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Adsorption Studies of Trimethoprim Antibiotic on Powdered and Granular Activated Carbon in Distilled and Natural Water

Michael A. Opanga[1,4], Vincent O. Madadi[1], Shem O. Wandiga[1,2], Holiness M. Nose[3], Charles W. Mirikau[1], Mamo Umuro[1,4]

[1]Department of Chemistry, School of Physical Sciences, College of Biological and Physical Sciences, University of Nairobi, P. O. Box 30197-00100, Nairobi, Kenya

[2]Institute of Climate Change and Adaptation, College of Biological and Physical Sciences, University of Nairobi. P. O. Box 30197-00100, Nairobi, Kenya

[3]Department of Pure and Applied Sciences, Technical University of Kenya, P. O. Box,52428-00200 Nairobi, Kenya

[4]Department of Promotive and Preventive Health, National Public Health Laboratory, Ministry of Health, P.O Box 20750- 00202 Nairobi, Kenya

ABSTRACT

Contamination of drinking water sources by Pharmaceuticals and Personal Care Products (PPCPs) has raised concerns due to associated negative effects on the ecosystem, which include reproductive and hormonal malfunctions in some living organisms. In addition, occurrence of antibiotics in aquatic environment has been associated with development of antimicrobial resistance. However, the conventional water and wastewater treatment technologies are not effective at removing such organic micro-pollutants from the source waters, hence most of such contaminants find their way through the systems with minimal restrain. Hence accelerated effort to find technologies to enhance removal of recalcitrant organic micro-pollutants from the water and wastewater. The objective of this study was to investigate the removal of Trimethoprim (TMP) from natural water using Powdered Activated Carbon (PAC) and Granular Activated Carbon (GAC). Adsorption experiments were conducted following batch process using natural water and distilled water. We also investigated the effect of pH changes on adsorption of TMP from the water. We obtained better performance for PAC in the removal of TMP compared to GAC. The removal efficiency decreased as a function of TMP concentrations in the aqueous solution. The optimal pH for adsorption was found to be 7, whereas pH values below or above 7 exhibited decreased adsorption of the antibiotic. There was no significant difference in the adsorption of TMP in both natural water and distilled water, which was attributed to limited organic matter in the natural water that was used.

Keywords : Atibiotic Pollution, Activated Carbon Adsorption Studies, PAC and GAC, Natural and River Water

I. INTRODUCTION

Contamination of water resources by emerging organic micro-pollutants is an issue of recent concern.1 Whereas the pharmaceuticals are present in waters at very low concentrations, they have been detected in drinking water sources globally including the USA[2], Europe and Asia.[3] According to Ternes and coworkers[4], the primary route of entry for these pharmaceuticals into water supply system is through releases from wastewater treatment plants (WWTPs). In addition, pharmaceuticals may also enter the

wastewater system as metabolic excretes and through illegal discard of expired drugs down the drain.[4] However, most pharmaceuticals in wastewater pass through WWTPs into the environment unrestrained by the current primary and secondary treatment stages.[5] This is partly because these treatment stages focus on removal of conventional impurities such as suspended solids, turbidity, colour and microbiological organisms.[6] Biological oxygen demand (BOD) and nutrient levels are minimized by secondary treatment while disinfection removes pathogens before the effluent is released.[7] The conventional treatment technologies are not devised to effectively remove most organic micro pollutants such as PPCPs, hence most of such contaminants are not effectively removed.[2]

The increasing public concerns and awareness on safety of drinking water has driven consumers to use carbon related systems to purify drinking water at the point of use[8], making activated carbon filtration one of the most widely employed technologies in point of use drinking water treatment. However, the nature of activated carbon, composition of water and operating parameters can affect adsorption efficiency of activated carbon.[9] Adsorption involves accumulation of solute (adsorbate) on a surface of a solid or a liquid (adsorbent) forming a molecular or atomic film. Atoms at the surface are not entirely surrounded by other atoms, hence they experience bond deficiency and are energetically favorable for bonding to the adsorbate.

The most frequent and widely used classes of pharmaceuticals include antibiotics, analgesics, anti-inflammatory, antiseptics and antiepileptic drugs.[10] Most of them are sold over the counter without any prescription. However, routine monitoring of PPCPs in water and wastewater treatment plants are rare, and even the occurrence of PPCPs in effluent is not well regulated.[11] The public concerns and perception over possible ecosystem and adverse health effects related with exposure to PPCPs have led to increased study of their fate in the course of wastewater treatment in most developed countries.[10, 12, 13] Since most of the wastewater treatment plants are not devised to eliminate PPCPs, pharmaceutical composites end up in environment and cause a threat to wildlife, and difficulties to drinking water treatment facilities.[14,15,16,17]

PPCPs effects include short-term and long term poisoning, antibiotic resilience of microorganism and endocrine disrupting effects.[18] In addition, monitoring actions and precautions for PPCPs have not been instituted in most Wastewater Treatment Plants (WWTPs), and discharge regulations and standards do not exist for most PPCPs,[18] especially in developing countries.

In Kenya, PPCP contamination has become an issue of concern,[19] due to increasing levels of antibiotic resistance that may compromise the fight against disease causing micro-organisms.[20] Data on environmental residues of PPCPs in Ngong River is limited, despite the fact that the river water is widely used to irrigate vegetables along the river profile, and watering livestock. The goal of this work was to investigate the performance of activated carbon on the removal of Trimethoprim from the river water.

II. METHODS AND MATERIAL

A) Adsorption experiments:

Adsorption studies were carried out in duplicates following batch equilibration studies. 0.1 g of PAC and GAC were used separately for each experiment in 15 ml centrifuge tubes containing 10 ml of different initial concentrations of 1, 5, 10 and 20 mg/l of TMP solution. The tubes were agitated in a water bath shaker at 150 rpm and 24 ^{o}C for 1, 2, 4, 6, 8, 10, 12 and 24 hrs to establish the equilibration time. The solutions were centrifuged at 1,500 rpm for 3 minutes and the clarified supernatant solutions were filtered through 0.45 µl acetate micro filters. The filtered

solutions were transferred into 1.5 ml amber vials ready for analysis. The initial and equilibrium TMP concentrations were determined by peak area measurement using Shimadzu, Model LC-2040C 3D HPLC, at 275 nm. The peak areas were computed to TMP concentrations using standard calibration curve. The amount of adsorption at equilibrium, qe(mg/g) were calculated as shown in equation 1 below,

qe= (Co-Ce)V/M……Equation 1

Where Co and Ce (mg/l) are the liquid phase concentrations of TMP at initial and equilibrium, respectively. V is the volume of the solution in litres (L) and M is the mass of dry adsorbent used in grams (g). M HCl and NaOH solutions were used to adjust the pH of samples in order to study the effect of pH on removal efficiency. The pH measurements were made using a Metrohm 744 pH meter model for all experiment. Activated carbon 0.1 g was added to 10 ml of 1, 5, 10 and 20 mg/l solutions of TMP in centrifuge tubes. The pH values of the solution were set at pH 1, 2, 4, 6, 7, 9, 10, 11and 12. The solutions were agitated at room temperature on digital shaker at 150 rpm for 24 hours. Removal of antibiotics was measured after agitation and the concentrations of TMP analyzed on a Nexera-i LC-2040C 3D Liquid chromatograph.

B) Analysis of TMP:

Nexeira-I LC-2040C 3D liquid chromatograph (Shimadzu, model LC-2040C 3D) with UV/VIS detector was used for the analysis of the TMP. All separations were performed by Kromasil 100-5C18 column (0.25 m long and 4.6 mm diameter). The mobile phase was 0.05M KH_2PO_4. Elution was carried out by isocratic mixture of 75:15:10 for buffer: Acetonitrile: Methanol. The flow rate was 1.0 ml/minute, injection volume was 20 µl and detection was conducted at a wavelength of 275 nm. Determination of TMP concentrations was conducted by comparing the peak areas of chromatograms of samples and their respective external reference standards.

III. RESULTS AND DISCUSSION

A) Calibration curve for TMP:

Calibration of HPLC was effected by analysis of standard solutions of TPM. Good linearity of 0.996 was obtained between the instrument response and concentration of the standards as shown in Figure 1.

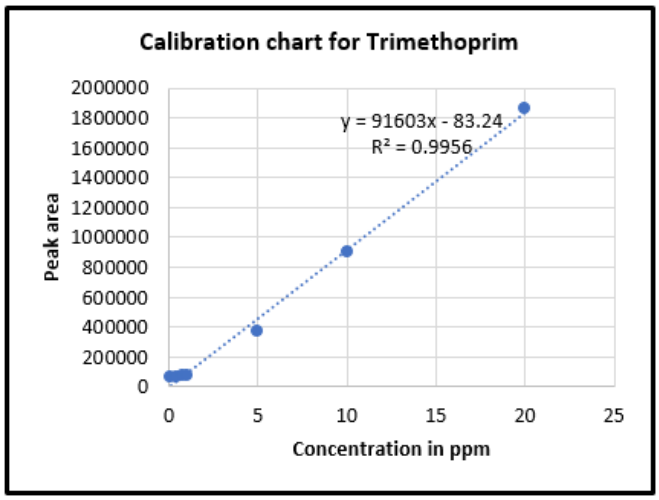

Figure 1. Calibration curve for Trimethoprim

B) Effect of Contact Time on Adsorption of TMP on activated carbon

The adsorption data for the uptake of TMP versus contact time at different initial concentrations used ranging from 1 mg/L to 20 mg/L. All experiments were conducted at pH 7 with constant agitation of 150 rpm. The amount of activated carbon used was kept constant at 0.1 g. Figure 2 shows that adsorption increased with increase in contact time until the equilibrium after 6 hours.

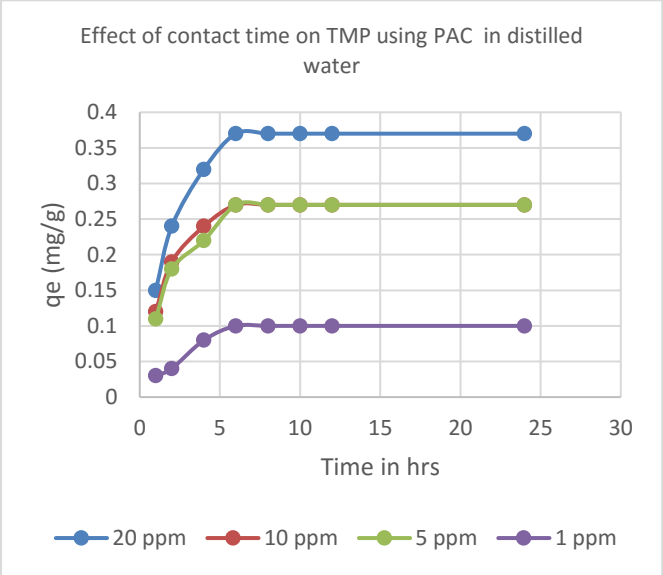

Figure 2. Effect of contact time on adsorption of TMP on PAC in Distilled water.

The results of adsorption of Trimethoprim on GAC in distilled water is shown in Figure 3. The data shows increase in adsorption until 6 hours suggesting attainment of the equilibrium. The amount adsorbed increased from 1 mg/L to 20 mg/L solutions.

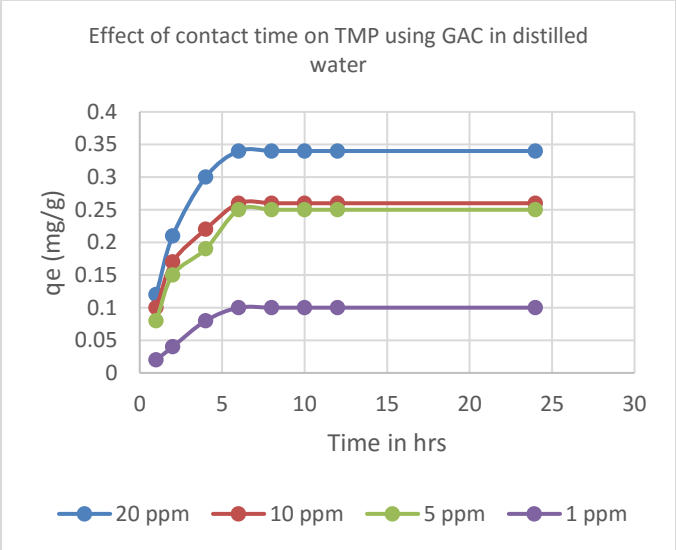

Figure 3. Effect of Contact time on adsorption of TMP antibiotics on GAC in distilled water

The effect of contact time on adsorption of Trimethoprim on PAC in Surface water is shown in Figure 4 below. Adsorption increased with contact time up to the 6th hour and plateaued.

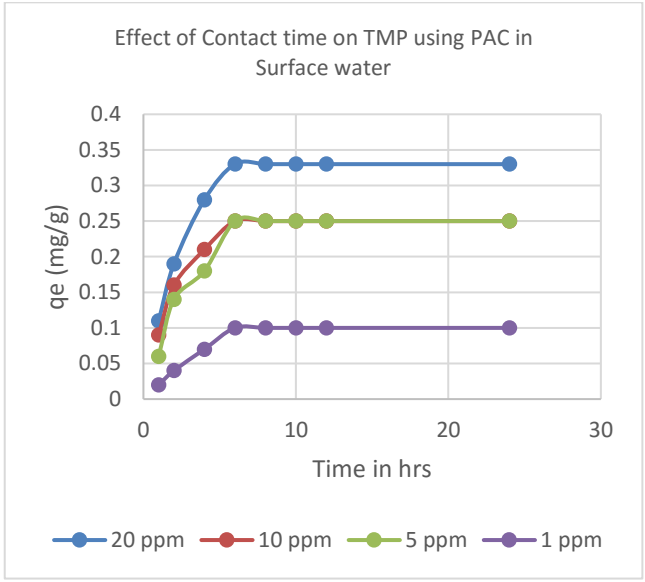

Figure 4. Effect of Contact time on adsorption of TMP antibiotics on PAC in surface water

The effect of contact time on adsorption of Trimethoprim antibiotics on GAC in Surface water is shown in Figure 5 below. The data shows that adsorption capacity increased with increase in contact time until equilibrium is reached. In addition, adsorption of Trimethoprim on GAC in surface water increased with increase in concentrations up to the 20 mg/L investigated.

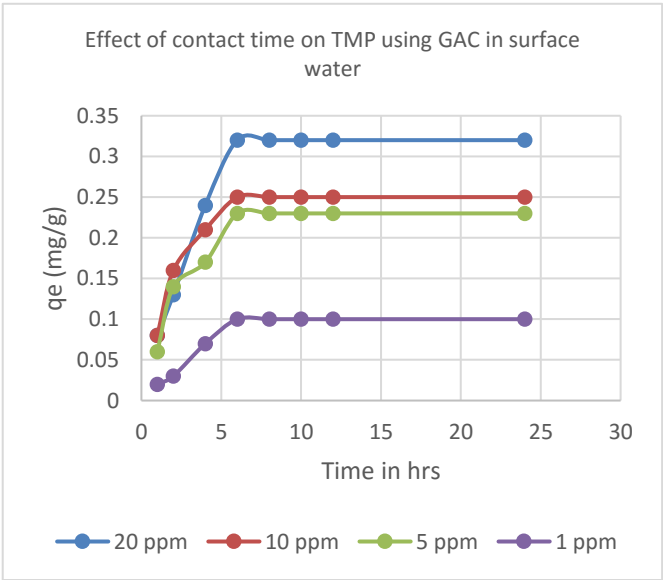

Figure 5. Effect of Contact time on adsorption of TMP antibiotics on GAC in surface water.

Adsorption of TMP was notably greater for PAC than on GAC, suggesting better performance of PAC than GAC in removing the antibiotic from both distilled

and surface water. Maximum removal of TMP was observed for 1 mg/L solution, with both PAC and GAC achieving 100% removal for both surface and distilled water. However, the removal efficiencies decreased as the concentrations of TMP increased for 5, 10 and 20 mg/L solutions. Table 1 below summarizes maximum removal of GAC and PAC after 24 hours of equilibration.

Table 1. Removal rate of GAC and PAC after 24 hrs Adsorption for TMP

Type of Water	Type of Activated Carbon	Concentration (ppm)	% Removal
Distilled	PAC	1	100
		5	53.8
		10	27.2
		20	18.6
	GAC	1	100
		5	50.6
		10	26.3
		20	17.2
Surface	PAC	1	100
		5	50.2
		10	25.8
		20	16.5
	GAC	1	100
		5	47.3
		10	25.3
		20	16.2

The decrease in removal efficiency with increasing concentration of TMP could be attributed to increase in the number of particles in the solution compared to available active sites for adsorption, hence increased competition for attachment of the particles to the fixed number of active sites on GAC or PAC. Hence lower % adsorption compared to available number of the adsorbate.

Higher removal rate for PAC were was observed compared to GAC, which could be explained by the packing of activated carbon. The PAC contained small particles, hence larger surface area for the adsorption compared to GAC which had larger particles, hence smaller surface area.

B) Effect of PH on Trimethoprim:

pH affects the surface charge on activated carbon, since above pH 7 there is an increase in hydroxyl ions. This causes the activated carbon and the TMP species in the solution to be negatively charged and hence reduces the sorption process by electrostatic repulsion. At higher pH values there is production of aqua-complexes which reduces the adsorption capacities of activated carbon (Figure 6).

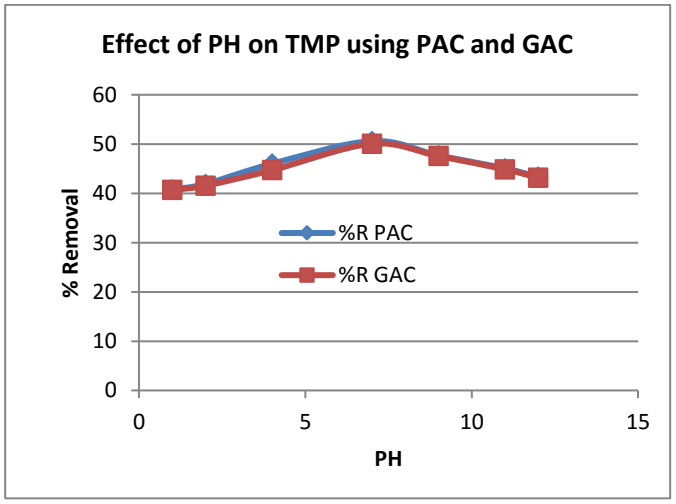

Figure 6. Effect of pH on TMP using PAC and GAC as an adsorbent

C) Adsorption Experiments:

Adsorption isotherms show the relationship between the amount of substance adsorbed and the remaining concentration in aqueous media, at equilibrium. In this study, two adsorption models were applied; the Langmuir and Freundlich isotherms. Langmuir isotherm described by the equation below[21] was used to determine the values of maximum.

$$Ce/Qe=1/BQe+ Ce/Qm \quad \ldots \quad \textbf{Equation 2.}$$

Where B is a Langmuir constant (L/g); Qm is the maximum sorbate uptake per unit mass of the

adsorbent (mg/g); Qe is the adsorbed amount on unit mass of the adsorbent mg/g and Ce is the equilibrium concentration of sorbate in solution. The values of Q_m and B computed from the slopes and y intercepts are shown in Table 2 where Q is the maximum adsorbate that can be adsorbed on the surface (adsorption capacity) and B is the isotherm constant. The results shown in Table 2 yielded values of QB less than one. According to Musa and coworkers[22] larger values of b and QB suggest favorable adsorption process. Therefore, since the value of QB was less than 1 for TMP on activated carbon was not favorable.

Table 2. Maximum uptake for antibiotics on PAC and GAC in distilled and surface water

Active Content	Water type	Activated Carbon Type	Equation	Q (mg/g of activated carbon)	QB	B(l/g)	R^2
TMP	Surface	GAC	Y=12.51x+1.96	0.51	0.08	0.16	0.73
		PAC	Y=10.84x+1.97	0.51	0.09	0.18	0.76
	Distilled	GAC	Y=12.51x+1.96	0.51	0.08	0.16	0.73
		PAC	Y=9.08x+1.95	0.50	0.11	0.22	0.88

From the table it can be concluded that the results yielded fairly good correlation coefficient. It can also be noted that there was no significant difference in maximum adsorption uptake between distilled water and surface water. This means that the surface water had minimal organic matter dissolved in to it.

1) Freundlich Isotherm

The Freundlich isotherm is based on the log transformation of the equation 2 and 3 below.

$$q_e = k_f c_e^{1/n} \ldots\ldots\ldots\ldots \quad \textbf{Equation 2}$$

$$\text{Log } q_e = \text{Log } k_f + 1/n \text{ Log } c_e \ldots \quad \textbf{Equation 3.}$$

Where,

k_f = Freundlich constant related to the bonding energy 1/n is the heterogeneity factor, n (g/l) is a measure of the deviation from linearity of adsorption or the degree of nonlinearity between solution concentration and adsorption.

Freundlich isotherm supposition is based on uniformity of active sites energy, or the fact that different functional groups are adsorbed on the surface by different energies. In this case sorption can happen in multilayer manner. Graphs of log Qe versus log Ce were plotted for TMP. The values of K_f and n computed from the slopes and y intercepts of the graphs are shown in Table 3.

Table 3. Freundlich isotherms values

Active Content	Water type	Activated Carbon Type	Equation	K_F	1/n	n	R^2
TMP	Surface	GAC	Y=0.38x-0.92	0.40	0.38	2.63	0.83
		PAC	Y=0.37x-0.91	0.40	0.37	2.70	0.78
	Distilled	GAC	Y=0.39x-0.90	0.41	0.39	2.56	0.79
		PAC	Y=0.38x-0.90	0.41	0.38	2.63	0.79

For Freundlich isotherms if the value of n is below unity, then the adsorption is a chemical process; otherwise the process is a physical process. In Table 3which summarized the results of this study the n value obtained for AMX, SMX and TMP were above one. This suggest that the adsorption was a physical process. The values of regression coefficients R^2 are regarded as a measure of goodness of fit of the experimental data to the isotherm model. Hence the R^2 of Langmuir and Freundlich isotherm in this study, better fits were obtained for Freundlich isotherm model. This suggests that adsorption of TMP followed multilayer adsorption.

IV. CONCLUSIONS AND RECOMMENDATIONS

Adsorption of TMP was greater on PAC than on GAC, showing that PAC was a more effective at removing these antibiotic contaminants from water than GAC.

Adsorption in distilled water was higher than in surface water suggesting that the real time application of both PAC and GAC would be affected by artifacts such organic matter and other co-contaminants in natural water.

Maximum antibiotic uptake (Qm) for TMP was 0.50 mg/g in distilled water using both PAC and 0.51 mg/g for TMP using GAC. For surface water, 0.51mg/g was obtained for TMP using both PAC and GAC. From the adsorption experiments there was no significant difference in maximum antibiotic uptake between distilled water and river water. Adsorption of TMP on activated carbon followed Freundlich isotherm and was a physical process. Adsorption was strongly influenced by the electrostatic interactions as evidenced by changing adsorption capacities at different solution pH values. In addition, adsorption was also influenced by the active content of the antibiotic in question and its pka.

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