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Original Research Paper

Removal of Sulfamethoxazole from Wastewater by Adsorption and Photolysis

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ABSTRACT

Antibiotics are emerging contaminants which affect human health, livestock, aquatic life and also resist biological wastewater treatment. Therefore, it is imperative to remove them from wastewaters. The present investigation is aimed at removal of sulfamethaoxazole (SMX) using adsorption and advanced oxidation processes (AOPs) and to determine efficacy of various adsorbents and study their adsorption kinetics. The aqueous solution of sulfamethoxazole (SMX) was treated using GAC, PAC and activated alumina. Advanced oxidation processes (AOPs) were conducted using photolysis (UV treatment) and photolysis with H_2O_2 (UV + H_2O_2 treatment). Adsorption of SMX on GAC and PAC was found to be rapid. Adsorption of SMX on GAC and PAC followed pseudo first order kinetics. PAC was found to be more effective. Removal of SMX after 120 min at a dose of 5 g/L using PAC, GAC and activated alumina was 73.4%, 34% and 15.5%, respectively. In case of PAC, only intraparticle diffusion was operating, whereas for GAC both intraparticle diffusion and surface adsorption were operating concurrently. Removal of SMX using UV treatment and UV treatment in presence of H_2O_2 was found to be 7.65% after 80 min and 7.67% after 110 min, respectively. Activated carbon was found to have superior behaviour as compared to activated alumina for the adsorption of SMX.

INTRODUCTION

Antibiotics are the most important group of pharmaceuticals used but due to improper disposal and via urine and faecal matter, unmetabolized antibiotics enter into sewage effluents. This group of pharmaceuticals is discharged mainly from private households and hospitals (Giger et al. 2003), runoff from animal feeding operation, from compost made of animal manure containing antibiotics (Ötkar & Balciolu 2005), and by application of antibiotics on livestock production (Arikan et al. 2008).

Antibiotics are a diverse group of drugs which can be divided into several subgroups, such as α -lactams, quinolones, tetracyclines, macrolides, sulfonamides and others. Among all these antibiotics, sulfa drugs have been largely detected in wastewater. The highest median influent concentrations of sulfamethoxazole, trimethoprim, ciprofloxacin, norfloxacin and cephalexin have been found to be 360, 340, 3800, 170, and 4600 ng/L, respectively in WWTP in Brisbane, Australia (Barceló & Patrovic 2008). Sulfamethoxazole (SMX) in combination with trimethoprim is largely used to treat respiratory diseases like pneumonia, coccidiosis, diarrhoea and gastroenteritis. They subsequently generate residues due to excretion of unmetabolized or active metabolites (Dantas et al. 2008).

If antibiotics are not degraded or eliminated during sewage treatment, they reach surface waters, groundwaters and finally to drinking water (Kümmerer 2003, Sponza & Demirden 2007). The removal of low concentration of antibiotics is challenging but essential.

In the present study, removal of sulfamethoxazole (pure form) is chosen for study. Although, sulfa drugs are present in low concentration and their concentration do not exceed any current water standards; their existence in the environment may have ecotoxicological effects (Shamsa & Amani 2006).

As far as detection of SMX in water is concerned, various techniques have been used, e.g., HPLC (Nebot et al. 2007), capillary electrophoresis end-column electrochemical detection (You et al. 1998), mass spectrometry, liquid chromatography-tandem mass spectrometry (Giger et al. 2003, Conley et al. 2008), spectrophotometric method (Shamsa & Amani 2006, Nagaraja et al. 2007), mass spectrometry (Dost et al. 2000), electroanalytical determination (Souza et al. 2008) GC-MS (Koutsouba et al. 2003) and pressurized liquid extraction (Nieto et al. 2007). In the present study, removal efficiency of SMX from wastewater was determined using UV spectrophotometric method (Shamsa & Amani 2006).

There are several methods available for removal of sulfamethoxazole from wastewater. It includes coagulation, adsorption (Adams et al. 2002), oxidation using chlorination (Debordea & Guntena 2008), ozonation (Dantas et al.

2008), H_2O_2 , UV light (Gonz'alez et al. 2007), biological anaerobic process using UASB (Sponza & Demirden 2007) membrane separation, nanofiltration, and reverse osmosis (Kosutic et al. 2007). In the present work, adsorption using granular activated carbon (GAC), powdered activated carbon (PAC), aluminium oxide and AOPs, viz. photolysis, and photolysis with H_2O_2 techniques have been studied for removal of SMX in aqueous solution. Study of kinetics of removal of sulfamethoxazole using GAC and PAC with different kinetic models has also been made.

MATERIALS AND METHODS

Sulfamethoxazole (SMX) (M.W. = 253.28, minimum assay: 98.0%, melting point: 166-169°C, Make: Himedia Laboratories (India) was used in the study. Another reagents like ethanol (minimum assay: 99.9%, AR Grade), aluminium oxide active acidic (molecular weight: 101.96, particle size: 70-230 mesh, Make: CDH, India), powdered activated charcoal (PAC) (Make: E. Merck), granular activated carbon (GAC) (partical size: 2.0-5.0 mm, Make: CDH), hydrogen peroxide (AR Grade, Make: Rankem, India) and Hydrochloric acid (AR Grade, Make: Rankem, India) were used in the present experimental work. Chemical structure of SMX is shown below:



Quantitative determination of SMX: The quantitative determination of SMX has been made by measuring optical density at 271 nm on a UV-Visible Spectrophotometer of Make: EC Model GS5075. For this purpose, 20 mg/L stock solution of SMX was prepared. For the quantitative detection of SMX, spectrophotometric method (Shamsa & Amani 2006) was used. A schematic diagram of photochemical reactor used in the study is shown in Fig. 1.

Removal of SMX: Removal of SMX from water was made using adsorption and photolysis. For determination of the effect of adsorbent concentration on removal of SMX by adsorption, experiments were conducted using different concentrations of GAC, PAC and aluminium oxide activated acidic. For this purpose, 100 mL of 20 mg/L solution of SMX was treated with different adsorbents. For mixing the solution, flask shaker was used. After 120 min, the removal of SMX using these adsorbents was determined by using following expression:



Fig. 1: Schematic diagram of photochemical batch reactor experimental setup.

$$q_t = \frac{(C_0 - C_t)V}{W} \qquad \dots (1)$$

The percentage of SMX removed (R%) from the solution was calculated using the following equation.

$$R\% = \frac{C_0 - C_t}{C_0} \times 100 \qquad \dots (2)$$

Effect of adsorbent contact time on removal of SMX was established for GAC and PAC. For this purpose, 100 mL of 20 mg/L solution of SMX was taken in 250 mL conical flasks and 5 g/L GAC and 5 g/L of PAC were added separately.

Another method used for removal of SMX was advanced oxidation process (AOPs). Two AOPs (photolysis and photolysis with H_2O_2) were conducted for removal of SMX at 35°C. Both these experiments were conducted in a 5 L capacity photochemical batch reactor. Three litres sample of concentration 20 mg/L SMX was used for treatment process. UV treatment was operated using a 3 × 8 W low pressure mercury lamp. In UV process, treated water was continuously recirculated in the reactor. For photolysis with H_2O_2 process, H_2O_2 solution with a concentration of 0.0396 mM was used.

Adsorption kinetics: The kinetics of SMX adsorption on GAC and PAC are required for selecting optimum operating conditions for the full-scale batch process. The process of SMX removal from aqueous phase by GAC and PAC may be represented by pseudo first-order (El Nemr 2009, Ahmaruzzaman 2008), pseudo second-order (El Nemr 2009, Ahmaruzzaman 2008), Elovich (El Nemr 2009) and intraparticle diffusion (El Nemr 2009) kinetic models. The conformity between experimental data and the model-predicted values have been expressed by the correlation coefficient R^2 .

Pseudo first-order kinetic model: The kinetic data were treated with the Lagergren first-order model, which is the

earliest known one describing the adsorption rate based on the adsorption capacity. It is generally expressed as follows (Ahmaruzzaman 2008).

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \qquad \dots(3)$$

Pseudo second-order kinetic model: Integrated rate equation for pseudo second-order model is given by following equation (Demirbas & Nas 2009).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad \dots (4)$$

The initial sorption rate (h) may be calculated by the following expression.

$$h = k_2 q_e^2$$
 ...(5)

Elovich kinetic model: Elovich kinetic equation is another rate equation based on the adsorption capacity, which is generally expressed as (El Nemr 2009, Augustine et al. 2007).

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \qquad \dots (6)$$

If SMX adsorption by GAC and PAC fits the Elovich model, a plot of q_t versus $\ln t$ should yield a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta) \times \ln(\alpha \beta)$. Thus, the constants can be obtained from the slope and intercept of the straight line.

Intraparticle diffusion model: The adsorption process required a multi-step involving the transport of solute molecules from aqueous phase to surface of the solid particles followed by diffusion of the solute molecules into interior of the pores, The second step diffusion is usually a slow process, and is therefore, rate-determining step. The intraparticle diffusion model is explored by using the following equation.

$$q_t = K_{dif} t^{0.5} + C^* \qquad ...(7)$$

The plot of q_i versus $t^{0.5}$ may present a multi-linearity correlation, which indicates that two or more steps occur during adsorption process. The intraparticle rate constant K_{dif} is directly evaluated from the slope of the regression line and the intercept is C^* . The values of C^* provide information about the thickness of the boundary layer (El Nemr 2009, Mak et al. 2009).

RESULTS AND DISCUSSION

Experiments were conducted to study effect of adsorbent concentration on removal of SMX, effect of adsorbent contact time on removal of SMX, extent of adsorption on GAC and PAC with time, and kinetics of adsorption and SMX removal using photolysis. The results of the above have been



Fig. 2: Comparison of adsorbent dose on % removal of SMX using GAC, PAC and activated alumina (temp: 20°C, initial SMX concentration: 20 mg/L).



Fig. 3: Effect of contact time on removal of SMX using GAC and PAC.



Fig. 4: Comparison of SMX adsorption using GAC and PAC.

presented in the following subsections.

Effect of adsorbent concentration on removal of SMX: Fig. 2 shows percent removal of SMX using different adsorbents with varying doses of GAC, PAC and Activated alumina. It may be observed that with increase in the dose of GAC, removal of SMX also increases. 34% removal of SMX from 20 mg/L solution was achieved after 120 min at 6 g/L dose of GAC. In a previous study for removal of tetracycline from raw water (synthetic and river) using GAC filtration, more than 68% removal of incoming tetracycline has been reported for an initial concentration is 10 µg /L (Choi et al. 2008).

It is obvious that removal is 71% for SMX using 1 g/L PAC after 180 min. No noticeable change was observed in

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removal of SMX with PAC at a dose greater than 1g/L. Therefore, in case of PAC, small dose of adsorbent (1g/L) is sufficient for removal of SMX. In a previous study for antibiotic removal, a mixture of carbadox, sulfachlorpyridazine, sulfadimethoxine, sulfamerazine, sulfamethazine, sulfathiazole, and trimethoprim with initial concentration of 20 mg/L of each antibiotic in distilled water, the percent removal of each of the antibiotics ranged from 57 to 97% and 81 to 98% for PAC dosages of 10 and 20 mg/L, respectively (Adams et al. 2002).

Table 1: Parameters of pseudo-first order and pseudo-second order kinetic models for adsorption of SMX using GAC and PAC at 20°C (Initial concentration of SMX: 20 mg/L).

Sl. No.	Type of adsorbents	$q_{e, exp} \ mg/g$	Pseudo-First order Kinetics				Pseudo-Second order Kinetics		
			$q_{e'calc,} mg/g$	$k_{I_i} min^{-1}$	R ²	$q_{_{e,calc,}} \ \mathrm{mg/g}$	k _{2,} g/mg.min	\mathbb{R}^2	<i>h,</i> mg/g.min
1. 2.	GAC PAC	1.08 3.06	1.95 3.41	0.029 0.023	0.862 0.9715	1.90 3.92	0.0036 0.0049	0.530 0.913	0.0129 0.0753

Table 2: Parameters of Elovich kinetic model and intraparticle diffusion for adsorption of SMX using GAC and PAC at 20°C (Initial concentration of SMX: 20 mg/L).

S. no.	Type of adsorbents	Elovich kinetic model			Intraparticle diffusion		
		α mg/g.min	β g/mg	R ²	K _{dif} mg/g.min ^{0.5}	\mathbb{R}^2	C*, mg/g
1 2	GAC PAC	0.0322 0.337	2.11 1.522	0.932 0.905	0.102 0.235	0.930 0.918	- 0.161 0.057

Table 3: Comparison of removal of SMX by various treatment processes.

S. No.	Treatment process	Maximum % removal	Dose of adsorbents/ UV/UV + H ₂ O ₂	Duration
1.	Adsorption using different GAC dose	28.0%	5 g/L	120 min
2.	Adsorption using PAC dose	75.3%	5 g/L	120 min
3.	Adsorption using activated alumina dose	15.5%	5 g/L	120 min
4.	Photolysis with UV	7.65%	-	80 min
5.	Photolysis with UV+ H_2O_2	7.67%	0.0396 mM (H ₂ O ₂)	110 min

It may be also observed that using activated alumina the removal of SMX was 11% at a dose of 1g/L which increases to 16% at a dose of 5 g/L, further, beyond 5 g/L, it becomes almost constant. The removal pattern of SMX using activated alumina shows an unpredictable behaviour during adsorption experiments. It has been reported that tetracycline gets transformed during surface interaction with aluminium oxide. It appears that a similar phenomenon might have occurred in the present case.

Effect of adsorbent contact time: Effect of adsorbent contact time on removal of SMX was established for GAC and PAC with 20 mg/L solution of SMX using 5 g/L GAC as adsorbent with agitation at 20°C. It can be observed from Fig. 3 that concentration of SMX reduced from 20 mg/L to almost 14 mg/L after 165 minutes. Initially, drop in concentration is sharp but becomes constant after 120 min at a concentration of 14.4 mg/L.

According to Fig. 3, as contact time of SMX and GAC increases percentage removal also increases for initial two hours but after that it becomes constant. Maximum removal obtained is 27.27% after 120 min when 0.5 g of GAC is used as adsorbent with 20 mg/L solution of SMX. Fig. 3 also shows removal patterns of SMX using 5 g/L of PAC. In this process, after 195 min, the removal of SMX becomes

constant at a percentage removal of 77.27% and final concentration of sulfamethoxazole remain in solution is 4.5 mg/L. This shows that after 3.5 h, no further removal occurs.

SMX adsorption on GAC and PAC: Fig. 4 illustrates the comparative performance of GAC and PAC as adsorbent for SMX removal. SMX-GAC curve shows a sharp increment in adsorbed amount of SMX initially but after this, GAC gets saturated of SMX. SMX-PAC curve represents adsorbed amount of SMX near saturation after 195 min of contact time.

It can be seen from Fig. 4 that the saturation of GAC for SMX is reached after 135 min and after that no adsorption occurs. The equilibrium adsorption concentrations for GAC and PAC were achieved after 135 min and 195 min respectively.

Kinetics Study

Pseudo first-order kinetics model for SMX: The Pseudofirst order plot, for SMX adsorption on GAC and PAC are illustrated in Fig. 5 (a) and (b). From the plot, the pseudofirst order rate constant, k_i and the equilibrium sorption capacity, $q_{e,ealc}$ were computed.

The values of $q_{e,calc}$, k_1 and \mathbb{R}^2 for adsorption are given in

Table 1. It may be observed that the values of k_1 for GAC and PAC are 0.029 min⁻¹ and 0.23 min⁻¹, respectively. The equilibrium adsorbed values calculated from pseudo first order kinetics have been 1.95 mg/g and 3.68 mg/g.

Pseudo second-order kinetic model: The Pseudo-second order plot for SMX adsorption on GAC and PAC are plotted and R² values for GAC and PAC obtained were 0.5306 and 0.9136 respectively. Calculated values of parameter of Pseudo-second order kinetic model, viz. k_2 , $q_{e,cak}$, R² for SMX adsorption on GAC and PAC are given in Table 1.

It may be observed from Table 1 that $q_{e,calc}$ values calculated from pseudo first order model and pseudo second order kinetics model are nearly equal. Considering R² values, pseudo-first order kinetics for PAC is appears to be applicable. It may further to be noted that $q_{e,calc}$ value of equilibrium adsorbed phase concentration of SMX using pseudofirst order kinetic model ($q_{e,calc} = 3.68 \text{ mg/g}$) is nearer to the practical q_e value ($q_{e,exp} = 3.06 \text{ mg/g}$). Therefore, it indicates that pseudo first-order kinetic model is applicable in case of SMX-PAC interaction during its adsorption on PAC. In a similar manner, q values calculated from pseudo first order model and pseudo second order kinetics model for GAC are nearly equal and considering R² values, pseudo first order kinetics for GAC appears to be more applicable. In addition, $q_{\rm a}$ value calculated (1.95 mg/g) is nearly equal to practical $q_{\rm a}$ value of 1.90 mg/g. Therefore, pseudo first order kinetic model is applicable to SMX-GAC interaction.

Elovich kinetic model for SMX using GAC: The Elovich kinetics plot for SMX adsorption on GAC and PAC are illustrated in Figs. 6 (a) and (b).

Values of Elovich kinetics parameters, viz. α and β using GAC and PAC are given in Table 2.

Intraparticle diffusion model for SMX using GAC : Figs. 7 (a) and (b) show an intraparticle diffusion plots for adsorption of SMX on GAC and PAC. Both the curves show low linearity for the adsorption of SMX by GAC which indicates that both of surface adsorption and intra-particle diffusion are involved in the rate-limiting step. However, still there is no sufficient indication about that which of the two steps was rate-limiting. It has been reported that for intraparticle diffusion to be sole rate-limiting step, it is essential for the q. versus t^{0.5} plots to pass through the origin (El Nemr 2009), which is not the case in this study. It has been reported elsewhere that when the q versus $t^{0.5}$ plot does not pass through the origin, points towards some degree of boundary layer diffusion (Badmus & Audu 2009). This further confirms that the intraparticle diffusion is not only the rate limiting step but rate of adsorption may also be controlled by kinetics model, all of which may be operating simultaneously.

Values of parameters of intraparticle diffusion model, viz. K_{dif} and C^* obtained in the present study are given in Table 2. Fig. 7 (b) shows low linearity for the adsorption of SMX on PAC. Considering the fact that in this case, q_i versus t⁴ plot pass through the origin, it may be concluded that intraparticle diffusion was operating during the SMX-PAC interactions.

Comparative study of the kinetic models: Four kinetic models were studied for adsorption of SMX on GAC and PAC. Parameters pertaining to pseudo first order and pseudo second order kinetics are presented in Table 1 and parameters of Elovich and intraparticle diffusion models are presented in Table 2.

Removal of SMX by photolysis: Fig. 8 (a) shows percent removal of SMX with time using photolysis, and percent removal of SMX using photolysis in presence of H_2O_2 in Fig. 8 (b).

It may be observed from Fig. 8 (a) that a maximum removal of 7.6 % was obtained by UV treatment which was achieved in 1 h and 20 min. It is also observed that initial removal increases but after 50 min it becomes almost constant. Earlier, it was reported that when photolysis of amoxicillin (AMX), ampicillin (AMP) and cloxacillin (CLX) with an initial concentration of 104, 105, 103 mg/L, respectively, degradation obtained was 2.9, 3.8 and 4.9% for AMX, AMP and CLX respectively after 5 h of photolysis. Further, from Fig. 8 (b) it is obvious that maximum percent removal of SMX in case of $UV + H_2O_2$ treatment obtained was 7.6%. The removal of SMX using $UV + H_2O_2$ shows a similar trend as being noticed in case of UV treatment. A comparative assessment of removal of SMX by adsorption with different adsorbents used and photolysis processes are shown in Table 3.

It is obvious that percent removal of SMX is maximum in case of adsorption using PAC followed by GAC and activated alumina. The removal of SMX using photolysis process is only 7.6%.

CONCLUSIONS AND RECOMMENDATION

PAC has been found to be effective in removal even at low dose of 0.2 g/L. Removal increases from 1 to 34% as the concentration of GAC varies from 0.5 g/L to 6 g/L. In case of PAC, when dose increases from 0.2 g/L to 5 g/L, % removal increases from 61.7% to 73.4%. Similarly, for activated alumina it increases from 1.4% to 15.5% for the same adsorbent dose range.

Maximum removal of SMX was found to be 77.27% with PAC for a contact time of 195 min, but only 27.27% of SMX was removed using GAC after 135 min. Furthermore, adsorption of SMX on GAC and PAC follows pseudo first order kinetics. Value of k_1 for GAC and PAC is 0.029 and 0.023 min⁻¹ respectively. Study of Elovich model indicates that rate of adsorption was 0.0322 mg/g min for GAC and 0.337 mg/g min for PAC. Study of intraparticle diffusion concluded that for SMX adsorption on PAC, only intraparticle diffusion was operating, whereas for GAC both intraparticle diffusion and surface adsorption were operating concurrently.

Removal of SMX using UV treatment and UV treatment in presence of H_2O_2 was found be 7.65% after 80 min and 7.67% after 110 min, respectively. It indicates that H_2O_2 has little effect. Comparison of removal of SMX by adsorption and photolysis indicates that higher removal was obtained in adsorption.

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Nomenclature

- $C_0 =$ Initial SMX concentration, mg/L
- $C_t = SMX$ concentration at time t, mg/L
- C^* = Intercept of q_t vs ln t plot
- h = Initial sorption rate, mg/g.min
- k_1 = Pseudo first-order rate constant of adsorption, (min⁻¹)
- k_2 = Pseudo Second-order rate constant of adsorption, (g/mg.min)
- K_{dif} = Intraparticle diffusion rate constant, (mg/g.min^{0.5})
- q_e = Adsorption capacity at equilibrium, mg/g
- $q_{e, exp}$ = Adsorption capacity at equilibrium, determined by experiments, mg/g
- $q_{e^{*}calc}$ = Adsorption capacity at equilibrium, calculated for kinetics, mg/g
- q_{t} = Adsorption capacity at time t, mg/g
- V = Volume of SMX solution, L
- W = Mass of the adsorbent, g
- α = Initial adsorption rate (mg/g.min)
- β = Desorption constant (g/mg)

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