. In experimental studies related to adsorption, it has been determined that the DCF sorption capacity of SWCNT, MWCNT, and PAC adsorbents is higher at acidic pH values rather than alkaline pH values. Meanwhile, it was reported that the adsorption process of DCF on SWCNT, MWCNT, and PAC was defined by the Freundlich isotherm model rather than that by Langmuir. In other words, the values of fitting parameters related to isotherms in all pH represent a multi-layer adsorption process. On the other hand, experimental studies were carried out to display the effect of ionic strength using NaCl. There was no change in DCF adsorption capacity up to 0.6 M concentration, while there was a significant increase in DCF adsorption capacity as the ionic strength increased at concentrations greater than 0.6 M. In addition, it was observed that much higher amounts of DCF removal were achieved in coagulation studies using CNTs. Compared with adsorption and conventional coagulation, the highest DCF removal was obtained as a result of combined coagulation experiments with SWCNT + Alum (93.1%). Therefore, the results of this study also revealed that the combined coagulation process with CNTs used as an aid coagulant instead of coagulation and adsorption may be more effective in the removal of micropollutants such as DCF in water resources.

CONFLICT OF INTEREST

There is no conflict of interest between the authors.

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