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Biosorption Of Cadmium In Liquid-Solid Circulating Fluidized Bed

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Abstract: Heavy metal pollution has become a major concern all over the world with rapid growth in industrialization, particularly Cadmium which is highly carcinogenic. Our present work is mainly focused on hydrodynamics of liquid solid circulating fluidized bed (LSCFB) and biosorption of cadmium using immobilized micro organism in a LSCFB. In this paper, work is carried out to estimate the solids circulation rate, Solids holdup using sodium alginate beads of 4mm diameter and density of 1010 kg/m^3. Cadmium concentration at regular intervals was determined by EDTA titration with xylenol orange as indicator and hexamine as buffer. (1 ml of 0.05M EDTA = 5.621 mg Cd.) was determined to verify Cadmium biosorption efficiency of batch and LSCFB studies. Based on batch study 48 strain microorganism was selected for immobilization and cadmium biosorption studies. The measured solids circulation rate and solid holdup were found to be a function of the fundamental variable viz. liquid velocity, viscosity, density. The cadmium biosorption efficiency in batch and in LSCFB respectively and found to be depending on the strain of micro-organism used, time , quantity of micro-organism used and initial cadmium concentration.
Keywords- LSCFB, Solid holdup, Solid circulation rate, Biosorption.

1.INTRODUCTION

New processes in biochemical technology, water treatment, petroleum and metallurgical industries, continuous adsorption and desorption to recover gaseous pollutants and reusable compounds, etc have led to the need of new types of liquid-solid contacting equipment. One of these is the liquid-solid circulating fluidized bed (LSCFB) [1-5]. The LSCFB consists of two columns the riser and the down comer. The riser operates at high liquid velocity greater than the terminal velocity of the particle and the particles are carried up the riser column. The entrained particles are collected at the top and recirculated to the bottom of the riser column through the downcomer to maintain the required solid hold up in the riser. Hydrodynamic studies are important to properly design an industrial LSCFB system and it is important to optimize the conditions required for the biosorption studies. The flow characteristics in a LSCFB system has been shown to be very different from a conventional liquid-solid fluidized bed and from a gas-solid circulating fluidized bed as reported in studies [3, 5]. The principal interest in LSCFB is it can handle reaction and regeneration simultaneously. Q-D. Lan [6]have successfully demonstrated the LSCFB for the continuous recovery of protein from the cheese whey under various operating conditions. Amarjeet et al [7] verified continuous enzymatic polymerization of phenol which shows that the enzymatic reaction and the regeneration of the biocatalysts can be carried out simultaneously and independently in LSCFB system. Hydrodynamics studies have been carried out in cold model LSCFB ion exchange system for cesium removal [8].

Heavy metal pollution problem arises with areas of intensive industry. Cadmium and its compounds are extremely toxic even in low concentration and will bio-accumulate in organism and in ecosystem. Nickel-Cadmium batteries are one of most popular cadmium based products. The search for new technologies involving the removal of toxic metals from wastewaters has directed attention to biosorption, based on metal binding capacities of various biological materials. Biosorption is a highly sought after method of waste water treatment and heavy metal removal. Hence, there was plenty of available literature on biosorption. However, there was not much of literature available on liquid solid fluidized beds or biosorption in them. Ahalya et al, 2003,[10] studied the biosorption of heavy metals. They explained the various mechanisms of biosorption taking place. They reported that temperature in the range of 20 – 35^oC will not affect the biosorption performance. pH was determined as the most important parameter affecting the performance. Biomass concentration was found to inversely affect the biosorption capacity. They also suggested a wide variety of immobilization techniques such as adsorption on inert supports, entrapment in polymeric materials and cross linking. Hima Karnika Alluri et al, 2004[11] performed biosorption experiments for Chromium, Copper, Cadmium and Nickel using the biomass of different Pseudomonas species. The maximum adsorption capacity was found to be the highest for Nickel followed by Cadmium, Copper and Chromium. They also studied the pretreatment, immobilization and desorption of biomass for the biosorption process. They suggested the immobilization of the biomass by entrapment in polymeric matrices such as sodium alginate or polyacrylamide. Dilute mineral acids such as HCl, H_2SO_4 and HNO_3 was found to aid in desorption. They suggested that increasing the pH results in subsequent increase in the overall negative charge on the surface of cells which favour metal adsorption, Vijayaraghavan et al, 2008 [12] did a detailed study on bacterial biosorption and biosorbents. A detailed description of isotherm models of biosorption, such as Langmuir isotherm and Freundlich isotherm were presented. They also suggested pretreatment of the biomass by chemical and biological means. Jianlong Wang et al ,2008 [13]studied different types of biosorbents for heavy metal removal. They reviewed the biosorption performance of different bacterial biosorbents In this paper, work is carried out to estimate the solids circulation rate, Solids holdup Cadmium concentration at regular intervals by EDTA titration with xylenol orange as indicator and hexamine as buffer.(1 ml of 0.05M EDTA = 5.621 mg Cd.) and to determine Cadmium biosorption efficiency of batch and LSCFB studies.

2. MATERIALS AND METHODS

Figure 1 shows the details on the experimental setup. It consists of an Acrylic riser column of 1000 mm height, 50 mm internal diameter, a liquid solids separator, a device for measuring the solids circulation rate, a storage vessel serving as solids reservoir and an inclined solids feed pipe connecting the storage vessel and the base of the riser. The base of the riser has perforated distributor for flow liquid into the riser. The distributor plate has holes of 3 mm diameter, arranged in triangular pitch. Rota meter of maximum 600 LPH is used to measure the liquid flow rate. Tap water, as fluidizing liquid is pumped from the reservoir into the riser column. The ball valve present in the top of the solid reservoir is shutdown to collect the solid in the graduated tube the solid circulation rate and the Pressure drop is found using the digital manometer.

The liquid- solids separator performs the operation of separating particles from the liquid and the particles flow down to the particle storage vessel. The device for measuring the flow rate of the particles located at the top of the storage vessel is graduated to give the amount of solids collected at a known time. A ball valve at the bottom of the device enables the solid to accumulate in the graduated tube for a known time. This is done by closing the ball valve. The height of the solids accumulated in the tube is recorded to give the weight of solids circulating per unit time. Alginate beads are used as the solid medium in this present study.

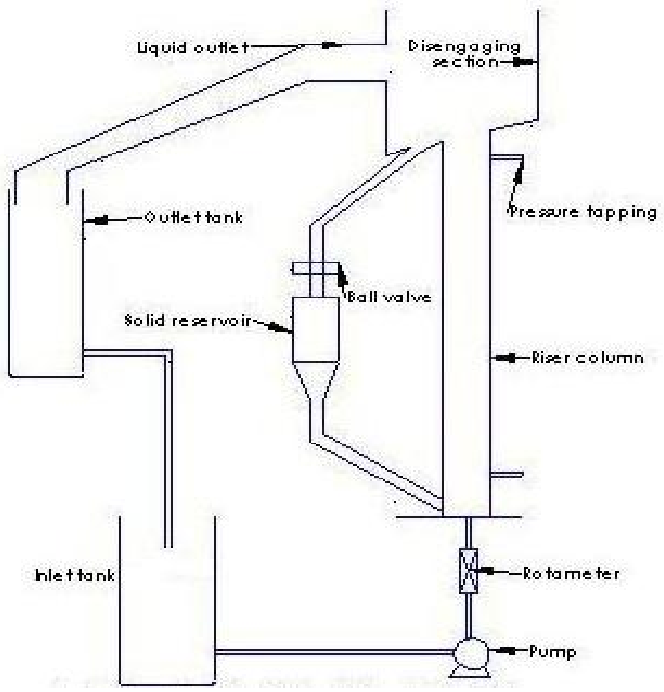

Fig. 1 Schematic diagram of the experimental setup

2.1Preparation of Beads

Sodium alginate powder is mixed well into water and 0.5 M calcium chloride solution is prepared. The prepared sodium alginate solution is taken in a syringe and dropped into the calcium chloride solution. The opening of the syringe tip determines the diameter of the alginate bead formed in the calcium chloride solution. The beads once full formed are washed with fresh calcium chloride solution to make it harder. Properties of alginate beads are given in Table 1.

Table 1: Properties of alginate beads

Solid material	Alginate Beads
dp, mm	4
ρ_s , kg/m^3	1010
Ut , m/s	0.033
ε_s, Void Fraction	0.08

2.2 Theory and Calculations

The solids circulation rate is given by:

$$G_s = \frac{H°}{t}, (kg/m^2 s) \qquad (1)$$

The solids circulation begins only when the true velocity equals the terminal velocity of the particle, Ut The solids hold up is measured by noting the pressure gradient at different locations along the riser. The average solids hold up is determined for each measured section from the pressure gradient; the wall friction effects may be neglected.

$$£_s = \frac{\Delta°}{°_s} . \frac{H}{\Delta z} \qquad (2)$$

The results obtained was compared with empirical correlations developed by Zheng [3]

$$1 - £ = \frac{G_s^{*\,0.8}}{0.25 U_l^{*\,1.9}} \qquad (3)$$

where G_s^* is the dimensionless solids circulation rate and is defined as

$$G_s^* = \frac{G_s}{(«°_l \Delta°)^{1/3}} \qquad (4)$$

and U_l^* is the dimensionless superficial liquid velocity, defined as

$$U_i^* = U_l \left(\frac{°_l^2}{«g\Delta°} \right)^{1/3} \qquad (5)$$

2.3Batch Sudies- Selection of microorganism for cadmium biosorption

There are number of micro-organisms available to study the cadmium biosorption. Five different micro-organisms named as 1A, 12**,** 48**,** Pseudomonas sp, Saccharomyces cerevisiae (Baker's yeast) are selected. Batch studies are performed for the five different strains with an initial cadmium sulphate solution concentration of 560 mg/100 ml. The concentration of cadmium is determined after 5 hours and 24 hours as given in Table 2. It can be observed that the micro-organisms 48 and yeast has high cadmium biosorption capacity and hence selected for the batch study

2.4Batch study using selected micro-organisms

Strain 48 and yeast strains are selected for the batch study. 100 ml of nutrient broth is prepared and 2 ml of 24 hr subculture is added to the nutrient broth along with the cadmium sulphate salt. Samples of 10 ml were withdrawn from the mixture for every hour for 5 hours and the corresponding cadmium concentrations in 48 strain and yeast is found and tabulated.

Table 2: Absorption of cadmium by different strain

strain	5^{th} hour reading	24^{th} hour reading
1A	39.84	57.89
12	28.81	54.88
48	*59.89*	*74.93*
Pseudomonas	27.81	61.90
Yeast	*47.86*	*67.91*

Strain 48 is selected for immobilization and cadmium biosorption studies. The strain is sub-cultured for 24 hours in an incubator. 3% sodium alginate solution was prepared and 20 ml of culture is added to 100 ml of alginate solution. Subsequently 500 ml of 0.5M calcium chloride solution was prepared and the alginate mixture is dropped into the calcium chloride solution. The beads once completely formed are washed with fresh calcium chloride solution to make it harder.10 g. of the immobilized alginate beads is taken in a conical flask along with 100 ml of cadmium sulphate solution of concentration 560 mg Cd/100ml. 10 ml of samples were taken out at the end of every hour for 5 hours and the cadmium concentration was determined and tabulated.

2.5Biosorption studies in LSCFB

Alginate beads containing the immobilized cells of 48 strain is taken in the riser column such that it occupies $1/4^{th}$ (25%)of it's volume. cadmium sulphate salt is accurately weighed and mixed with 50 liters of distilled water and taken in the feed tank. The pump is switched on and the flow rate is set to an optimum of 350 LPH determined by hydrodynamic studies. The stop watch is started simultaneously. 10 ml of initial sample is withdrawn to check the cadmium concentration. Samples were withdrawn every one hour interval till the consistent reading is obtained which denotes the maximum biosorption capacity of the immobilized micro-organism.

3.RESULTS AND DISCUSSION

3.1Effect of solid circulation rate and solid holdup in LSCFB(using alginate beads)

It can be analyzed from Fig.2 that when the flow rate of liquid inlet is increased, the solid circulation rate increases up to the flow rate of 350 LPH after which the solid circulation rate decreases. when the flow rate increases more solids gets entrained into the disengaging section as a result of which crowding of solids occurs near the entrance of the down comer which provides hindrance or a resistance for the circulation of solid and hence the solid circulation rate decreases when set a flow rate of above 350 LPH. Thus the optimum flow rate for the operation of the scaled down LSCFB for alginate beads of 4 mm can be taken as 350 LPH. From the Fig 3 it can be observed that when the flow rate of liquid inlet is gradually increased, the solid hold up in the riser decreases. This trend can be explained as when the flow rate increases more solid gets flushed into the disengaging section as a result of which the solid content in the riser column decreases linearly.

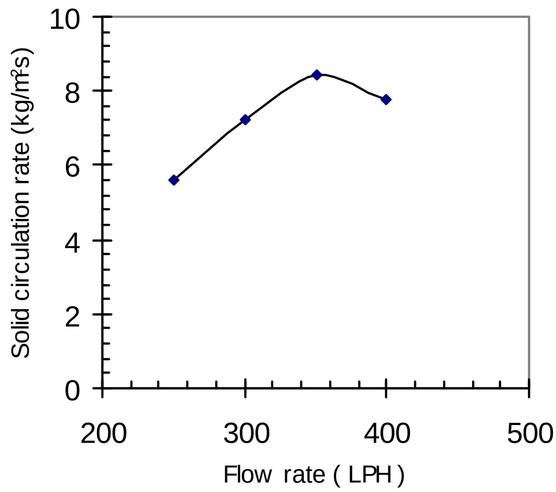

Figure 2 Flow rate Vs Solid circulation rate (Kg/m^2s)

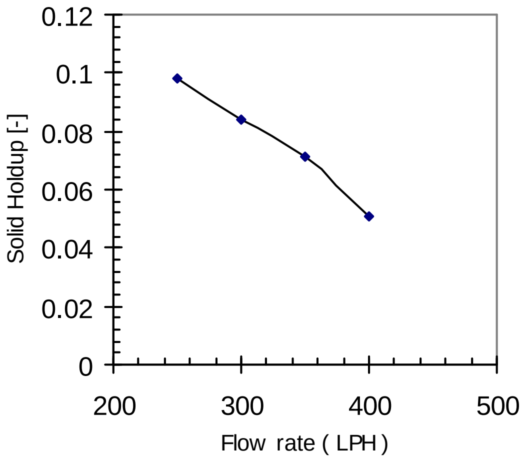

Figure 3 Flow rate (LPH) Vs Solid holdup

3.2 Batch study using selected micro-organisms

It can be observed from the Fig.4 that when the time progresses the cadmium concentration in the solution decreases and reaches almost a constant value. The final cadmium concentrations for 48 strain and yeast were analyzed to be 191.114 mg Cd/100 ml and 264.187 mg Cd/100 ml respectively. It can be observed from the Fig.5 that when the time progresses the efficiency `of cadmium removal increases and reaches a constant value. Which denotes the micro-organism reaching it's full biosorption capacity. The efficiency of 48 strain was found to be higher (65.91%) as compared to the yeast strain (52.8%).

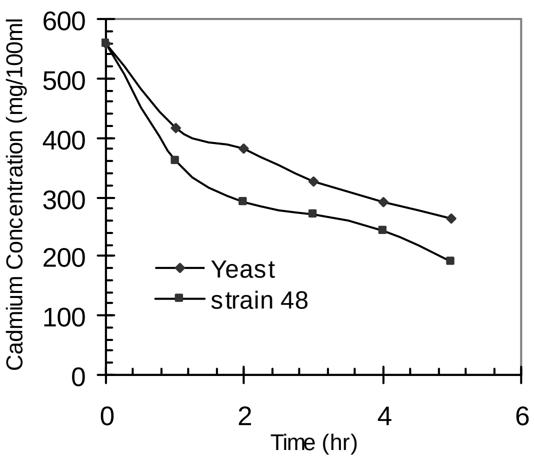

Figure 4 Time (hour) Vs Cadmium Concentration (mg/100ml)

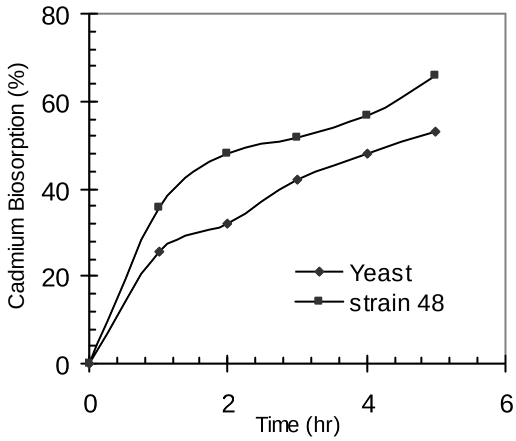

Figure 5 Time (hour) Vs Cadmium removal (%)

3.3 Batch study using immobilized micro-organisms

It can be seen from the Fig.6 that when the time progresses the concentration of cadmium reduces gradually and reaches 185.493 mg/100 ml after 5 hours. It can be observed in the Fig.7 that as the time progresses the cadmium removal efficiency increases gradually and reaches a peak value of about 66.91%. The increase in the efficiency from batch to immobilization can be accounted as the empty alginate beads also adsorb cadmium to certain extent.

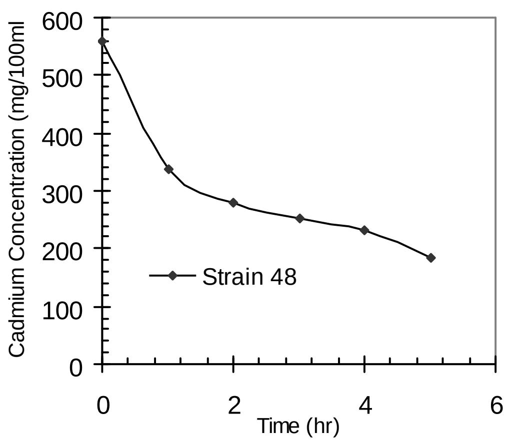

Figure 6 Time (hour) Vs Cadmium concentration (mg/100 ml)

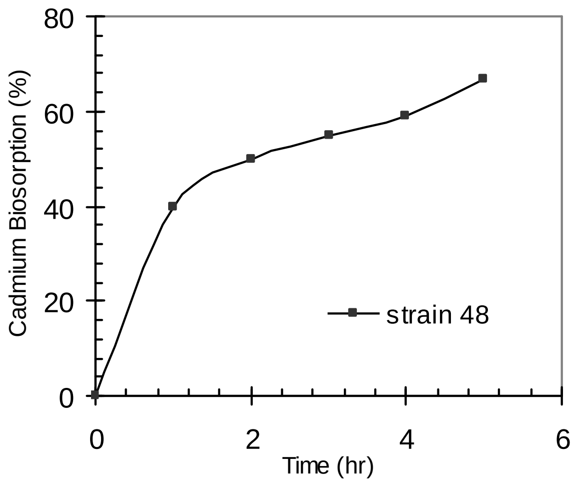

Figure 7 Time (hour) Vs Cadmium removal

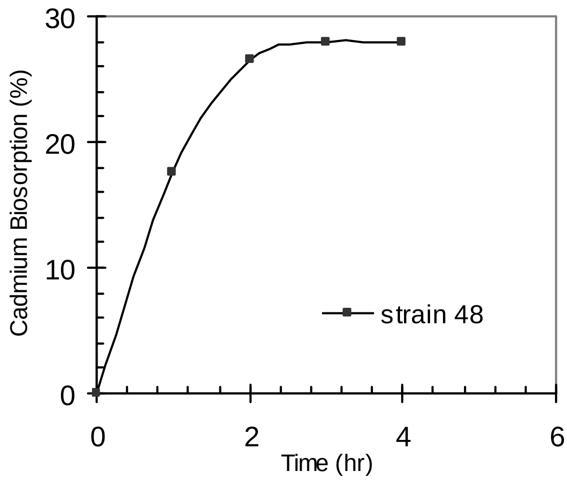

Figure 9 Time (hour) Vs Cadmium removal

3.4 Biosorption studies in LSCFB

The immobilized cells were fed into the riser column. The pump is switched on and set to an optimum flow rate of 350 LPH. The cadmium concentration at the beginning was determined to be 436.63 mg Cd/100 ml. the samples were withdrawn after every hour and the concentration was determined. The final concentration was found to be 314.776 mg Cd/100 ml. The reading was found to be consistent for the third and the fourth hour reading which denotes the micro-organisms reaching their maximum biosorption capacity. Figs 8 and 9 shows that the maximum efficiency (27.90 %) was obtained after the fourth hour. The efficiency of cadmium biosorption can be higher when the initial cadmium concentration was less. This is because the cadmium biosorption capacity of the organisms remains the same and hence major portion of cadmium would be removed when its inlet concentration is less.

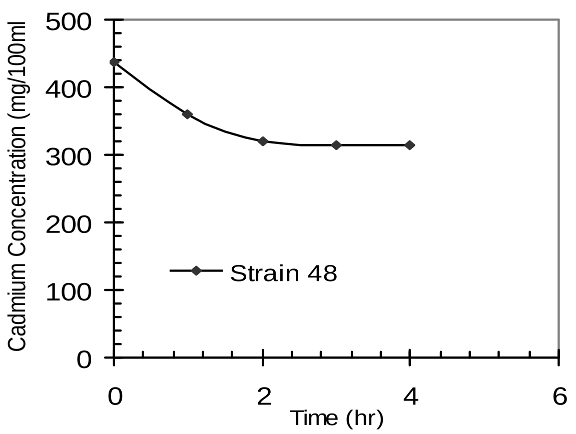

Figure 8 Time (hour) Vs Cadmium concentration (mg/100ml)

4.CONCLUSION

The study covering the hydrodynamics such as solid circulation rate, solid holdup and biosorption of cadmium was made and it can be analyzed that the Liquid solid circulating fluidized bed has an excellent hydrodynamic behavior and applications in waste water engineering. Heavy metal removal from waste water is a serious problem that the industries are facing at the present days because of the stringent norms required as per the pollution control board. The above work throws light on the biological approach of reducing the cadmium concentration in the waste water. LSCFB method of cadmium biosorption may be applied in the electronic industries where the cadmium content in the outlet spent water is very high. This research work, which removes the highly carcinogenic cadmium contents from waste water, might be used for great extent and it also helps in chemical engineering by providing greener and eco-friendly processes.

NOMENCLATURE

d_m - mean diameter of the particle, m
dp - particle diameter, m
g - Acceleration due to gravity, m/s^2
Gs - Solids circulation rate, $kg/m^2 s$
Gs* - solids circulation rate expressed in dimensionless quantity
H - Height of solids accumulated in the calibrated tube, m
L - Length of the column, m
k_1, k_2 - constants
ΔP - pressure drop, N/m^2
t - Time taken, s
U - Liquid Velocity
Umf - minimum fluidization velocity, m/s

Symbols

ε - bed voidage

ε_S - solids holdup

ε_l - liquid holdup

ε_{mf} -voidage at minimum fluidization conditions

ρ_l - density of liquid , kg/m^3

ρ_s - density of solids, kg/m^3

μ - viscosity of liquid, kg/m.s

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