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Original Research Paper

Removal of Amoxicillin in Wastewater Using Adsorption by Powdered and Granular Activated Carbon and Oxidation with Hydrogen Peroxide

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ABSTRACT

Antibiotics disposed into wastewater reach wastewater treatment plants and surface waters and act as micro-pollutants. As antibiotics pose various problems related to treatment and reuse, it is imperative to remove them from wastewater. In the present paper, adsorption studies have been carried out for removal of amoxicillin using powdered activated carbon (PAC) in a batch mode and granular activated carbon (GAC) in a continuous packed bed column. Removal of antibiotics has also been made using oxidation by H_2O_2. The techniques used for detection of antibiotics require elaborate analytical instrumentation. Being inexpensive and simple technique, monitoring of concentration during removal has been made using COD determination in the present work. It has been found that concentration of amoxicillin has a straight line relationship with COD. Batch adsorption using PAC shows that a maximum of 70% removal can be obtained for a 200 mg/L solution of amoxicillin using a dose of 600 mg/L of PAC. Maximum removal of 60% was obtained for a concentration of 200 mg/L of amoxicillin with a constant dose of 500 mg/L of PAC. In continuous packed bed adsorption using GAC, 90% COD removal was obtained at saturation. A maximum removal of 80% is obtained at a concentration of 200 mg/L of amoxicillin and 24.2% at 1000 mg/L through GAC column. Furthermore, oxidation removes a maximum of 90% COD using a dose 441 mM/L of H_2O_2 (30% w/v). Removal of COD increases from 10% to 60% on increasing dose of H_2O_2 from 44 mM/L to 220 mM/L. Considering removal efficiency, both oxidation and adsorption techniques have their advantages and limitations. Nevertheless, adsorption using activated carbon and oxidation using H_2O_2 provide simple and satisfactory methods to remove antibiotics from wastewater.

INTRODUCTION

Antibiotics are of great importance for therapeutic purposes in human and veterinary medicine (Sorenson et al. 1998). The presence of antibiotics detected in aquatic environment becomes important as it leads to rise of refractory and even toxic pollutants. Presence of antibiotics in wastewater arises from different sources like discharge from domestic wastewater treatment plants (WWTP) (Giger et al. 2003), pharmaceutical companies (Arslan-Alaton et al. 2004), runoff from animal feeding operation, and from compost made of animal manure containing antibiotics (Ötkar et al. 2005), and by application of antibiotics on livestock production (Arikan et al. 2008). Human beings are the primary source of pharmaceutical antibiotics in the environment (Matsui et al. 2008). Excreted non-metabolized antibiotics enter wastewater streams through hospital effluent and domestic sewage systems (Sorenson et al. 1998). If antibiotics are not degraded or eliminated during sewage treatment, they reach surface water, groundwater and drinking water (Kümmerer 2003).

In WWTP, the presences of antibiotics make an increase in organic load and may disturb the process of biological removal of organic matter. COD removal efficiency also decreases due to bacterial toxicity of antibiotics and their recalcitrance (Sponza et al. 2007, González et al. 2007, Reif et al. 2008). Moreover, the characteristics like toxicity, biodegradability and inhibition has a correlation with their removal in biological treatment (Dantas et al. 2007).

The appearance of bacterial strains that are resistant to antibiotics is a result of abuse of antibiotics. This phenomenon is known as antibiotic resistance (Li et al. 2008). The presence of antibiotics in wastewater may cause bacterial resistance in human beings and livestock when water is reused. The selection and development of antibiotic-resistant bacteria is one of the greatest concerns with regard to the use of antimicrobials (Kümmerer 2003). Enteric microorganisms carrying resistance genes are found in WWTP (Andersen 1993). Development of antibiotic resistance in pathogens causes problems in clinical treatment and serious problems for human health (Bautitz et al. 2007). In industry, presence of antibiotics in water may inhibit bacterial culture during fermentation process. It is apparent that impurities in the waste fermentation broth, particularly biopolymers or macromolecules can seriously affect the crystallization of antibiotics. The residual antibiotics in the fermentation waste not only cause the loss of product but also suppress microbial growth in downstream biological wastewater treatment (Li et al. 2004b). Hence, it is imperative to remove antibiotics from wastewater.

There are several methods available for removal of antibiotics from wastewater. It includes coagulation (Choi et al. 2008), adsorption (Adraiano et al. (2005), oxidation using chlorination (Debordea et al. 2008), ozonation (Balciglu et al. 2004), H_2O_2, UV light (Arslan-Alaton & Dogruel 2004, Arslan-Alaton & Gurses 2004), biological anaerobic process through UASB (Sponza et al. 2007), membrane separation, ultrafiltration, reverse osmosis (Li et al. 2004a, Zhang et al. 2006), and electrochemical removal (Jara et al. 2007). Extent of removal and rates vary greatly depending on the treatment utilized, its duration and the concentration and physical properties of the pharmaceuticals in the influent.

In the present paper, adsorption studies have been carried out using powdered activated carbon (PAC) in a batch mode and granular activated carbon (GAC) in a continuous packed bed column. Further, removal of antibiotics has also been made using oxidation by H_2O_2 and breakthrough curve has been drawn for amoxicillin adsorption in a packed bed of GAC. As far as detection of antibiotics in water is concerned, various techniques have been used to detect antibiotics in water like HPLC (Stackelberg et al. 2007), capillary electrophoresis (Santos et al. 2007), mass spectrometry, liquid chromatography-tandem mass spectrometry (Giger et al. 2003, Conley et al. 2008), and spectrophotometric method (Chatzitakis et al. 2008, Adriano et al. 2005, Gutiérez et al. 1998, Zhang et al. 2006), etc. Being inexpensive and simple technique, monitoring of concentration during removal has been made using COD determination in the present work. The purpose of this work is to remove amoxicillin as well as to evaluate percentage removal of amoxicillin using GAC and PAC in continuous and batch modes respectively.

MATERIALS AND METHODS

Amoxicillin: Amoxicillin trihydrate IP, (Make: Ranbaxy Laboratories) of trade name of MOX equivalent to amoxicillin 500 mg has been used in the study. Amoxicillin powder was dissolved in distilled water for overnight as it is sparingly soluble in water.

Characteristics of water sample containing amoxicillin: In the present work, the concentration of amoxicillin in water has been correlated with wastewater parameters such as COD, BOD, electrical conductivity, pH, etc. The amoxicillin solution was kept below 5°C in refrigerator in order to prevent degradation.

Adsorption using powdered activated carbon (PAC): PAC used was manufactured by MERCK (India) Ltd. Different doses of PAC (100 to 700 mg/L) were added in antibiotic sample of 200 mg/L concentration. COD of each sample was measured. In second set of experiment, solutions with different concentrations of amoxicillin ranging from 200 to 1000 mg/L were prepared. A fixed quantity of PAC, i.e. 500 mg/L, was added to each of the above sample and were stirred using magnetic stirrer for 30 minutes. The contact time of 30 minute was found adequate for stable removal to PAC-amoxicillin system. These solutions were then filtered using vacuum filtration. COD of filtrate was calculated using dichromate open reflux method (APHA 1989).

Adsorption using granular activated carbon (GAC): GAC (manufactured by CDH Pvt. Ltd., New Delhi) packed column was used for the adsorption experiments. The column was of 10-mm internal diameter and 150-mm length**.** Inlet feed rate of 180 mL/min was given from a pump using a control valve. A solution of 200 mg/L amoxicillin was allowed to pass through the bed. Outlet samples from bed were collected at an interval of 1 min for 12 min. COD of all the samples was measured using dichromate reflux method. The COD values obtained in above step were used to develop break-through curve. In a second set of experiment different concentrations of amoxicillin, ranging from 200 to 1000 mg/L, were filtered through the GAC column and the outlet samples were collected to assess removal of amoxicillin. COD of each outlet sample was measured and a curve was plotted between % COD removal and concentration of amoxicillin.

Removal using hydrogen peroxide: Water containing amoxicillin concentrations of 200 to 1000 mg/L were again used in this study also. A fixed quantity of H_2O_2 (441.17 mM/L), 30% w/v was added to each of the above samples and a contact time of 16 h was provided. COD values of these solutions were measured. In second set of experiment different doses of H_2O_2 in the range of 44.11-220.55 mM/L (5-25 mL/L of 30%w/v) were added in antibiotic sample of 200 mg/L concentration and COD of each was measured.

RESULTS AND DISCUSSION

Characteristics of water sample containing 200 mg/L amoxicillin are given in Table 1.

Calibration of amoxicillin concentration in terms of COD: The Value of COD of a synthetic sample prepared in laboratory containing 200 mg/L of amoxicillin in distilled water was 3300 mg/L and that of 1000 mg/L amoxicillin was 29700 mg/L. It can be observed from Fig. 1 that concentration of amoxicillin can be represented by a straight line relationship between COD and concentration for the concentration range of 200 to 1000 mg/L. The straight line curve can be represented by equation: $y = 33x – 3300$ and $R^2 = 1$.

Table 1. Characteristics of aqueous solution of amoxicillin concentration (200 mg/L).

S. No.	Parameter	Value
1	BOD_3 at 27ºC	3.5 mg/L
2	pH	7.9
3	Electrical Conductivity	46 µS/cm

Adsorptive removal of amoxicillin using PAC: Separate treatability studies were conducted on

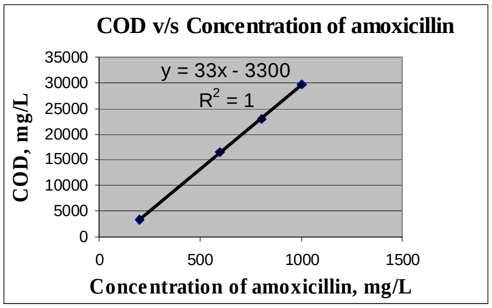

Fig. 1: Calibration curve for COD v/s concentration.

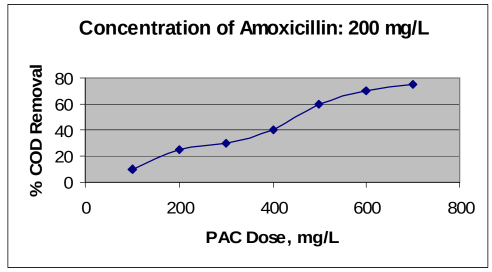

Fig. 2: % COD removal v/s PAC dose for 200 mg/L amoxicillin concentration.

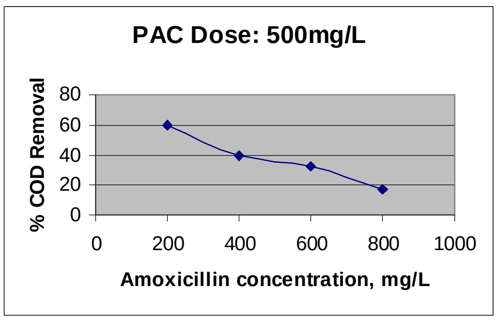

Fig. 3: % COD removal v/s amoxicillin concentration for a dose of 500 mg/L PAC.

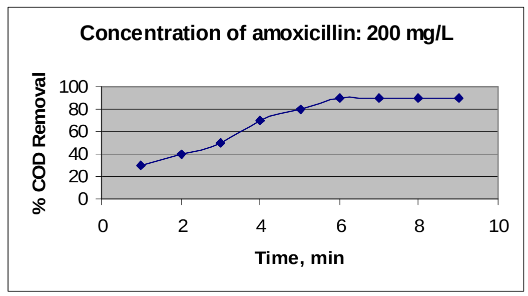

Fig. 4: Breakthrough curve for 200 mg/L amoxicillin using GAC filtration.

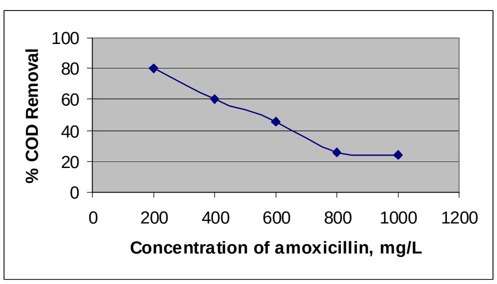

Fig. 5: % COD removal v/s concentration of amoxicillin for GAC filtration.

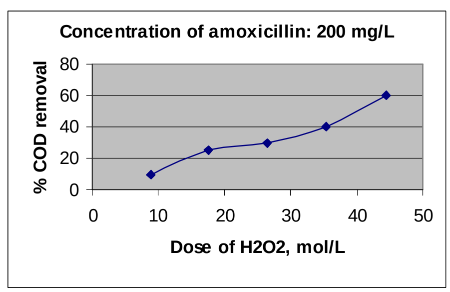

Fig. 6: % COD removal v/s dose of H_2O_2.

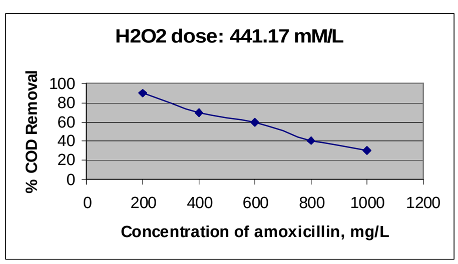

Fig. 7: %COD removal for different concentrations of amoxicillin at fixed dose of H_2O_2 (441.17 mM/L).

synthetic aqueous solution of 200 mg/L of amoxicillin. Amoxicillin was removed through adsorption during selected doses of PAC in a batch study. Fig. 2 provides evidence that with increased doses of PAC, removal of antibiotic also increases due to adsorption phenomenon. It may be observed from Fig. 2 that at a dose of 100 mg/L, COD removal was 10%, which increased up to 75% by using a dose of 700 mg/L PAC.

In a previous study of antibiotic treatment, a mixture of carbadox, sulfachlorpyridazine, sulfadimethoxine, sulfamerazine, sulfamethazine, sulfathiazole and trimethoprim with concentration of 20 mg/L of each antibiotic in double 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).

Batch adsorption from different concentrations of amoxicillin using fixed dose of PAC: The batch adsorption experiment was performed with different concentrations of amoxicillin and a fixed concentration of PAC at the rate of 500 mg/L. It was observed that % COD removal decreases with increase in amoxicillin concentration. It is evident from Fig. 3 that at a concentration of 200 mg/L, COD removal was 60% and on increasing concentration up to 800 mg/L, removal decreased to 17.14%.

In a previous study for antibiotic removal (tetracycline) from waste liquor coming from tetracycline (TC) production, the addition of PAC to the wastewater reduced fouling of RO membrane. In this study, addition of 8 mg/L PAC marginally improved the integrated UF-RO process. In this process, removal of COD after UF membrane was found to be 55% only (Zhang et al. 2006).

Adsorptive removal of amoxicillin through GAC column: A breakthrough curve for % COD removal for continuous amoxicillin adsorption in a packed column of GAC is shown in Fig. 4. It may be observed that COD removal increased with time. The curve shows, breakthrough is occurring at 3 min and was saturated after 6 min for a solution of 200 mg/L of amoxicillin. Maximum COD removal obtained was 90% at 6^{th} minute.

Adsorptive removal of amoxicillin for different concentrations in a continuous mode using GAC filtration: Different concentrations of amoxicillin, ranging from 200 to 1000 mg/L, were passed through the GAC column. Maximum removal was obtained with a concentration of 200 mg/L of amoxicillin, and removal decreased with higher concentrations. At amoxicillin concentration of 200 mg/L and 1000 mg/L, COD removal was 80% and 24.2% respectively (Fig. 5).

In a previous study for removal of antibiotics (tetracycline) from raw water (synthetic and river) using GAC filtration, more than 68% removal of incoming tetracycline (initial concentration 10 μg/L) has been reported. GAC column used was of 50 mm in i.d. and of 2000 mm length (Choi et al. 2008).

Removal by oxidation using hydrogen peroxide: COD removal obtained in case of oxidation of amoxicillin at a fixed concentration of 200 mg/L by hydrogen peroxide was up to 60%. As concentration of hydrogen peroxide increased, COD removal increased. Different concentrations of H_2O_2 in the range of 44.11 mM/L (5 mL/L), 88.22 mM/L (10 mL/L), 132.33 mM/L (15 mL/L), 176.44 mM/L (20 mL/L), and 220.55 mM/L (25 mL/L) were used, and COD removal increased from 10% to 60%, as depicted in Fig. 6.

A previous study of photo-fenton reactions at different concentrations of H_2O_2 were carried out to investigate the influence of hydrogen peroxide in the degradation of a 200 mg/L SMX (sulphamethoxazole) solution. With respect to COD, the removal achieved at the end of the reactions increased from 12 to 92.5% depending on the hydrogen peroxide doses (from 50 to 1000 mg/L) (González et al. 2007).

When a constant dose of H_2O_2 was applied at the rate of 441.17 mM/L (50 mL/L) on different concentrations of amoxicillin, it was observed that with an increasing concentration of amoxicillin from 200 mg/L to 1000 mg/L, the COD removal efficiency decreased from 90% to 30% as shown in Fig. 7.

A part of the present work has also been presented in our previous work (Pachauri et al. 2008). In a previous study for removal of antibiotic (penicillin group) from penicillin formulation water (initial concentration: 400 mg/L) using fenton process conducted with 20 mM H_2O_2 + 1 mM Fe^{+2} at pH 3, it was observed that COD removal was 56% (Arslan-Alaton et al. 2004).

CONCLUSION

With increased doses of PAC, removal of antibiotics also increases through adsorption phenomenon. Results show that a maximum of 75 % COD removal can be obtained by using 700 mg/L PAC dose. COD removal decreases as concentration of amoxicillin increased from 200 mg/L to 800 mg/L with a fixed dose of PAC at the rate of 500 mg/L. Results indicate that a maximum of 60% removal is obtained in the solution of amoxicillin with concentration of 200 mg/L whereas 17.14% removal is obtained with concentration 800 mg/L.

Results of continuous adsorption using GAC bed of 15 cm height and 1 cm in diameter show, breakthrough is occurring at 3 min and is saturated after 6 min for a solution of 200 mg/L of amoxicillin. At saturation a maximum of 90% COD removal can be obtained. When varying concentrations of amoxicillin solution were passed through GAC column, a maximum of 80% removal was obtained with 200 mg/L concentration. For 1000 mg/L, concentration of amoxicillin decreased to removal 24.2%. Results of oxidation using constant dose of hydrogen peroxide show that for varying aqueous concentrations of amoxicillin from 200 mg/L to 1000 mg/L, a maximum of 90% COD removal can be obtained by using 441.17 mM/L (50 mL/L, 30% w/v) of hydrogen peroxide dose at amoxicillin concentration of 200 mg/L.

Percent removal of COD can be increased with a higher dose of hydrogen peroxide. For an amoxicillin solution with concentration of 200 mg/L, the dose of hydrogen peroxide is increased from 44.11 mM/L to 220.55 mM/L, removal increased from 10% to 60 %. BOD_3 at 27ºC above a concentration of 200 mg/L was found extremely low. It appears that all the bacteria which were fed through seeded solution were killed at a dose of 200 mg/L of amoxicillin and above. It indicates that presence of antibiotics in wastewater affects performance of biological treatment process.

Considering removal efficiency, each removal technique has its own advantages and limitations. Nevertheless, adsorption using activated carbon and oxidation using H_2O_2 provide simple and satisfactory methods to partially remove antibiotics from concentrated wastewater that may be emanating from antibiotics manufacturing plant of bulk drugs as well as formulation industry. Furthermore, such techniques will improve the treatability of wastewater containing antibiotics by biological treatment processes which is widely accepted for this purpose.

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