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SYNERGISTIC EFFECTS OF ALUM AND POWDERED ACTIVATED CARBON ON THE REMOVAL OF NON-STEROIDAL ANTI-INFLAMMATORY DRUGS BY COAGULATION–FLOCCULATION

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Abstract

This study aimed to enhance the removal of non -steroidal anti-inflammatory drugs during coagulation-flocculation in the presence of aluminum sulfate alone and then in combination with powdered activated carbon. The Jar-Test was performed in the laboratory on aromatic organic compound (diclofenac) dissolved in distilled water. The purpose of the tests was to evaluate the removal efficiencies of diclofenac for variable doses of reagents and pH. The interactions of organic compound in the presence of the coagulant combined with the powdered activated carbon would be surface mechanisms (physical adsorption, ligand exchange or complexation on the surface of flocs of aluminum hydroxide or powdered activated carbon). Findings demonstrated that the addition of powdered activated carbon notably improved diclofenac removal, particularly under near-neutral pH conditions.

Keywords: Coagulation-flocculation; aluminium sulphate; powdered activated carbon; non -steroidal anti-inflammatory drugs; mechanisms.

Introduction

Non-steroidal anti-inflammatory drugs (NSAIDs) are a class of pharmaceuticals commonly administered for pain management, fever reduction, and inflammation control. Due to their widespread and prolonged usage, reports of associated adverse effects have significantly increased. Clinical findings associate prolonged NSAID intake with elevated risks of nephrotoxicity, cardiovascular complications, and gastrointestinal disorders (Brune and Patrignani, 2015).

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Their extensive consumption has contributed to growing concern over their environmental persistence and ecotoxicological impact. NSAIDs are characterized by poor biodegradability, chemical stability, and a strong potential for bioaccumulation. These properties contribute to their continued presence in various environmental compartments.

Frequent detection of NSAIDs such as diclofenac, ibuprofen, and naproxen has been documented in surface waters, effluents from wastewater treatment facilities, and occasionally in potable water sources. Empirical data compiled globally indicate that these compounds are among the most recurrent pharmaceutical pollutants in aquatic systems, representing approximately 15% of total pharmaceutical contaminants identified in international water quality surveys.

Concentrations ranging from nanogram to microgram levels per liter have been reported for several NSAIDs, including ketoprofen, mefenamic acid, and diclofenac. These residues are predominantly introduced into the environment through treated wastewater discharges. Detection of NSAIDs has been confirmed in diverse aquatic matrices, including rivers, coastal waters, groundwater, wastewater effluents, and sewage sludge (Lakshmi et al., 2024).

Toxicological studies have established that NSAIDs exert detrimental effects on aquatic organisms. These include impaired reproductive capacity, abnormal growth patterns, and altered behavior in species such as fish, amphibians, and invertebrates (Schwaiger et al., 2004). Phytoplankton exhibit the highest sensitivity, with documented acute toxicity across multiple trophic levels, including marine microbes and benthic invertebrates (Ruiz and Font, 2011).

Bioaccumulation of NSAIDs such as diclofenac and ibuprofen has been observed in the liver, kidney, gill, and muscle tissues of exposed aquatic organisms. Renal histopathology and subcellular damage have been recorded in rainbow trout. Measured environmental concentrations of diclofenac in natural and treated waters have exceeded levels considered critical for aquatic toxicity. Furthermore, degradation products of ibuprofen and naproxen formed through photolytic processes may possess enhanced toxicity compared to their parent compounds (Kümmerer, 2009).

Conventional wastewater treatment technologies often fail to fully eliminate pharmaceutical residues. The removal efficiency of NSAIDs is largely influenced by their interaction with particulate matter, which facilitates their separation through physicochemical approaches like coagulation, sedimentation, and flotation, or through biological degradation pathways (Roberts and Thomas, 2006).

In contrast to surface and wastewater datasets, information on NSAID occurrence in tap and drinking water remains limited, especially within low- and middle-income countries.

In this study, the aim is to evaluate the effectiveness of coagulation-flocculation using aluminum sulfate in combination with powdered activated carbon on simple organic molecules considered to be refractory because they represent an emerging environmental concern. The tests concern pharmaceutical substances (diclofenac). The aim is to optimize the use of the coagulant reagent (aluminum sulfate) in conjunction with the addition of an adsorbent material (powdered activated carbon) to achieve maximum removal of the aforementioned compound.

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MATERIALS AND METHODS

Preparation of reagents

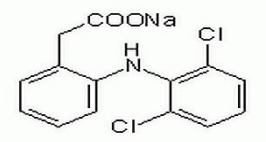
- A stock solution (10 g/L) was prepared by dissolving aluminum sulphate ($Al_2(SO_4)_3,18H_2O$) into distilled water. For this, the stock solution was occasionally changed.
- The powdered activated carbon (PAC) had a particle size of 20 µm and specific surface area equal to 658 m^2/g.

Preparation of diclofenac solutions

Distilled water (pH from 6.07 to 6.79 and conductivity from 2 to 5 µs/cm) .

Diclofenac, at concentrations varying from 2 to 15 mg/L, was added to distilled water. The pH was adjusted as needed by means of 0.1 N HCl and NaOH solutions

Table 1: Main physico-chemical properties of diclofenac sodium (Anses, 2019).

Diclofenac (DFC)	
Chemical formula	
Molecular formula	$C_{14}H_{10}Cl_2NNaO_2$
Molecularweight	318.13 g mol^{-1}
Water solubility	Soluble in water to 50mg/ml.
Log Kow	0.7-1.2
pKa	4.15
log Dow	1.15

Diclofenac analysis

DFC, an aromatic organic compound, was determined using an OPTIZEN 2120 UV UV-visible spectrophotometer equipped with quartz cells and a 1 cm optical path. The wavelength used is 276 nm and corresponds to the maximum absorbance.

The residual concentrations were determined from the absorbance calibration curves (Fig. 2).

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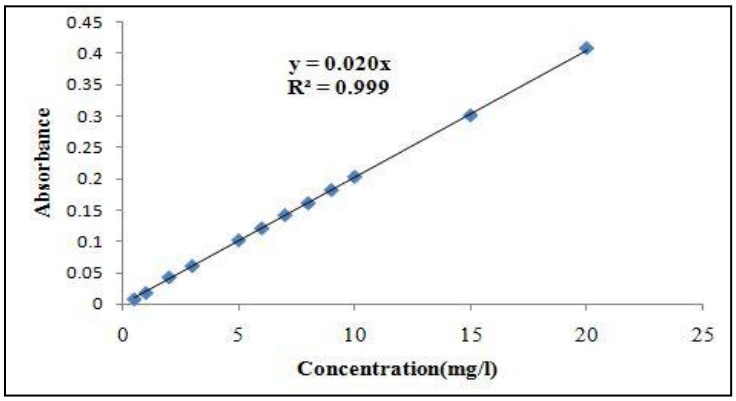

Figure 2: Calibration curves of diclofenac in distilled water(Wave length λ= 276nm)

Description of jar test

The flocculation of diclofenac was carried out in accordance with the jar-test analytical procedure. The equipment used in this test consists of a flocculator with 6 stirrers (Fisher 1198 Flocculator), with a rotational speed that can be varied from 0 to 200 rpm, in order to simulate the dynamics of the coagulation-flocculation process. This apparatus allows for the simultaneous stirring of the solutions contained in a series of 500 ml beakers. Note that each sample was agitated at the speed of 200 rpm for a period of 2 minutes after the addition of the coagulant. Afterwards, the speed was reduced to 60 rpm for a 30 minutes flocculation period. Finally, the flocswere allowed to settle for 30 minutes, before filtration through a 0.45 µm cellulose membrane. The samples were then withdrawn for analysis. In addition, the diclofenac level in the supernatant, after filtration, was monitored by means of the UV absorption test using a UV–Vis spectrophotometer (UV – visible OPTIZEN 2120UV) at 257 nm. A linear correlation was established between the UV reading and the organic compound content, for every type of water.

The removal efficiency of diclofenac was calculated as follows:

$$E\% = \frac{C_0 - C_f}{C_0} \times 100$$

Where C_0 is the initial concentration of the organic compound before adding the coagulant, and C_f is the final concentration of the organic compound after addition of the coagulant.

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RESULTS AND DISCUSSION

Effect of coagulation-flocculation in the presence of aluminum sulfate alone

Prior to testing the dose effect of powdered activated carbon (PAC), synthetic solutions of the organic compounds are prepared at a concentration of 5 mg/l diclofenac in distilled water with pH adjusted to 7. These solutions are jar tested with coagulant alone to obtain the optimum dose of aluminum sulfate. The results obtained are shown in Figure 1.

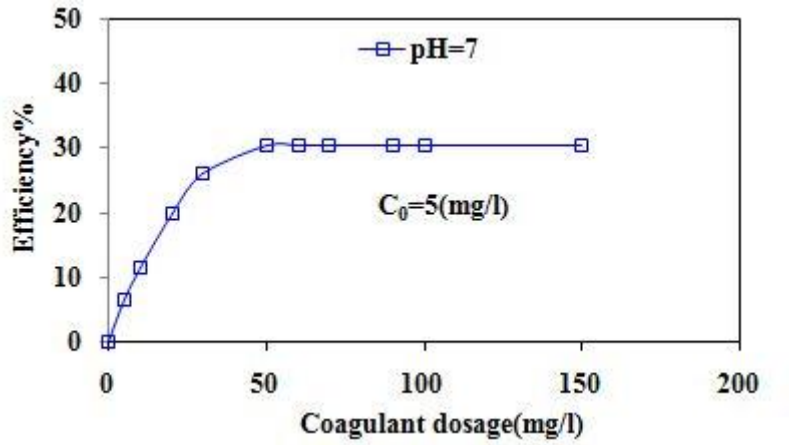

Figure 1: Effect of Aluminum Sulfate Dose on Diclofenac Removal in Distilled Water

[Diclofenac]= 5mg/l ; pH = 7.

Just as has been observed for simple phenolic or carboxylated compounds (Achour and Guesbaya, 2005; Bacha and Achour, 2013), we can observe for diclofenac as well, an increase in elimination yields with the dose of coagulant introduced. However, there is an optimum dose above which yields stabilize. The results in Figure 1 show that the optimum dose of coagulant in distilled water at neutral pH 7 is 50mg/l.

Elimination yields remain fairly average (around 60% at optimum) compared with those obtained by flocculation of humic substances (Bacha and Achour, 2023).

At neutral pH, the removal of these compounds by aluminum sulfate likely occurs through the formation of insoluble salts involving either soluble or insoluble cationic aluminum species monomeric or polymeric in interaction with organic matter. Additional surface-level processes, such as complexation or ligand exchange with hydroxyl groups present on aluminum hydroxide flocs, may also contribute to the elimination mechanism (Bacha and Achour, 2025; Bacha and Achour, 2017).

Effect of aluminum sulfate/activated carbon combination for various CAP dosages

Once the optimum dose of coagulant has been determined, increasing amounts of CAP (0 to 100 mg/l) are combined with this dose of diclofenac. CAP levels are introduced during slow agitation with pH adjustment to 7. The results obtained are shown in Figure 2.

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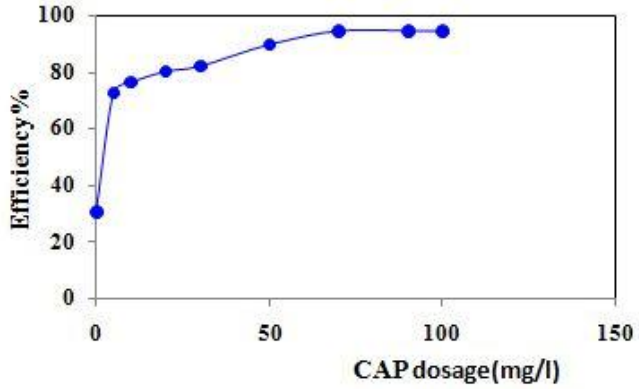

Figure 2: Removal of Diclofenac by Powdered Activated Carbon Combined with the Optimal Dose of Aluminum Sulfate in Distilled Water

[diclofenac] 5mg/l ; pH = 7.

The introduction of powdered activated carbon (PAC), combined with the optimum dose of coagulant (50 mg/l), significantly improves diclofenac removal yields (94.29%). It should also be noted that these efficiencies increase as the added CAP content increases.

The enhanced removal of diclofenac observed with the combined use of aluminum sulfate and PAC is likely due to the adsorption of diclofenac molecules onto the PAC surface. Given the mesoporous structure of the PAC used, the small size of diclofenac molecules may enable their diffusion into the internal pores. Similar performance was previously reported with this PAC in adsorption experiments involving paracetamol in distilled water (Bacha and Achour, 2018).

Table 2 summarizes and compares the removal efficiencies obtained using the coagulant alone and in combination with powdered activated carbon.

Table 2 : Summary of Diclofenac (5 mg/L) Removal Results Using Aluminum Sulfate Alone (AS) and in Combination with PAC (AS + PAC)

	Diclofenac	
	Aluminum sulfate alone	**Aluminum sulfate + CAP**
Optimal coagulant dosage(mg/l)	50	
Optimal CAP dosage(mg/l)		90
Efficiency%	29,52	94,29

According to Yuasa et al., (1997), activated carbon has a higher adsorption coefficient for low molecular weight fractions than for high molecular weight fractions. for low-molecular-weight fractions than for high-molecular-weight fractions. high-molecular-weight fractions. The literature also states that unlike aliphatic organic molecules, aromatic molecules are well molecules are well eliminated by retention on activated carbon (Bacha and Achour, 2018). The

compounds tested would be retained on activated carbon, as for most organic molecules in water, by physical adsorption. physical adsorption.

Indeed, all the studies carried out by Didier (1997) on five different activated carbons led to the conclusion that the mainmain adsorption mechanism for the pollutants studied (phenols and phthalates)is physisorption in the porosity of activated carbons. Similarly, the studyadsorption of organic molecules (phenol, paranitrophenol, benzoic and salicylic acidsbenzoic, salicylic and picric acids) on activated carbons, both raw and treated treatment, indicates that adsorption phenomena are essentially due to Van der Wallsdue to Van der Walls interactions, highlighted by their energetic aspect (Julien et al., 1994).

CONCLUSION

This study aimed to enhance the removal of diclofenac through coagulation-flocculation using aluminum sulfate in combination with powdered activated carbon (PAC).

Experimental results and analysis highlighted the influence of operational parameters, including reagent doses and pH, on removal efficiency. Under neutral pH conditions, diclofenac showed moderate removal by aluminum sulfate, primarily through surface-specific mechanisms involving hydrolyzed aluminum species.

The addition of PAC significantly improved removal efficiency for diclofenac, especially in the pH range of 4 to 7. The low molecular weight and functional groups attached to the aromatic rings of diclofenac may also contribute to their reactivity. The predominant mechanisms appear to involve surface interactions and/or complexation processes.

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