

STUDY ON REMOVAL OF CADMIUM FROM WATER ENVIRONMENT BY ADSORPTION ON GAC , BAC AND BIOFILTER

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ABSTRACT

The Contamination of water by toxic heavy metals is a world-wide environmental problem. Discharges containing Cadmium, in particular, are strictly controlled due to the highly toxic nature of this element and its tendency to accumulate in the tissues of living organisms. Low concentration (below 5 mg/L) of Cadmium is difficult to treat economically using chemical precipitation methodologies. Ion exchange and reverse osmosis while can guarantee the metal concentration limits required by regulatory standards, have high operation and maintenance costs. The goal of this research was to determination of efficacy of using GAC , Biofilm and BAC columns to treat low concentration Cadmium bearing water streams and was to determination of the effects of temperature and pH on the adsorption isotherms. Studies were conducted to delineate the effect of pH, temperature, initial Cd and adsorbent concentration on adsorption of Cd²⁺ by GAC , BAC and Biofilm. Breakthrough curves for removal of 0.5 mg/L Cd²⁺ by GAC, Biofilm and BAC columns at two contact times were plotted. Batch adsorption and column data are compared, pH is shown to be the decisive parameter in Cd removal for GAC but not for BAC or biofilter. Lagergren plots confirms applicability of first-order rate expression for adsorption of Cd by GAC, BAC and Biofilm. The adsorption coefficient (K_{ad}) for BAC were 2-3 times greater than those with plain GAC. Bed Volumes of water containing 0.5 mg/L Cd²⁺ treated at breakthrough for GAC , Biofilm and BAC columns were 45, 85 and 180 BV respectively. BAC is more efficient than GAC in the removing of Cd from water environment.

Keywords: Cadmium ,adsorption, GAC, BAC , Biofilter

INTRODUCTION

Cadmium is introduced in to bodies of water from smelting, metal plating, Cadmium-Nickel batteries, phosphate fertilizer, mining, pigments, stabilizers, alloy industries and sewage sludge. The harmful effects of Cadmium include a number of acute and chronic disorders, such as "itai-itai" disease, renal damage, emphysema, hypertension, and testicular atrophy (1). The drinking water guideline value recommended by World Health Organization (WHO), is 0.005 mg Cd/L. Low concentration (less than 5 mg/L) of Cadmium is difficult to treat economically using chemical precipitation methodologies. Ion exchange and reverse Osmosis while can guarantee the metal concentration limits required by regulatory standards, have high operation and maintenance costs (2).

Although the ability of activated carbons to remove Cadmium in high concentrations from wastewater has been established by numerous researchers (3-9), very few articles are available on the use of activated carbon to remove Cadmium in low concentration from contaminated surface or subsurface waters (10). Activated carbon has been an effective adsorbent for the removal of many organics substances in water, its use for metal removal from water is rather rare. Several reports of Cadmium removal from aqueous solutions by biosorption with micro-organism generated biomass have been published (11-14).

The underlying objective behind using GAC as a support for biofilm has been , therefore, to provide the foundation for remediation processes that can provide metal biosorption concurrently with removal of non-metal contaminants such as organic compounds. J.A. Scott and A. M. Karanjkar studied Cadmium (in high concentration) adsorption on to Biofilm covered Granular Activated Carbon (15-17). There is not any study on removal of low concentration of Cadmium by Biofilm/GAC. The objective of this study was to investigate the adsorption characteristics of Cadmium (less than 5 mg/L) on to plain (non-biofilm) GAC , Biofilm and Biofilm/GAC , and also was to determine the effects of temperature and pH on the Cadmiumuptake by plain GAC and Biofilm/GAC.

The goal of this research was to demonstrate the efficacy of using biofilm covered granular activated carbon columns to treat water contaminated by low concentration (0.5 mg/L) of Cadmium.

MATERIALS AND METHODS

The granular activated carbon used in this study was Darco 12-20 mesh supplied by Aldrich. Carbon was washed with double distilled water and dried in an oven at 120 C for 24 hours. All the Cadmium solutions were prepared using Cd(NO₃)₂·4H₂O and the solution pH was adjusted with HNO₃ and NaOH 0.01N. Experimental data for the adsorption isotherms were obtained as follows. A predetermined mass of plain GAC and Biofilm/GAC were contacted with a fixed volume of a Cadmium solution of known initial concentration. The Cadmium solution remained in contact with adsorbent until equilibrium was reached. Batch sorption studies were performed at an ionic strength of 0.01 (added as NaCl) at different temperature

(5C , 15C , 25C) and at different pH (5 , 7 and 8.5). The contact time were selected on the basis of preliminary experiments that demonstrated that the equilibrium were established in 4 hours for GAC and Biofilm and 1.5 hours for Biofilm/GAC

For isotherm studies , a series of 250 mL Erlenmeyer flask were employed. Each Erlenmeyer flask was filled with 100 mL adjusted pH of Cadmium solution of varying concentration (0.25- 0.5 – 1.0 – 2.5 and 5.0 mg/L). For each concentration 4 Erlenmeyer flask were employed. A known amount of adsorbent (plain GAC and Biofilm/GAC separately) (0.05- 0.1 – 0.15 and 0.2 gr) was added in to each Erlenmeyer and agitated for the desired time periods. After this periods the solution was filtered using Glass Fiber (GF/A) filter and analysed for the concentration of the metal ions remaining in the solution by Chem Tech Alpha 4 Atomic Absorption Spectrophotometer. Conditions for the Spectrophotometer was an acetylene – air flame under oxidizing conditions at 228.8 nm wavelength.

Three columns including GAC, Biofilm and Biofilm/GAC were used in this study. The length of the columns was 52 Cm and inner diameter of column was 14 Cm. One column was packed with 12-20 mesh sand and this column is named as biofilm column. Another column was packed with 12-20 mesh GAC. Seeded nutrient medium (2000 mg/L Sodium acetate as the sole carbon source , 500 mg/L NH₄NO₃, 500 mg/L KH₂PO₄, 200 mg/L CaCl₂ and 200 mg/L MgSO₄) was circulated (upflow , 25 C , pH=7) for two days through GAC and sand columns.

Biofilm samples for batch biosorption test were detached and collected from the sand media. Cadmium binding isotherms were produced by measuring the amount of Cadmium bound by biomass from solutions containing a range of Cadmium concentrations. Eighty three (83) mg samples of biomass (dry weight) were mixed with 100 mL aliquots of aqueous Cadmium solutions with Cd(II) concentrations of 0.2 – 0.5 – 1.0 – 2.0 and 5.0 mg/L . The mixtures were placed for six hours on a shaker to ensure that equilibrium was attained. The mixtures were then filtered through 0.45-micrometer membrane filter to remove the biomass. The final concentration of unbound Cadmium was determined by AAS and the metal loading on the biomass calculated. After two days circulating of culture medium through sand and GAC columns, the culture medium was replaced with a solution containing 0.5 mg/L Cd(II) for uptake studies by Biofilm/GAC , Biofilm (sand column) and plain GAC columns. Columns were operated in the upflow mode. Effluent samples were collected from the columns and acidified and the concentration of Cd(II) was determined by AAS.

RESULTS AND DISCUSSION

Calculated values of correlation coefficients (R²) at different pH value are given in table 1. According to Langmuir model, reasonable straight –line correlations (R²) were achieved for Cd(II) adsorption by GAC and Biofilm , because R² for Langmuir isotherm were greater than for the Freundlich isotherm. For adsorption of Cd(II) by GAC/Biofilm, the correlation coefficients showed that in general the Freundlich model fitted the results better than the Langmuir model.

Table 1- Freundlich and Langmuir isotherm correlation coefficients (R²) for adsorption of Cd(II) on GAC , Biofilm and GAC/Biofilm at different pH

pH	Langmuir Model			Freundlich Model		
	GAC	Biofilm	GAC/Biofilm	GAC	Biofilm	GAC/Biofilm
5.5	0.9245	0.8641	0.6653	0.8549	0.9314	0.8329
7.0	0.8922	0.8565	0.6878	0.8747	0.8295	0.8152
8.0	0.9153	0.8823	0.6547	0.8431	0.8162	0.8571

As illustrated in figure 1 , where adsorption isotherms of plain GAC, Biofilm and GAC/Biofilm is shown, biofilm immobilized over GAC clearly enhance the uptake of Cd(II). With regards plain GAC, Cd(II) uptake is generally low, but with biofilm immobilized over GAC particles, the Cd(II) uptake level can be increased 2 or 3 fold.

Figure 2 illustrates both the effectiveness of an immobilized biofilm in taking up Cadmium (0.5 mg/L), along with the influence of solution temperature on equilibrium Cd(II) loading levels. That is, the presence of the biofilm, estimated at around 80 mg (dry weight) per gram of GAC, results in a 2 to 3 fold increase in Cd(II) uptake when compared to plain (non-biofilm) GAC. Furthermore, over a temperature rise of 5-24C, the slight increase in metal uptake indicates physical adsorption, rather than metabolic activity as the prime factor in metal accumulation by the biofilm-GAC system.

The uptake of the Cadmium by plain GAC increased with an increase in temperature thereby indicating the process to be endothermic. Figure 3 shows the influence of solution pH on equilibrium uptake level. The experiments were carried out for pH values below the pH where chemical precipitation of the Cadmium hydroxide occurs. In these condition, metal removal can be related only to the adsorption process. The adsorption of Cd(II) on the plain GAC increases with the increase in pH.

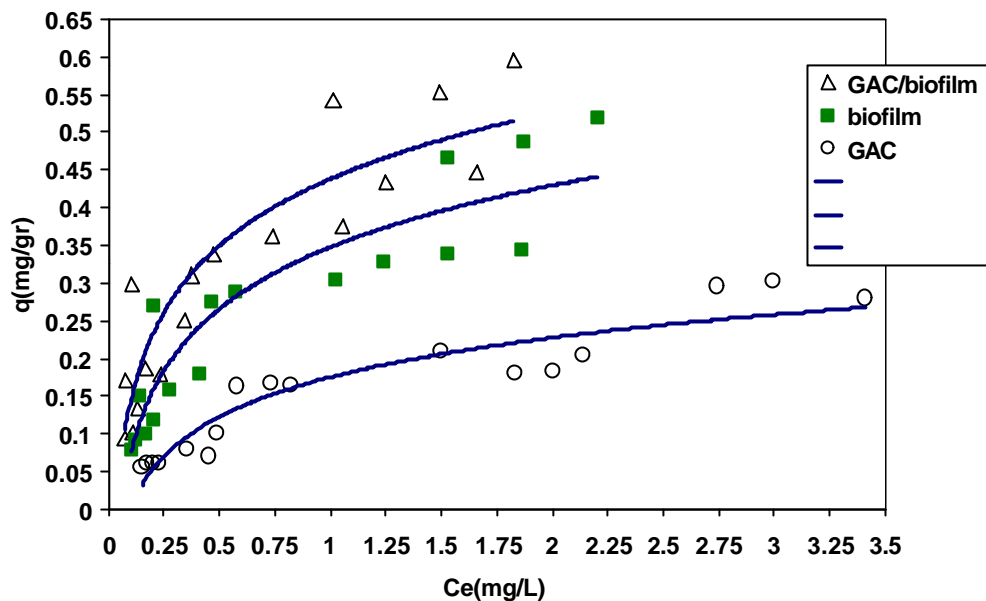


Fig.1- Isotherm plots for Cd(II) sorption by GAC , Biofilm and GAC/Biofilm

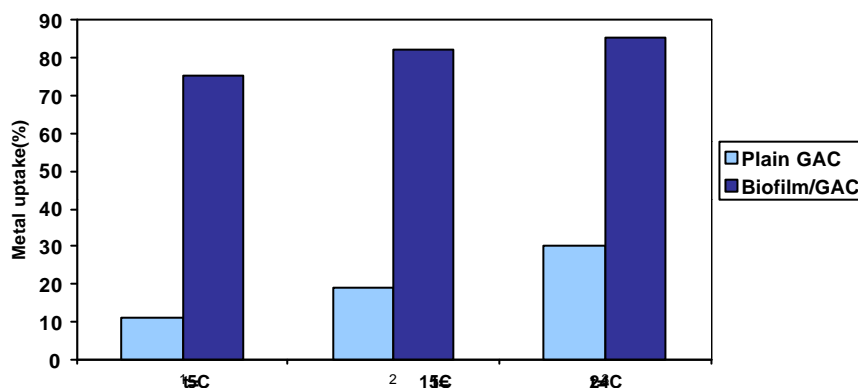


Fig.2- Effect of temperature on Cadmium uptake by Biofilm /GAC and plain GAC

The increase in Cd(II) removal as pH increases can be explained on the basis of a decrease in competition between proton and Cd(II) for the surface sites and by the decrease in positive surface charge, which results in a lower coulombic repulsion of the sorbing Cd(II). For the Biofilm/GAC system alkaline condition (pH=8) was found to have little effect on Cd(II) uptake (e.g. 0.23 mg Cd /gr GAC at pH 6.9 to 0.26 mg Cd / gr GAC at pH 8), whereas Cd(II) uptake in acidic condition (pH=5) was the same as natural condition (pH=6.9).

The Lagergren first-order rate equation is written as

$$\text{Log}(q_e - q_t) = \text{Log } q_e - K_{ad} / 2.303 t . \tag{1}$$

Where q_e and q_t are the amount of metal adsorbed (mg/gr) at equilibrium and time “t” respectively. For adsorption of Cd(II) by Biofilm/GAC, a plot of $\text{Log}(q_e - q_t)$ Vs “t” gives a straight line as can be seen in fig. 4, confirming the applicability of first-order rate expression. The adsorption coefficient (K_{ad}) for GAC, Biofilm and Biofilm/GAC were calculated from the slope of the plots separately and the values are presented in Table 2 .

Table 2: Calculated adsorption rate constants using GAC and Biofilm/GAC

Cd Concentration (mg/L)	Kad Biofilm/GAC (L/Min.)	Kad GAC (L/Min.)
0.25	2.1991	1.048
0.5	2.2280	1.108
1.2	1.9957	0.6819

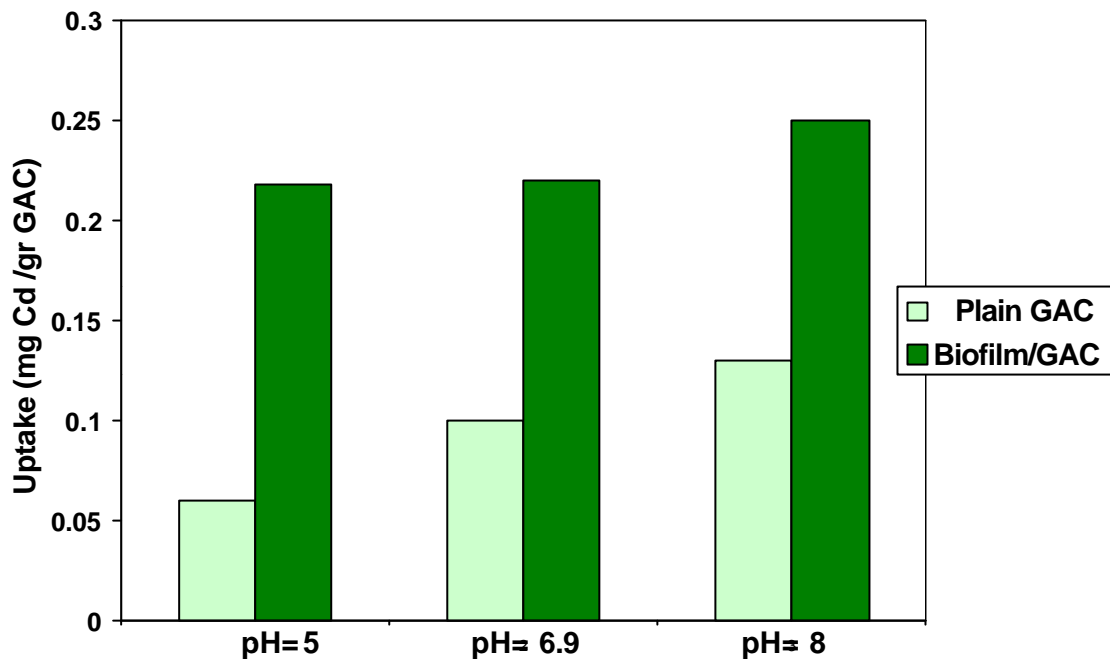


Fig.3 – Effect of solution pH on Cd uptake by Biofilm/GAC and plain GAC

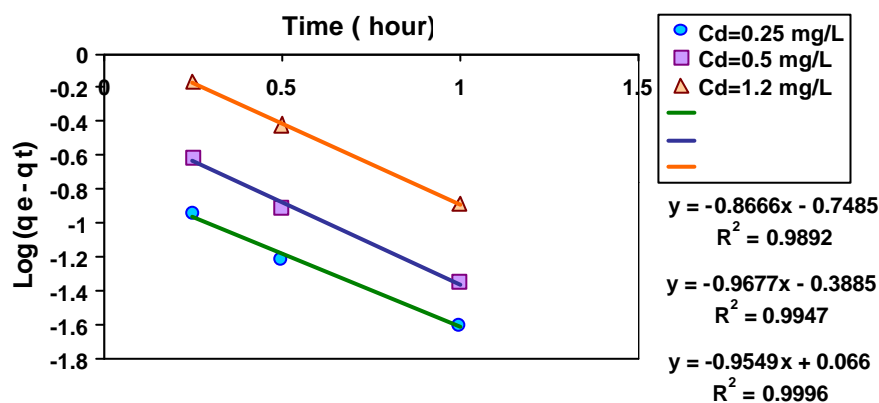


Fig.4- Lagergren plots for the adsorption of Cd(II) by Biofilm/GAC at pH=7, adsorbent dose 100 mg/L

The adsorption rate constants can be used for comparison between Biofilm/GAC, and GAC to adsorb Cadmium from aqueous solution. The data indicates that with Biofilm/GAC, higher rate of adsorption can be achieved, because Kad for Biofilm/GAC were 2-3 times greater than those with plain GAC. Normalized effluent Cadmium concentration (C_e / C_i) versus number of bed volumes (BV) treated for 0.5 mgCd/L by Biofilm/GAC column at pH=7, are presented in figure 5. This curve will be referred to as breakthrough curve. Breakthrough was defined at $C_e=0.01 C_i$. Breakthrough occurred at about 45, 85 and 180 bed volume for plain GAC, Biofilm and Biofilm/GAC columns respectively. The removal of Cadmium by a GAC column was increased by 400% when biofilm immobilized over GAC particles.

CONCLUSION

Granular Activated carbon (GAC) is well known as an excellent adsorber of organic pollutants from contaminated water streams. GAC by itself is not in general, however, an effective adsorbent for heavy metals. Whereas, it has been shown that with a biofilm attached to the GAC surface, the uptake rate and quantity of metal ions extracted from solutions can be significantly increased. As a consequence, by immobilizing bacterial biofilms, metal removal can be combined with the

adsorption of other contaminants such as organic residues. Biosorption has the potential to provide economic metal decontamination of low concentration waste streams, but leaves the problem of metal-laden biosorbent disposal. There are, however, significant industrial and environmental process opportunities from metal impregnated over GAC surfaces, as they can usefully enhance surfact activity. It is shown that it is possible to distribute metals over GAC by biosorption, through using attached biofilms. If the intention is to remove metals from contaminated streams, then ideally these biofilms should have a structure open enough not to negate the adsorption characteristics of the carbon surface for other contaminants, such as organic residues.

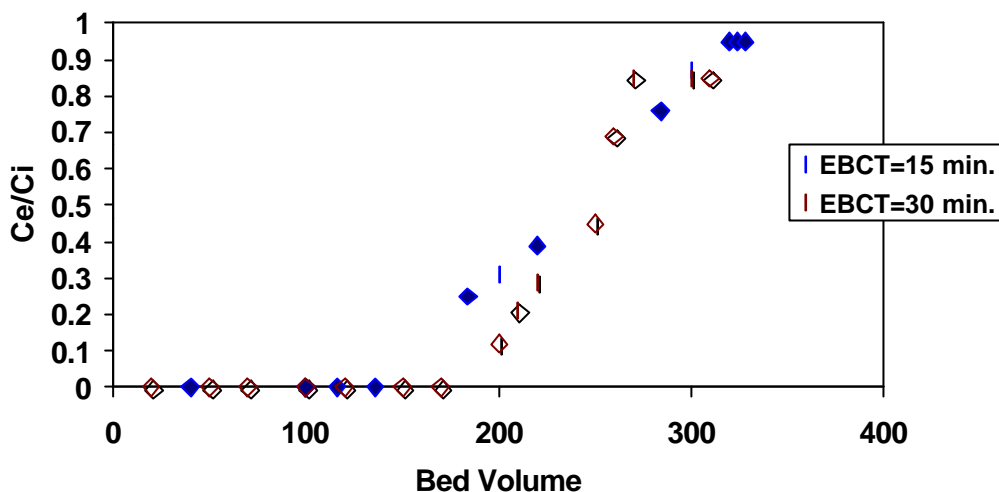


Fig.5- Breakthrough curves for 0.5 mg/L Cd(II) at different contact time and pH=7

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