UNESCO-IWRA ONLINE CONFERENCE

17-19 JANUARY 2023

3RD IN THE IWRA ONLINE CONFERENCE SERIES

Emerging Pollutants: Protecting Water Quality for the Health of People and the Environment

Removal of Pharmaceutical Pollutants Using Ceramic Membrane Filter.

EDITH NWAKAEGO OKEY

KNUST RWESCK Regional Water & Environmental Sanitation Centre Kumasi | Kwame Nkrumah University of Science and Technology

UNESCO United Nations Educational, Scientific and Cultural Organization · RC-IRBM Regional Centre for Integrated River Basin Management under the auspices of UNESCO

National Water Resources Institute Kaduna — Water for Development

18 January, 2023, 17:05 CET)

unesco Programme hydrologique intergouvernemental

IWRA International Water Resources Association

Study Background

- Emerging pollutants (Eps) are various chemicals that are not currently regulated but have the potential to enter the environment and have known or suspected negative impacts on the ecosystem and human health (Geissen et al., 2015). These pollutants can be pharmaceuticals hormones and steroids, personal care products, surfactants, agrochemicals, microplastics, among others (Ramírez-Malule et al., 2020).

- There is a worldwide concern about the inability of traditional WWTPs to completely remove pharmaceutical pollutants from wastewater, as highlighted by early research (Jelic et al., 2011; Kosma, Lambropoulou, and Albanis, 2014; Mceneff, Schmidt, and Quinn, 2014; Casas et al., 2015; Wang and Wang, 2016; Madikizela and Chimuka, 2017; Shraim et al., 2017; Stefanakis, 2017; Pereira et al., 2020).

- To address this inadequacy in conventional WWTPs and prevent the release of these compounds into the environment to protect human health and the ecosystem , a number of advanced treatment technologies have been developed and evaluated (Chonova, 2017; del Lamo et al., 2020; Castillo et al., 2020). Ozone/advanced oxidation processes (AOPs), activated carbon filtration, and membrane bioreactors are a few of the systems that have been examined (Castillo et al., 2020; Ajo et al., 2018; Souza et al., 2018).

- Although these systems produce high removal efficiencies, there are differences based on the pollutants and treatment methods. Furthermore, the construction and operation of such treatment methods are difficult and expensive to operate (Chonova, 2017; Castillo et al., 2020).

- It has become imperative to develop more efficient and cost-effective treatment technologies that can totally remove these contaminants from wastewater using readily accessible, affordable, and easy-to-assessment raw materials from the local area (Castillo et al., 2020).

Study Background Contd'

- Clay can be easily moulded into any shape that it retains when dry. Naturally occurring clays are widely used for contaminant remediation due to their easy availability, high adsorption capacities, high porosity, high cation exchange capacity, and high specific surface area (Chaari et al., 2020).

- Worldwide, clay has been used by man from time immemorial for both industrial and domestic applications. Today, clay is still very useful in the ceramics industry for processing several forms of ceramic materials (Yaya et al., 2017). The particular application of clay depends on its mineralogical, physical, and chemical properties (Momade and Gawu, 2009; Asamoah et al., 2018).

- Over the years, ceramic filters have been employed as an alternate technique of treating wastewater, stormwater, and drinking water (Wei, 2015; Tshishonga and Gumbo, 2017; Nair and Mophinkani, 2018; Akosile et al., 2020).

- In general, size exclusion, membrane adsorption, and charge repulsion are typically used in membrane processes to retain micropollutants. These removal processes are substantially influenced by various variables, including the characteristics of the membrane, the operating conditions and the characteristics of the particular micropollutant (Luo et al., 2014).

Research Aim and Specific Objectives

- Aim

- The main objective of this study is to investigate the suitability of the fabricated ceramic membrane filter (CMF) for pharmaceutical removal.

- **Specific Objectives**

i. To investigate the efficiency of the ceramic filter for the removal of pharmaceutical contaminants from the wastewater through the filtration experiments;

ii. To determine the effect of operating parameters such flow rate, pH and sludge retention time (SRT) on the pharmaceutical removal efficiency;

iii. To determine the effect of clogging on the CMF for 4 months continuous operation.

Materials and Methods

❑ Chemicals and Reagents

❖ Reference Standard

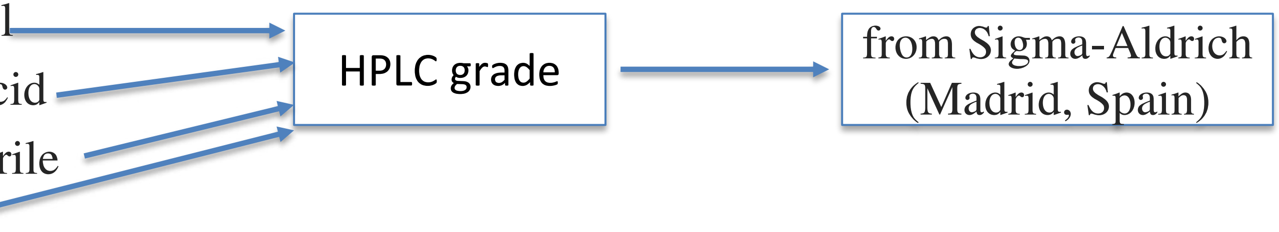
Ibuprofen, diclofenac, paracetamol, codeine, morphine and tramadol (purity > 99 %)

○ Cartridges

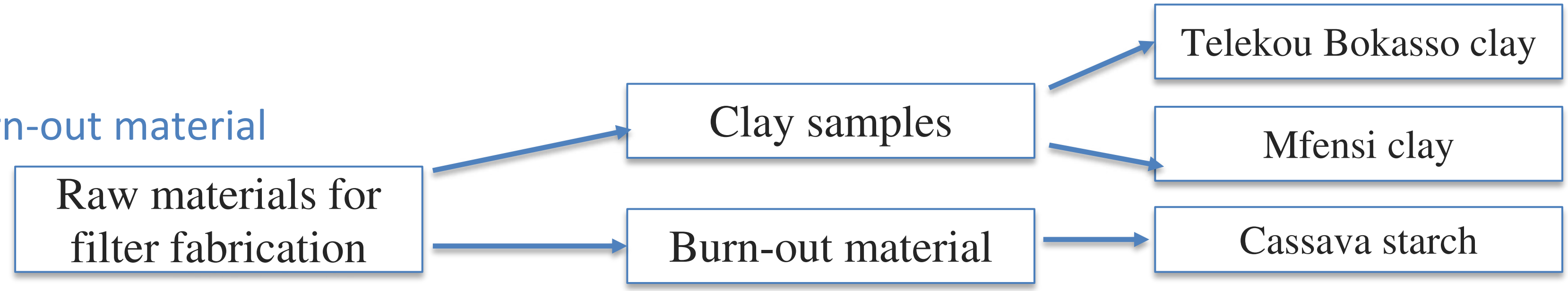
Oasis HLB SPE cartridges (6CC, 500 mg, Waters, Milford, MA, USA)

❖ Reagents

- Methanol
- Acetic acid
- Acetonitrile
- TFA



➢ Clay samples and burn-out material



Materials and Methods contd'

Preparation of HPLC Stock and Working Standard Solutions

Preparation of Stock Solutions

50 mg of individual compounds
+
50 mL of diluent → 1000 ppm

Preparation of Working Solutions

200 µL Stock solution → 10 mL Volumetric flask → Working solution

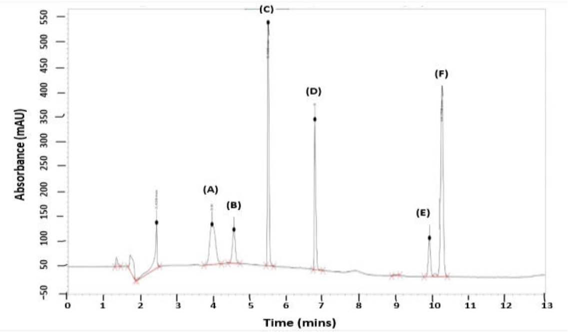
Conditions for HPLC Method Development

Proposed HPLC Operating Conditions

Stationary phase (Column)	Phenomenex Kromasil C8 (150 mm × 4.60 mm, 5 µm)
Wavelength (nm)	225
Detector	Photo diode array detector (PDA)
Eluent A	Water/0.05 % Trifluoroacetic acid (TFA) (pH 2.3)
Eluent B	Acetonitrile
Column temperature (^{0}C)	Ambient
Flow rate (mL/min)	1.0
Injection volume (µL)	20, full-loop injection
Elution mode	Gradient
Injector	Autosampler injection system

Gradient Table

Step Time (min)	Flow Rate (mL/min)	% A	% B
1.0	1.0	100.0	0.0
1.0	1.0	90.0	10.0
3.0	1.0	65.0	35.0
3.0	1.0	25.0	75.0
4.0	1.0	25.0	75.0
0.1	1.0	90.0	10.0
3.0	1.0	90.0	10.0



The chromatogram for the HPLC analysis of the six (6) target compounds

Retention time

Analytes	Retention Time (Mins)
Morphine (A)	3.953
Paracetamol (B)	4.550
Codeine (C)	5.488
Tramadol (D)	6.769
Diclofenac (E)	9.915
Ibuprofen (F)	10.258

UNESCO-IWRA ONLINE CONFERENCE 17-19 JANUARY 2023 3RD IN THE IWRA ONLINE CONFERENCE SERIES

Ceramic Membrane Filter (CMF) Fabrication Processes

Percentage composition of clay materials, grog and cassava starch

Filter code	Flow rate (mL/h)	Clay % by (wt)	Starch % by (wt)	Grog % by (wt)	Firing Temperature (°C)
1	10	90	5	5	900
2	50	80	15	5	900
3	150	70	25	5	900
4	300	60	35	5	900

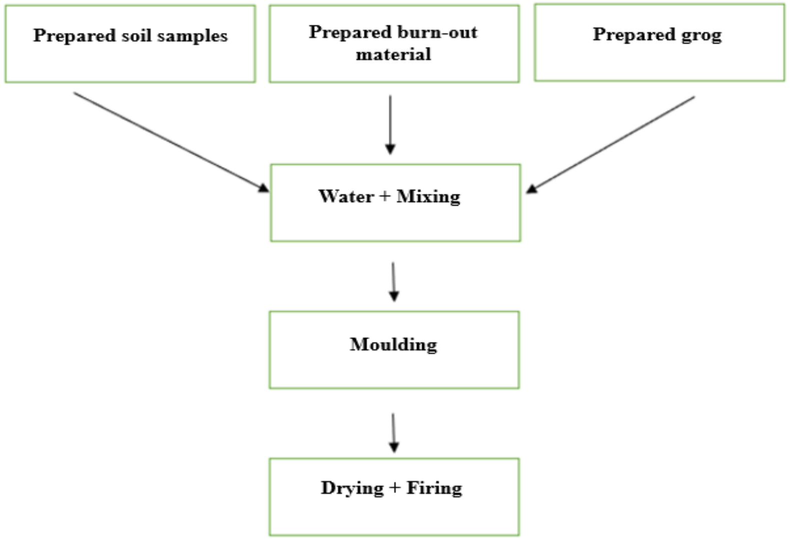


Diagram showing different processes of producing the ceramic filters

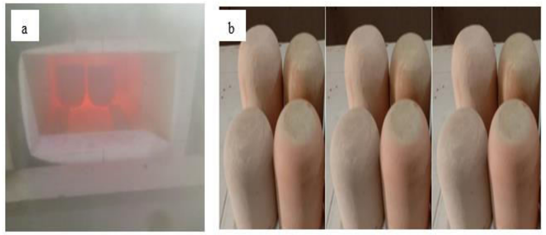
Plaster of Paris (POP) mould used in forming the filters

Pouring of the paste into the POP (a) and formation of the filter (b)

Filters drying at room temperature after pressing (a) and in the oven at 105 ± 5 ^{0}C (b)

Mixing of the raw materials

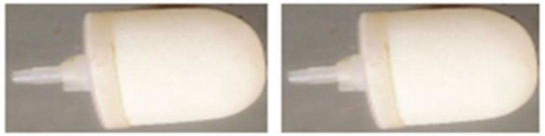
Formed filters ready for pressing



Filters during firing in the furnace (a) and after firing (b)

Ceramic Filtration Experiment

Filters without rubber caps



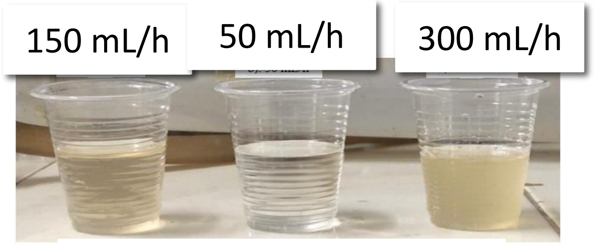
Filters with rubber caps

Characteristics of the ceramic filter and Operating conditions of the ceramic filtration process

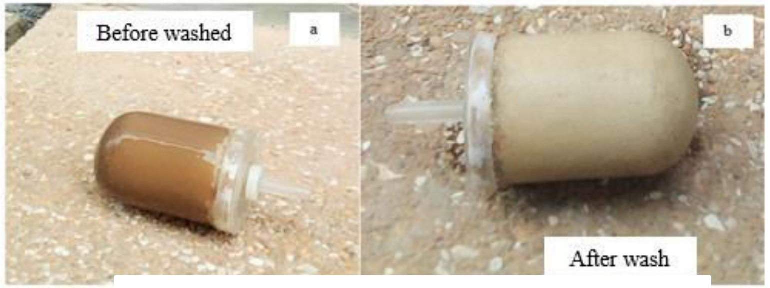
Characteristics of the Ceramic Filter	
Raw materials	Soil materials
Combustible material	Cassava starch
Inner diameter (cm)	4-5
Outer diameter (cm)	7-8
Thickness (cm)	1 - 2
Shape	Cylindrical
Flow rate (mL/h)	10-300
Operating Conditions of the Filtration Process	
Feed volume (mL)	100-400
Pressure (Kpa)	-
Filtration time (h)	1–10
Configuration	Completely submerged

Ceramic filtration set-up

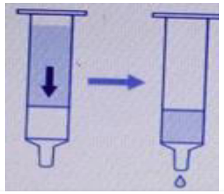
CMF treatment



Treated effluent at d/f flow rate



Filters after 8 weeks continuous operation



Conditioning

SPE set-up for sample extraction

- HPLC Analysis
- Equation for Removal Efficiency

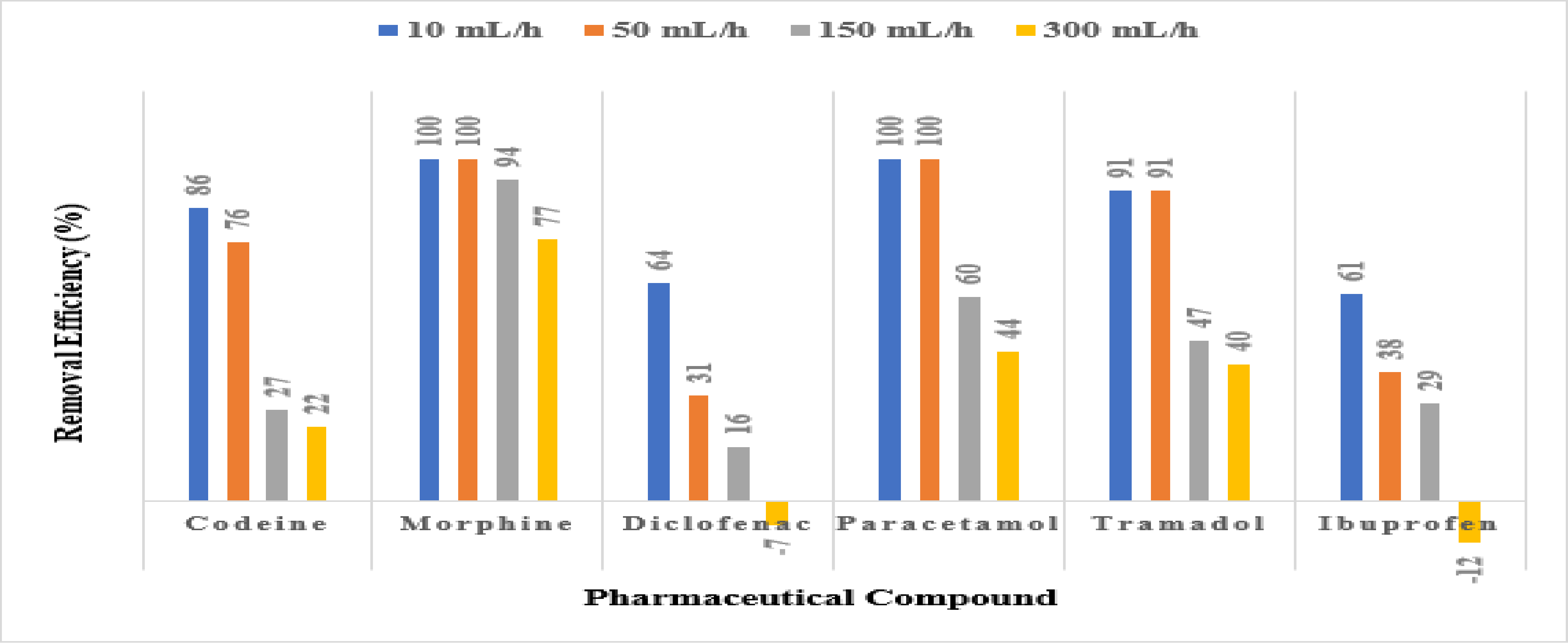
$$\% \text{Removal} = \frac{C_{inf} - C_{eff}}{C_{inf}} \times 100 \quad ....[1]$$

Results and Discussion

Application of CMF for pharmaceutical removal

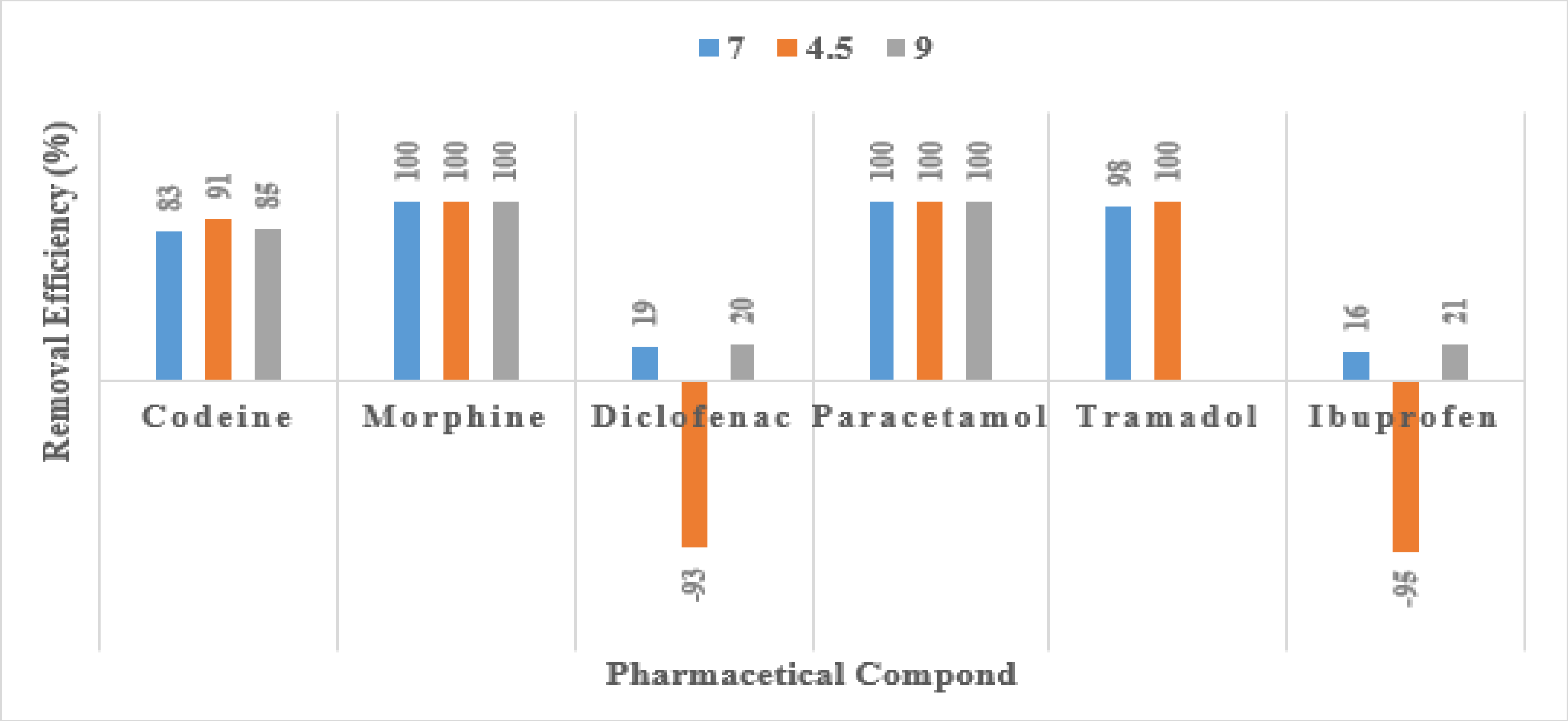
Compound	Influent (µg/L)	Effluent (µg/L)	Removal (%)
Paracetamol	25.3±0.059	0±0.00	100
Codeine	84.4±0.271	19.4±0.002	77
Tramadol	276.6±1.585	19.6±0.277	93
Diclofenac	13.5±0.359	10.9±0.106	19
Ibuprofen	46.9±0.306	39.5±0.045	16
Morphine	16.1±1.629	0±0.00	100

Effect of flow rate on pharmaceutical removal



Flow rate and removal efficiency

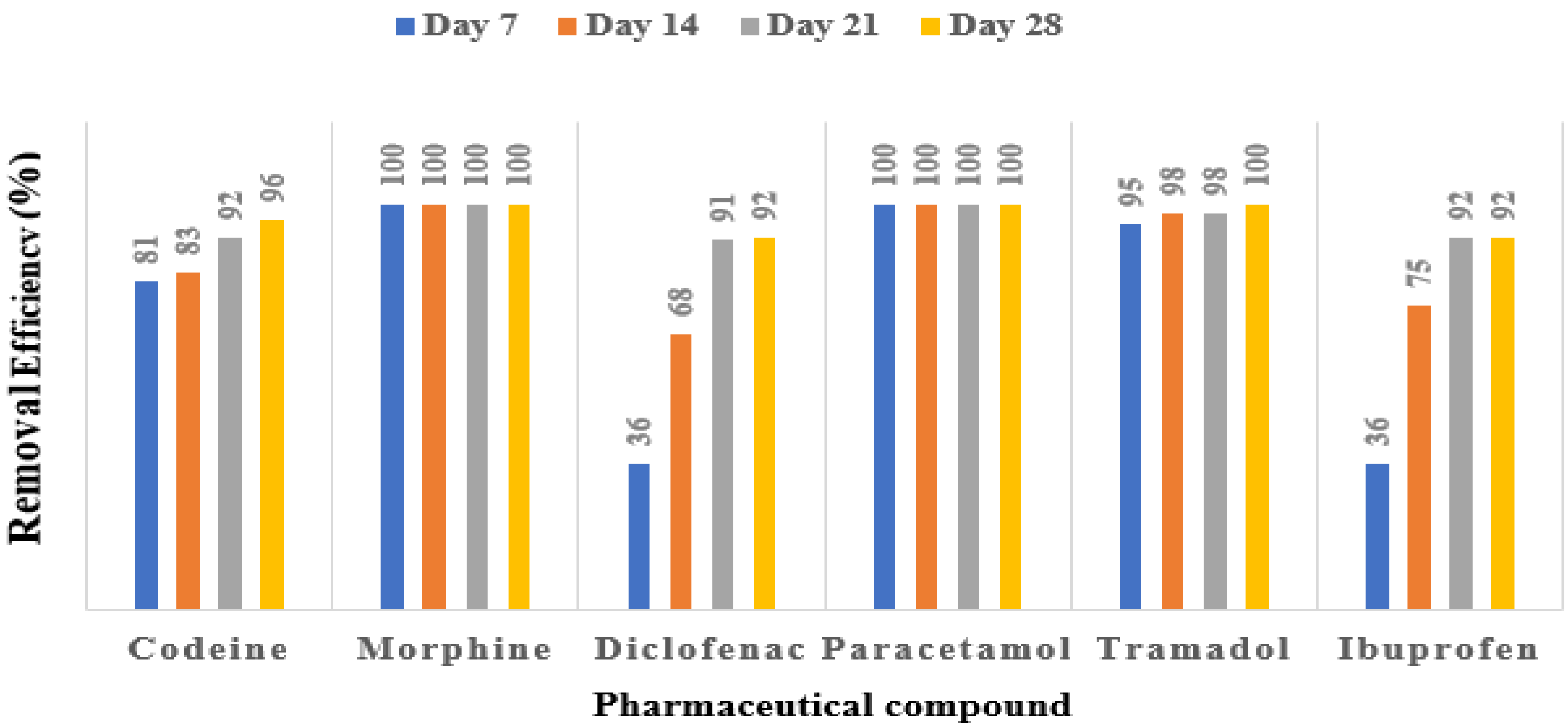
Effect of pH on pharmaceutical removal



pH and removal efficiency

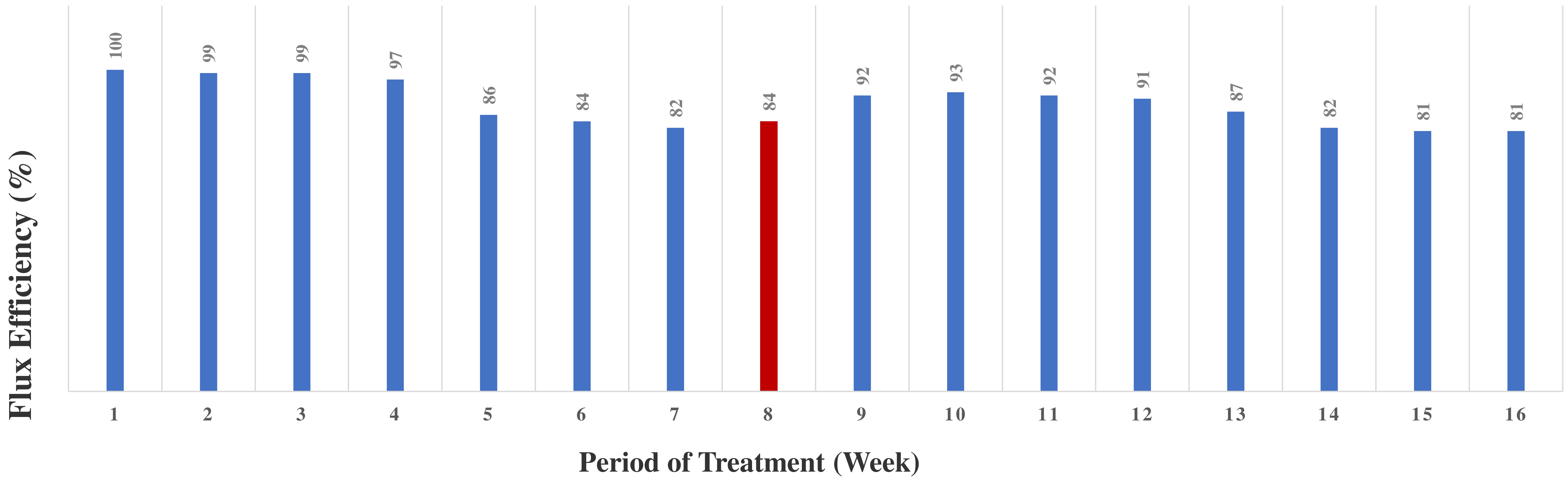
Effect of sludge retention time (SRT) on pharmaceutical removal

UNESCO-IWRA ONLINE CONFERENCE
17-19 JANUARY 2023
3RD IN THE IWRA ONLINE CONFERENCE SERIES



Effect of sludge retention time (SRT) on pharmaceutical removal efficiency

Effect of Clogging on Ceramic Membrane Filter Experiment



Flux efficiency across treatment periods

Conclusion

- The present study indicated that CMF experiments operated at a smaller flow rate combined with increased SRT achieved the best performance among the suited compounds.
- Considering the high removal rate of other pharmaceuticals under normal wastewater conditions, the CMF can be considered as an efficient and economical treatment method and could be applied in several related industries.
- The inability of the developed CMF to remove diclofenac and ibuprofen under normal wastewater conditions makes it easier for future researchers in the modification of the CMF with the objective of removing diclofenac and ibuprofen to an acceptable level.

UNESCO-IWRA ONLINE CONFERENCE
3RD IN THE IWRA ONLINE CONFERENCE SERIES

UNESCO-IWRA ONLINE CONFERENCE
17-19 JANUARY 2023
3RD IN THE IWRA ONLINE CONFERENCE SERIES

UNESCO-IWRA ONLINE CONFERENCE
3RD IN THE IWRA ONLINE CONFERENCE SERIES

EMERGING POLLUTANTS:
PROTECTING WATER QUALITY FOR THE HEALTH OF PEOPLE AND THE ENVIRONMENT

unesco Programme hydrologique intergouvernemental

IWRA International Water Resources Association

KNUST RWESCK Regional Water & Environmental Sanitation Centre Kumasi | Kwame Nkrumah University of Science and Technology

UNESCO United Nations Educational, Scientific and Cultural Organization | RC-IRBM Regional Centre for Integrated River Basin Management under the auspices of UNESCO

National Water Resources Institute Kaduna — Water for Development

Thanks for Listening

UNESCO-IWRA ONLINE CONFERENCE
3RD IN THE IWRA ONLINE CONFERENCE SERIES
EMERGING POLLUTANTS:
PROTECTING WATER QUALITY FOR THE HEALTH OF PEOPLE AND THE ENVIRONMENT
unesco Programme hydrologique intergouvernemental
IWRA International Water Resources Association