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University of Technology Sarawak

ORIGINAL ARTICLE

Applicability of Organic Polymer for Pharmaceutical Removal

*[1,2,3] Mohamad Faiz Mohd Amin, [1,2,3] Mohd Sukhairi Mat Rasat, & [1,2,3] Muhammad Iqbal Ahmad

[1] Faculty of Earth Science, Universiti Malaysia Kelantan, Kelantan, Malaysia.
[2] Sustainable Development Research Group, Universiti Malaysia Kelantan, Kelantan, Malaysia.
[3] Universiti Malaysia Kelantan-Tropical Rainforest Research Centre (UMK-TRaCe), Perak, Malaysia.

ABSTRACT - Pharmaceuticals have become one of the main concerns in environmental pollution nowadays especially when it comes to water treatment. Pharmaceuticals are not sufficiently removed in conventional sewage treatment plants and in order to prevent the spreading of contamination to groundwater and soils, the emission of some pharmaceuticals, which are considered to be priority compounds, is regulated through the European Water Framework Directive (2000/60/EC). The availability of advanced treatment techniques improves the removal of pharmaceuticals from wastewater. The introduction of organic polymers applied as coagulant and/or flocculant for wastewater treatment helps in reducing the quantities of pharmaceuticals in a more cost-effective way. The process described in this paper is based on the addition of organic polymers during the primary sedimentation process of wastewater treatment plants (WWTPs). Jar test studies were carried out with cationic polymers to study the removal of pharmaceuticals from different water samples (filtered wastewater and raw wastewater). All water samples were spiked with a mixture of pharmaceuticals, resulting in a total concentration of 2-15μg/L. In raw influent wastewater, three out of thirteen spiked pharmaceuticals showed a removal exceeding 85%, seven showed a removal between 80 and 60% and the rest between 50 to 30%. Filtered wastewater displayed almost similar results but showed a slightly higher removal of diclofenac, gemfibrozil and sulfamethoxazole compared to raw wastewater.

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INTRODUCTION

Pharmaceuticals are compound which are found in the μg/L or ng/L concentration range in the aquatic environment. Recent studies have indicated that these compounds are often detected in the aquatic environment and are therefore considered to be a potential threat to environmental ecosystems [1]. The way that these compounds enter the environment depends on their uses and the mode of application. The major routes seem to be urban runoff, municipal, industrial wastewater discharge, sludge disposal and accidental spills [2].

The current concern of pharmaceuticals in the receiving waters may also call for new approaches in wastewater treatment. WWTP are designed to deal with bulk substances that arrive regularly and in large quantities (primarily organic matter, nitrogen, and phosphorus). The quantities for pharmaceuticals are entirely different and cannot be seen as a bulk component. Pharmaceuticals are single compounds with each a unique behaviour in the treatment plant and they represent only a minor part of the wastewater organic load [3-8].

Current conventional WWTPs are capable in removing a part of the pharmaceuticals but still not effective and reliable [3-11]. The application of coagulation and flocculation with organic polymers as a substitute of metal ions can improve the removal of pharmaceuticals while enhancing the effluent quality.

*Corresponding Author: Mohamad Faiz Mohd Amin. Universiti Malaysia Kelantan (UMK), email:mohamadfaiz@umk.edu.my

But the need for a profound understanding of the coagulation and flocculation processes are of major importance since the concentrations of pharmaceuticals are extremely low.

The aim of this work is to comprehend the efficiency of polymer application as coagulant and flocculants in improving the pharmaceutical removal. The result is compared to several studies of metal coagulant in jar test experiment and full-scale treatment to see the extent of polymer in the pharmaceutical removal. This objective is based on the hypothesis that the distribution of pharmaceutical between solids and the aqueous phase can be modified by the addition of an organic polymer applied as coagulant and flocculants (more effective than metal coagulants/ flocculants). The insight on the influence particulate matter that exists in the wastewater toward the pharmaceutical removal has been studied.

MATERIALS AND METHODOLOGY

The wastewater used in this work was collected from a WWTP located in Leiden Zuid-West (South Holland). The WWTP treats the water of 126,000 inhabitants living in the area of Leiden Zuid-West, Voorschoten and Zoeterwoude-Dorp. The average daily flow is 24,000 m3. At the WWTP first of all removal of coarse solids takes place followed by nitrification and denitrification combined with chemical phosphorous removal and finally sedimentation. The main characteristics of the wastewater are: total suspended solids (TSS), 100–400 mg/L, total chemical oxygen demand (COD): 350–500 mg/L; Biological oxygen demand (BOD): 156.8 mg/L; total Nitrogen: 44.5 mg/L and total Phosphorus, 8.28 mg/L.

The pharmaceutical used in this work were Carbamazepine (CBZ), Diclofenac (DCF), Bezafibrate (BZF), Clofibric Acid (CA), Fluoxetine (FXT), Gemfibrozil (GEM), Ketoprofen (KPF), Metformin (MF), Metoprolol (MET), Phenazone (PHZ), Propranolol (PPN), Sulfamethoxazole (SMX) and Trimethoprim (TMP). These pharmaceuticals were spiked to 10 L of filtered and unfiltered wastewater in order to attain higher concentrations than those found in raw wastewaters. Once prepared, the resulting pharmaceutical concentrations were measured (Table 1). These values include both the background content (already present in sewage) and the spike. Two types of sample were prepared; 1. Filtered wastewater (filter with 0.45 µm column) and 2. Raw unfiltered wastewater.

The selection on the coagulant/flocculant is based on previous experiment (data not shown) of optimal turbidity removal. Out of twenty different types of polymer, four were chosen for further testing which consist of two cationic and two combinations of coagulant-flocculants (anionic and cationic type). The cationic combination of Nalco 8190 (High molecular weight (MW) coagulant) and Nalco 71413 (High MW cationic flocculant) were selected based on performance and low dosage requirement.

The coagulation–flocculation experiments were carried out in a jar tester with six glass beakers of 2 L. Nalco 8190 and Nalco 71413 were dosed with 15 ppm and 0.5 ppm respectively. The experiment was conducted at room temperature. The test included an initial 5 min period of rapid stirring (300 rpm) after the addition of the coagulant for destabilisation. Then it followed by 5 min of slow mixing (50 rpm) for emulsion breaking and floc formation, and finally 20 min period without mixing for floc separation. Since the objective of the work was to enhance pharmaceutical removal during sewage primary treatment, all the experiments were carried out at the neutral pH.

Standard wastewater parameter was analysed according to Standard Methods (APHA, 1999). The soluble content for the pharmaceuticals was determined after a solid-phase extraction (SPE) of 100 ml samples using 60mg OASIS HLB cartridges (Waters, Milford, MA, USA). All compounds were quantitatively eluted from the cartridge using 3 mL of ethyl acetate. The pharmaceutical concentration analysis was done by Het Water Labotarium (HWL, Harlem, the Netherlands). LC-MS-MS was used to determine the concentration of the investigated compounds in the SPE extract. Values given for the different samples correspond to the average value of two aliquots of each sample.

RESULTS AND DISCUSSION

The majority of pharmaceuticals in wastewater is assumed to be attached to colloidal and particulate matter. In the Netherlands, the greater part of data available on dissolved and particulate pollutants is determined by a separation diameter of 0.45µm. The selection of 0.45µm (<0.45 µm dissolved ; > 0.45 µm related to particle) is intentionally to distinguish the soluble and particle-related fractions. It is expected that by the filtration, the pharmaceutical is somehow positive of negatively removed based on soluble and particulate matter that exist.

Figure 1 shows the removals of pharmaceutical achieved during the jar test experiments. In general, all the compounds used in this experiment show a removal rate between 28 - 90% for the filtered and unfiltered wastewater. For the unfiltered wastewater, three out of thirteen spiked pharmaceuticals showed a removal exceeding 85%, seven showed a removal rate between 60 and 80% and the rest between 30 to 50%. Filtered wastewater displayed almost similar results but showed a slightly higher removal of DCF, GEM and SMX with 78, 86 and 93 % respectively. Given the smaller amount of particulate matter in filtered wastewater, it is expected that the mechanism of removal will be either charge neutralisation or polymer bridging.

CBZ and SMX show removal rates exceeding 90% for both filtered and unfiltered samples. This result is in contradiction to other authors who report on ineffectiveness of coagulation processes for the removal of CBZ in drinking water treatment plants as well as during primary treatment of municipal sewage [3-5]. The difference might be caused by the different type of coagulant and flocculant, dosage and stirring regime. However, since sorption to particulate matter is proven not to be the main mechanism for this compound [3-5], it is expected that direct interaction (charge neutralisation) with the polymer has taken place.

DCF shows a comparable removal rate during the experiments with an average removal of 60% for unfiltered and 75% for filtered wastewater. The unfiltered result is slightly lower than the 69-98% range reported by Amin [3-5]. The main reason on this compound removal can be due to the acidic nature of this compound (pKa~4), which in aqueous phase remains partially ionized. The polymer enhances the binding of DCF to the suspended solids throughout the trivalent cations, thus allowing a further removal from the water phase [6].

The different behaviour of each pharmaceutical obtained can also be explained by their different physico-chemical properties. Being a negatively charge compound, the good removal of GEM in filtered wastewater (85%) is expected to correspond directly to the ionic reaction (charge neutralisation) with the polymer. The unfiltered results show that the coagulation/flocculation process only entitles 45% of the removal which in the range of 16-70% suggested by Amin et al., [3-6]. This clearly shown that the particulate matter besides improving in the absorption of hydrophobic compound, also competes to interact with the polymer; so a smaller amount of GEM is removed in the unfiltered wastewater. Compounds such as DCF, CBZ, BZF, although characterised as highly hydrophobic, show quite a high removal even in filtered wastewater. The compound is preferable to be adsorb to particulate matter, but the scarcity of particles in the filtered matrix has changed the reaction mechanism. It is believed that the CD and MW of the applied polymer has played a role in the removal of this compound (charge neutralisation and bridging mechanism). For PHZ a removal rate of 30% was observed in unfiltered wastewater. This is comparable to results achieved by Amin et al., [6] who showed a removal rate for PHZ of 33%. For BZF a removal rate of 71% in unfiltered wastewater is in range of 27-83%.

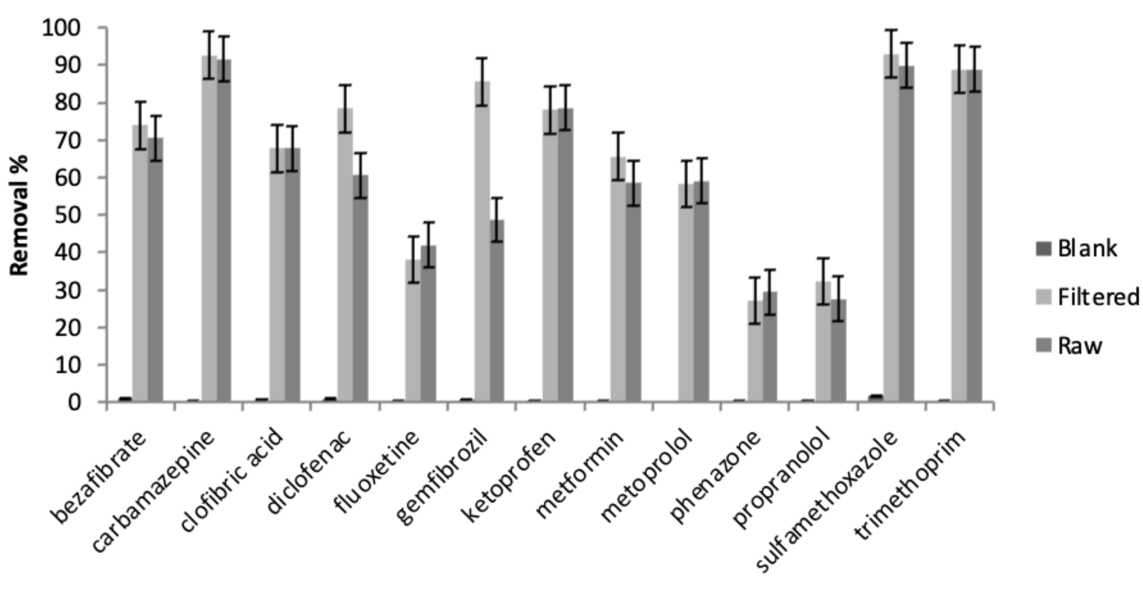

Figure 1: Removal efficiency from the aqueous phase obtained during the coagulation-flocculation jar test experiment.

CONCLUSION

Coagulation and flocculation with polymers can be a suitable pre-treatment option for pharmaceutical removal from wastewater. The highest removal efficiencies have been measured for CBZ and SMX (>90%). Other compounds are in removal range of 28%-85%. The increased removal efficiencies for filtered wastewater for compound like DCF and GEM are expected due to less competition (reduced particulate matter) for the polymer ionic charge and binding site.

The understanding on the positioning and fractionation (soluble, colloid-bind, etc.) of the pharmaceutical in wastewater is important in enhancing the removal process which specific type of coagulant/flocculants can be assigned. The main outcome of the introduction of polymer coagulants/flocculants is that the proposed strategy for wastewater treatment has two main advantages: (i) the removal of pharmaceutical is expected to be enhance up to 20% higher than the current metal coagulant (ii) hydrophobic pharmaceuticals, such as compounds that tend to be sorbed to particulate matter, are expected to be removed to a high extent, thus providing better effluent quality (overall process >95% pharmaceutical removal).

Given the comparison with establish researcher [2-5], the potential of polymer as coagulant and flocculants in removal of pharmaceutical is worth to be acknowledge. However, further research is needed to fundamentally establish polymer as the capable solution in enhancing the pharmaceutical removal from wastewater.

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REFERENCES

[1] Thani N S M, Ghazi R M, Amin M F M and Hamzah Z 2019 Phytoremediaton of heavy metals from wastewater by constructed wetland microcosm planted with alocasia puber *Jurnal Teknologi* **81** (5) 17-23.

[2] Aftar Ali N S, Muda K, Mohd Amin M F, Mohamed Najib M Z, Ezechi E H and Darwish M S J 2021 Initialization, enhancement and mechanisms of aerobic granulation in wastewater treatment Sep. and Pur. Tech. 260 118220.

[3] Mohd Amin M F, Heijman S G J and Rietveld L C 2014 The potential use of polymer flocculants for pharmaceuticals removal in wastewater treatment *Environ. Technol. Rev.***3**(1) 1–10.

[4] Mohd Amin M F, Heijman S G J, Lopes S I C and Rietveld L C 2014 Polyelectrolytes Ability in Reducing Atrazine Concentration in Water: Surface Effects *The Scientific World Journal* **2014** 1–6.

[5] Mohd Amin M F, Heijman S G J and Rietveld L C 2014 Nanoclay for micropollutant removal in wastewater-effective alternative? *Advanced Materials Research* **1024** 11-14.

[6] Mohd Amin M F, Heijman S G J and Rietveld L C 2016 Rietveld Clay-starch combination for micropollutants removal from wastewater treatment plant effluent *Water Science and Technology* **73**(7) 1719–27.

[7] Aftar Ali N S, Muda K, Mohd Amin M F, Mohamed Najib M Z, Ezechi E H and Darwish M S J 2021 Initialization, enhancement and mechanisms of aerobic granulation in wastewater treatment *Separation and Purification Technology* **260** 118220.

[8] Ibrahim Z, Mohd Amin M F, Yahya A, Aris A, Umor N A, Muda K and Sofian N S 2009 Characterisation of microbial flocs formed from raw textile wastewater in aerobic biofilm reactor (ABR) *Water Sci Technol* **60**(3) 683–688.

[9] Ibrahim Z, Mohd Amin M F, Yahya A, Aris A and Muda K 2010 Characteristics of developed granules containing selected decolourising bacteria for the degradation of textile wastewater *Water Sci Technol* **61**(5) 1279–88.

[10] Shaida N, Zulkrnin H, Rozhan N N, Zulkfili N A, Raihan N, Yusoff N and Amin M 2018 Larvicidal Effectiveness of Azolla pinnata against Aedes aegypti (Diptera: Culicidae) with Its Effects on Larval Morphology and Visualization of Behavioural Response *Journal of Parasitology Research*

[11] Thani N S M,Ghazi R M,Wahab I R A,Amin M F M,Hamzah Z,Yusoff N R N 2020 optimization of phytoremediation of nickel by alocasia puber using response surface methodology, Water (Switzerland), 12(10) 2707.