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Study of Cadmium Removal from Environmental Water by Biofilm Covered Granular Activated Carbon

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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 which 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 Cd^{2+} by GAC, BAC and Biofilm. Breakthrough curves for removal of 0.5 mg/L Cd^{2+} 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 confirm applicability of first-order rate expression for adsorption of Cd by GAC, BAC and Biofilm. The adsorption coefficient (K_{ad}) for BAC was 2-3 times greater than those with plain GAC. Bed Volumes of water containing 0.5 mg/L Cd^{2+} 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, Isotherm, GAC, BAC, Iran*

Introduction

Cadmium is introduced into the 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).

In general, the existence of heavy metals in the wastewater is very unfavorable to the growth of microorganisms. Industrial wastewater, such as that of the plating industry, often contains these ions. Even though heavy metal ions can be removed by physical-chemical treatment, e.g. coagulation and filtration, a part of them may remain in the water treated. When organic substances of lower concentration coexist with such ions, conventional biological removal processes may not be effective. Therefore, as an alternative, the Biological Activated Carbon (BAC) treatment may be adopted to clean up the wastewater (2).

GAC is in general not noted as a particularly efficient adsorber for metals, but with a suitable biofilm immobilized over GAC particles, the metal uptake level can be increased several fold. A combined biofilm/GAC system has been devised, therefore, to exploit the abilities of the biofilm to tackle metals and other contaminants (3).

Isothermal studies, used to assess the perform

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ance of a potential bioadsorbent, form an integral part of any bioadsorption study. Isotherms, determined previously for waste activated sludge bioadsorption by Bux et al (4), can accurately indicate the mechanism involved in microbe-metal interaction i.e. electrostatic, physical or chemical. Desirable isotherms should be steep from the point of origin, indicating a high affinity for the sorbate at low concentration. Likewise, a high saturation plateau ensures low residual concentrations of a particular metal species in the contaminated effluent once equilibrium is obtained (5). The mechanism of accumulation also dictates the ease of removal of adsorbate from loaded biomass i.e. the greater the degree of binding, the more stringent the method of recovery required (6). Bux et al (4) showed that activated sludge bioadsorption of Zn predominantly resembles a type II isotherm (according to classification by Brunaer (7), which indicates monolayer to multiplayer adsorption with increasing metal loading (8).

Much of the researches carried out so far on BAC has concerned the use of bacterial consortia such as activated sludge. Biological Activated Carbon (BAC) treatment, in which both adsorption and biological decomposition take place, has an advantage over conventional activated carbon treatment for the removal of organic substances. As the use of BAC treatment makes the whole facilities compact and the life of carbon longer, it has been attracting great attention as one of the most efficient advanced water treatment technologies, and is being applied to various treatment processes to remove pollutants. Weber reported an apparent increase in adsorption capacity with the removal of total organic carbon (TOC)by a combination of GAC and biofilm, provided by activated sludge (9).

The ideal biofilm will be one that retains bacteria through entrapment, but is open enough not to smother the GAC surface (i.e. so that it remains accessible for adsorption of organic residues etc.). Use of a support for immobilization of micro-organisms can also provide greater resistance against potentially toxic agents and increase metabolic activity (10).

Although the ability of activated carbons to remove cadmium in high concentrations from wastewater has been established by numerous researchers (11-17), very few articles are available on the use of activated carbon to remove cadmium in low concentration from contaminated surface or subsurface waters (18). 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 (19-22).

Scott and Karanjkar studied cadmium (up to 25 ppm) adsorption on to Biofilm covered granular activated carbon (23, 24). There is not any study on removal of low concentration (less than 5 ppm) of cadmium by Biofilm/GAC. 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. 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 cadmium uptake isotherms 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

All the experiments were conducted in accordance with ASTM 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 $(NO_3)_2.4H_2O$ and the solution pH was adjusted with HNO_3 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 (5°C, 15°C, 25°C) and at different pH (5, 7 and 8.5). The contact times were selected on the basis of preliminary experiments that demonstrated equilibrium in 4 h for GAC and Biofilm and 1.5 for Biofilm/GAC.

For isotherm studies, a series of 250 mL Erlenmeyer flask was 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 into each Erlenmeyer and agitated for the desired time periods. Afterwards the solution was filtered using Glass Fiber (GF/A) filter and analyzed for the concentration of the metal ions remaining in the solution by Chem Tech Alpha 4 Atomic Absorption Spectrophotometer. Conditions for the Spectrophotometer were 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 with an inner diameter of 14 cm. One column was packed with 12-20 mesh sand and was named as biofilm column. Another column was packed with 12-20 mesh GAC.

Nutrient medium (2000 mg/L sodium acetate as the sole carbon source, 500 mg/L NH_4NO_3, 500 mg/L KH_2PO_4, 200 mg/L $CaCl_2$ and 200 mg/L $MgSO_4$) was seeded by activated sludge taken from aeration tank of municipal sewage treatment plant and circulated (upflow, 25 C, pH=7) for two days through GAC and sand columns. The biofilm attached on the surface of activated carbon particles was bacterial consortia (activated sludge).

Biofilm samples for batch biosorption test (isotherm studies) 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. 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 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 the concentration of Cd (II) was determined by AAS.

Results

Calculated values of correlation coefficients (R^2) at different pH value are given in table 1. According to Langmuir model, reasonable straight-line correlations (R^2) were achieved for Cd (II) adsorption by GAC and Biofilm, because R^2 for Langmuir isotherm was greater than that of 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 (R^2) for adsorption of Cd(II) on GAC, Biofilm and GAC/Biofilm at different pH

	Langmuir Model			**Freundlich Model**		
PH	GAC	Biofilm	GAC/ Biofilm	GAC	Biofilm	GAC/ Biofilm
5.5	0.9245	0.8641	0.6653	0.8549	0.8314	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

The Langmuir model, considered valid for mono-layer adsorption on a surface containing a finite number of identical sites, assumes uniform energies of adsorption over the surface and no transmigration of adsorbate in the plane of the surface. The Langmuir expression can be represented by: $C_e/Q_e = C_e/Q_0 + 1/bQ_0$

Where:

C_e=equilibrium concentration (mg/L),

Q_e=equilibrium metal adsorbed (mg/gr GAC),

Q_o=adsorption capacity,

b= energy constant

A plot of C_e/Q_e against C_e should be a straight line, but Cd adsorption data on to GAC/Biofilm surface did not produce an acceptable approximation to linearity. Poor Langmuir model performance with GAC/Biofilm was linked to the assumption of uniform binding surface characteristics, whereas biofilm structure and coverage were non-homogeneous and this variability could result in different surface adsorption energies. In addition, a wide variety of biochemical functional groups within the biofilm could result in non-uniform electrostatic interaction and attachment. The linearised form of Freundlich equation can be represented by:

$\mathrm{Log}(X/M) = \mathrm{Log}\, K + 1/n\, \mathrm{Log}\, C_e$

The magnitude of n is an indication of system suitability, with values of n>1 representing favourable adsorption conditions. Unlike the Langmuir model, reasonable straight line correlation was achieved for Cd (21).

As illustrated in Fig. 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.

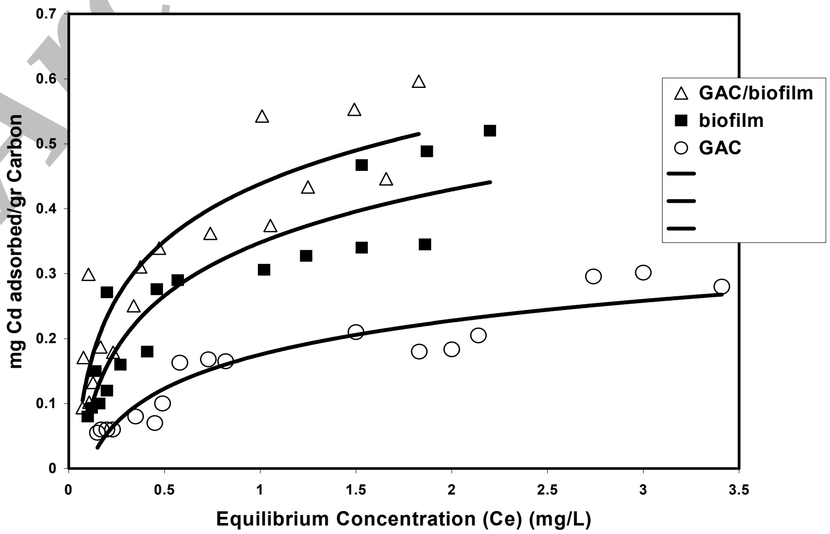

Fig.1: Isotherm plots for Cd(II) sorption by GAC, Biofilm and GAC/Biofilm

For divalent metal, biofilm/GAC equilibrium loading capacity was directly related to adsorption rate (24). Metal ion biosorption dynamics depends on factors other than surface binding, in particular inward diffusion through the biosorbent. Using Fick's second low of diffusion and assuming steady state conditions, an expression for divalent metal ion diffusion flux into a biosorbent has been drived and adapted to the biofilm/GAC system. They reported zinc and cadmium diffusivity in biosorption by Ca-alginate beads to be 1.02 x 10^{-7} and 1.34 x 10^{-7} Cm^2/s respectively, values of the same order of magnitude as those for the biofilm. There is dependence between diffusivity and equilibrium metal adsorbed, as the diffusion coefficient increased with loading. Such a relationship was also observed in adsorption of organics onto plain GAC and indicates an effective diffusion coefficient, related to metal ion concentration and hence subsequent uptake level (24).

Fig. 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 5-24°C, 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.

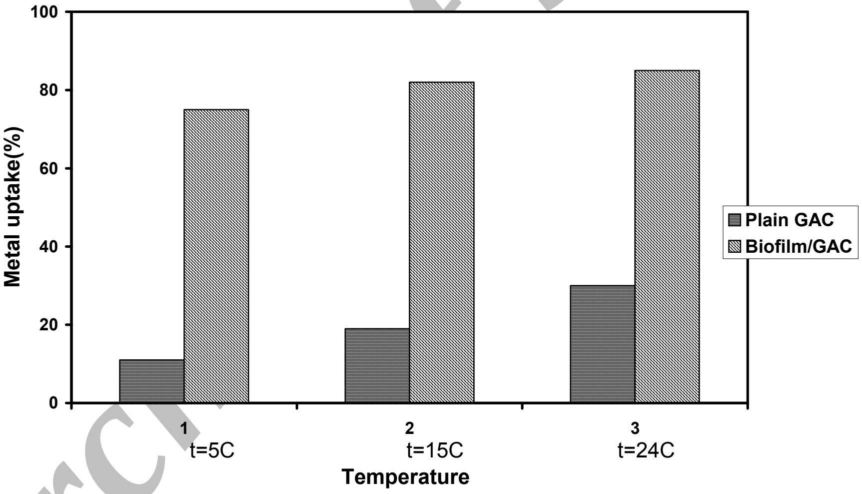

Fig.2: Effect of temperature on cadmium uptake by Biofilm /GAC and plain GAC

The uptake of the cadmium by plain GAC increased with an increase in temperature thereby indicating the process to be endothermic. Thermodynamic parameters, namely free energy, enthalpy and entropy of Cd and Zn adsorption onto GAC at three different temperatures were calculated by Dinesh Mohan and Kunwar Singh (2000). They reported a negative free energy value confirms the feasibility of the process and the spontaneous nature of adsorption, positive values of enthalpy indicate the endothermic nature of the process while the positive entropy reflects the affinity of the GAC for Cd and Zn (25).

Fig. 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 conditions, metal removal can be related only to the adsorption process. The adsorption of Cd (II) on the plain GAC increases with pH, simultaneously.

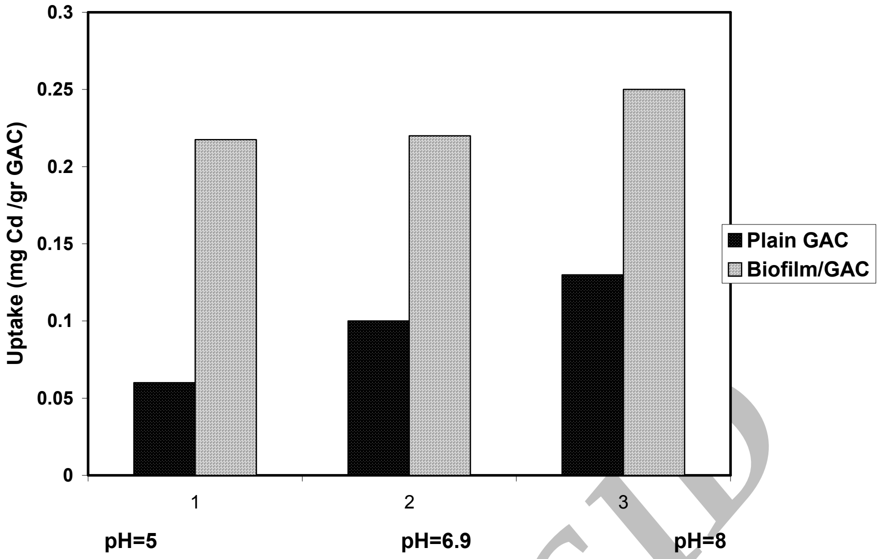

Fig.3: Effect of solution pH on Cd uptake by Biofilm/GAC and plain GAC

The Lagergren first-order rate equation is written as Log (q_e–q_t)=Log q_e–K_{ad}/2.303 t, where qe and qt 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 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 was calculated from the slope of the plots separatly and the values are presented in Table 2.

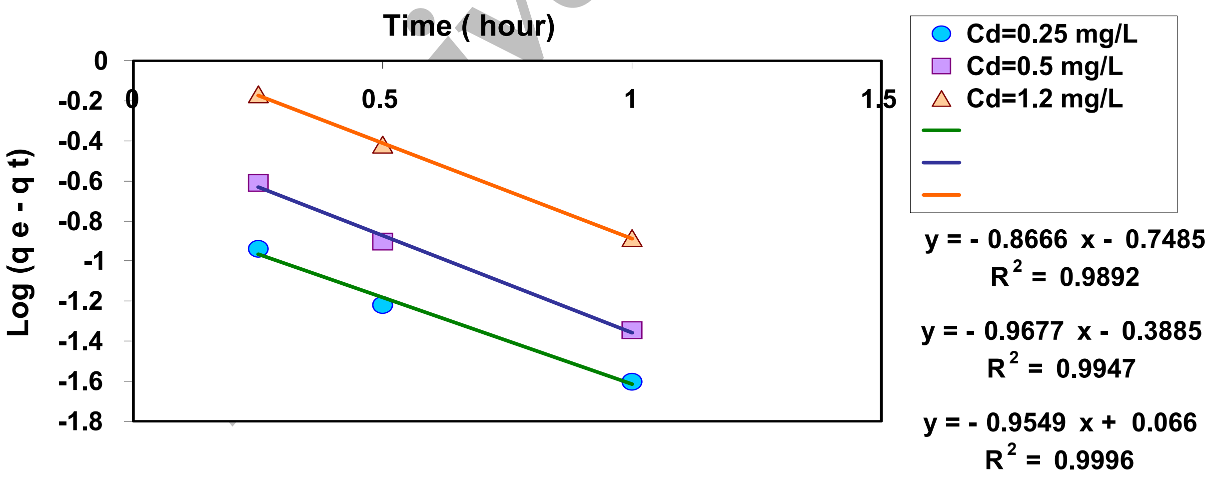

Fig.4: Lagergren plots for the adsorption of Cd(II) by Biofilm/GAC at pH=7

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

Cd Concentration (mg/L)	K_{ad} Biofilm/GAC (L/Min.)	K_{ad} GAC (L/Min.)
0.25	2.1991	1.048
0.5	2.2280	1.1080
1.2	1.9957	0.6819

Normalized effluent cadmium concentration (Ce/Ci) versus number of bed volumes (BV) treated for 0.5 mg Cd/L by Biofilm/GA C column at pH=7, are presented in Fig. 5. This curve will be referred to as breakthrough curve. Breakthrough was defined at C_e=0.01C_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.

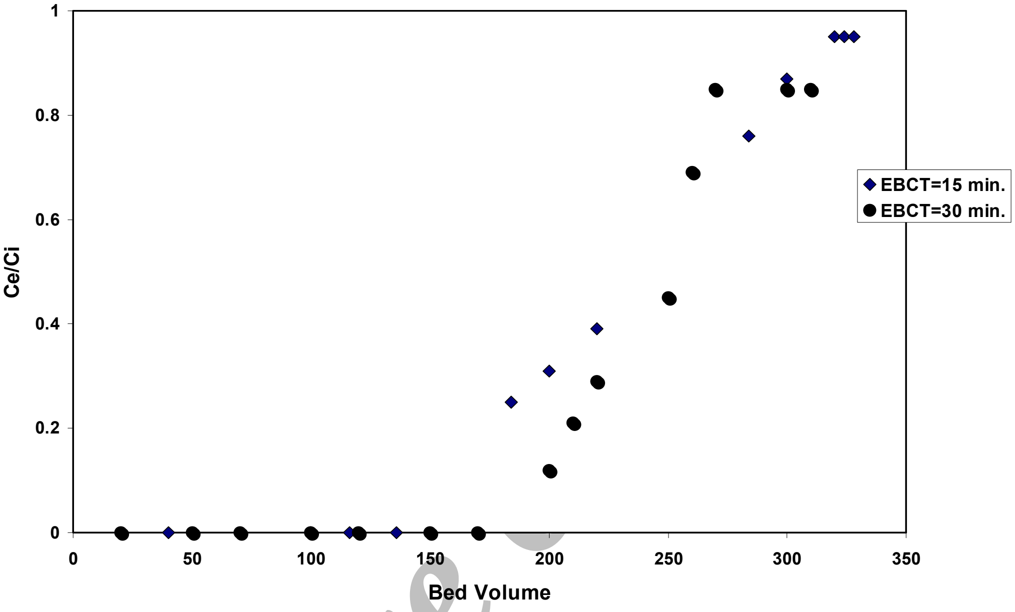

Fig.5: Breakthrough curves for 0.5 mg/L Cd(II) at different contact time and pH=7

Discussion

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 conditon (pH=8) was found to have little effect on Cd (II) uptake (e.g. 0.23mg Cd/gr GAC at pH 6.9 to 0.26mg Cd/gr GAC at pH 8), whereas Cd II) uptake in acidic condition (pH=5) was the same as natural condition (pH=6.9).

Leyva-Ramos R. (1) reported at initial pH below 2, Cd^{2+} did not adsorbed onto carbon, however, varying the initial pH from 3 to 4 resulted in an 8 to 9 fold increase in cadmium adsorption. The maximum adsorption of cadmium occurred at an initial pH of 8. In general, at an initial pH between 3 and 8, the amount of Cd adsorbed increased as initial pH increased.

At pH below 7, the Cd^{2+} ion predominates and pH values just below 9, Cd begins to precipitate out as $Cd(OH)_2$. At pH 8 the species distribution is approximately 90% Cd^{2+} and 10% $Cd(OH)_2$, this means that all the species occurring at pH 8 and below carry a positive charge either as Cd^{2+} or $Cd(OH)^+$ (26).

Budinova et al (16) studied metal ions removal from aqueous solutions using GAC. They found that with increasing of pH, Cd uptake has been decreased, and sorption isotherms are similar to Laungmier equations. Jaffar et al (1993) studied heavy metals removal using GAC column. The column removed 41-55% of metals (27). Brain et al (1994) defined breakthrough as C_e=0.03^{o}C (28). Seco et al (1999) studied effect of pH, metal and carbon concentration. They found that with increasing of pH and carbon concentration, cadmium removal was increased (29).

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 K_{ad} for Biofilm/GAC was 2-3 times greater than those of plain GAC.

In terms of process selection and design, the adsorption rate constants, K_{ad}, should provide indication of both the preferential uptake order and also importantly, comparison between biofilm/GAC and other biosorption systems. With biofilm/GAC, consistently higher rates of adsorption can be achieved for metals. The importance of this lies in the design of a process, in so much that residence times in contact columns are effectively reduced by increasing the rate of uptake.

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 surface 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.

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