

Adsorption Isotherm Study of Cadmium on Dairy Sludge Based Adsorbent

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Abstract

Aim of this research is to assess the potential of adsorbent derived from dairy industry sludge for the removal of cadmium from aqueous solution. Cadmium adsorption was studied in batch mode as a function of pH, adsorbent dose, contact time and initial metal ion concentration. The equilibrium uptake decreased with increasing adsorbent dose and increased with increasing cadmium concentration. The maximum cadmium removal was obtained at pH 6.0. The desorption efficiency of various desorbing agents is found in following order $\text{HCl} > \text{HNO}_3 > \text{EDTA} > \text{H}_2\text{SO}_4$. Langmuir, Freundlich and Temkin isotherms were tested on experimental adsorption data to represent the equilibrium between solid and liquid phases. Langmuir and Freundlich isotherm models provided a much better description of experimental data than Temkin isotherm model as revealed by high correlation coefficients (R^2). The maximum adsorption capacity obtained from Langmuir model equation was 24.75 mg/g of cadmium onto dairy sludge based adsorbent (DSBA). The results of present study revealed that cadmium is considerably adsorbed on dairy sludge and DSBA can be successfully used for separation of cadmium from waste stream.

Keyword: Adsorption, Cadmium, Dairy Sludge, Desorption Efficiency, Langmuir Isotherm

I. INTRODUCTION

Cadmium is the most common heavy metal used in industries as anticorrosive agent. Effluents discharged from metallurgy, electroplating, paint pigments, batteries, plastic manufacturing and alloy industries consists considerable amount of cadmium [1]. In 1817, Friedrich Stromeyer first time highlighted the kidney, bone and pulmonary damages by cadmium toxicity in human [2]. Eating food, drinking water, breathing or smoking are the major pathways through which cadmium enter into the human body [3, 4]. The major human health problems associated with long term exposure of cadmium are renal disturbances, hepatotoxicity, lung insufficiency, bone lesions, cancer, anemia, hypertension and weight loss [5-8]. Itai-Itai a well-known disease of bone occurred in Japan caused by the consumption of rice irrigated by the water contaminated with cadmium [9]. The International Agency for Research on Cancer (IARC) has classified cadmium and cadmium compounds as carcinogenic to humans and placed in Group 1 [10, 11]. So, there are sufficient reasons for the removal of cadmium from the wastewater to protect the human health as well as environment components.

Many conventional techniques, such as chemical precipitation, ion exchange, coagulation, electrolysis, activated carbon adsorption and membrane processes have been developed for the treatment of heavy metal laden wastewater. But, these are not only cost intensive and low efficient at lower metal concentration rather there are others disadvantages also such as secondary pollutants generation, high energy consumption, requirement of large quantities of chemical reagents [12-14]. As a consequence, there is a need of development of some cost effective alternative water treatment technologies for heavy metal removal. Through an appropriate selection of adsorbent, adsorption process can be a cost effective technology for the removal of heavy metals from the waste stream [14].

Water management is well documented in dairy industry but excess sludge management places a high financial burden. As handling of sludge accounts approximately 60% of the total treatment plant operating costs [15]. The sludge produced from the biological treatment can be used as adsorbent for the heavy metal removal as it is rich in organic and inorganic substances and microorganism [16, 17]. In the present investigation, adsorbent was prepared from dairy sludge and used to optimize its cadmium removal ability from the aqueous solution in batch mode operation. The effects of pH, adsorbent dose, contact time and initial metal ion concentration were studied. Equilibrium parameters were determined to understand cadmium adsorption mechanism on the dairy sludge based adsorbent.

II. MATERIALS AND METHODS

A. Preparation of Dairy Sludge Based Adsorbent:

The sludge was collected from Vita milk plant, Sirsa (29.5333° N, 75.0167° E) and it was first sorted by hand in order to discard the large impurities and then dried at 103°C in hot air oven for 24 hr. The dried sludge was then grinded, sieved to obtain particle size less than 0.5 mm and stored in desiccators prior to use. So prepared adsorbent was nomenclature as dairy sludge based adsorbent (DSBA).

B. Preparation of Cd(II) Solutions:

All chemicals used in present study were of analytical grade. The stock solution (1000 mg/L) of Cd(II) was prepared by dissolving CdCl₂.H₂O in double distilled water. The required standard solutions were further prepared by diluting stock solution. HCl and NaOH (0.1 M) were used to adjust the pH of solution.

C. Batch Equilibrium Experiments:

Cd(II) batch adsorption equilibrium experiments were studied as a function of pH, adsorbent dose, contact time and initial Cd(II) concentration. Effect of initial solution pH on adsorption capacity was investigated by using 250-ml Erlenmeyer flask containing 100 ml solution of 100 mg/L Cd(II) and 0.12 g of DSBA at pH range of 2-7. pH was adjusted using 0.1 M HCl and NaOH solution. Flasks were agitated on a shaker at 150 rpm for 180 min at 30°C to ensure that equilibrium was reached. Effect of contact time was studied from 15 min to 180 min with different adsorbent dose range from 2.5 g/L to 12.5 g/L at optimum pH obtained from above pH experiment and at constant initial Cd(II) concentration 100 mg/L, and temperature 30°C. The residual concentration of Cd(II) after each experiments was analyzed by using atomic absorption spectrometer (Lab India-AA7000). According to Equation (1) the percentage removal (%) or adsorption efficiency of Cd(II) was calculated as shown below.

$$\text{Removal \%} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

Equation (2) is used to calculate the amount of Cd(II) adsorbed, q_e (mg/g of DSBA).

$$q_e = \frac{v(C_0 - C_e)}{M} \quad (2)$$

where, q_e is the amount of Cd(II) adsorbed by DSBA (mg/g), C_0 is the initial concentration of Cd(II) (mg/L), C_e is the concentration of Cd(II) at equilibrium (mg/L), and v is the volume of the metal solution (L) and M is the weight of DSBA (g) [18].

D. Equilibrium Isotherm Models:

Adsorption isotherm studies were carried out with varying initial Cd(II) concentration from 20 mg/L to 200 mg/L at optimum pH and adsorbent dose obtained from above batch equilibrium experiments. Experiments were conducted in 250-ml Erlenmeyer flask containing 100 ml Cd(II) solution at 150 rpm and 30°C. Filtration was done with whatman filter paper 1 to separate adsorbent and the filtrate was analyzed by atomic absorption spectrometer. The removal percentage and uptake capacity were calculated [18]. The Langmuir, Freundlich and Temkin isotherm models were consider in this study to examine the relationship between sorbed (q_e) and aqueous concentrations (C_e) at equilibrium, for Cd(II) on DSBA.

E. Cd (II) Desorption Study:

Batch experiment is conducted to explore the reusability of the DSBA in a 250-ml Erlenmeyer flask containing 1 gm of Cd(II) loaded DSBA and 100 ml (0.1 M) of desorbing agent and this solution was agitated for 180 min at 30°C at 150 rpm. After that solution was filtered and filtrate was analyzed for the eluted Cd(II). Four type of desorbing agent were used in this study as Hydrochloric acid, Nitric acid, Sulphuric acid and EDTA. Equation (3) is used to calculate the desorption efficiency [19].

$$D = \frac{(C_e \cdot V)}{(Q \cdot W)} \times 100 \quad (3)$$

Where, D is the desorption efficiency in percentage, C_e is the Cd(II) concentration in the eluent, V is volume of the eluent, Q is Cd(II) uptake and W is the weight of the DSBA.

III. RESULTS AND DISCUSSION

A. Effect of pH:

Cd(II) adsorption by DSBA as a function of initial solution pH range from 2 to 7 was studied (Fig. 1). The result clearly demonstrated that Cd(II) uptake is strongly influenced by the solution pH. There was an increase in both percentage removal and uptake capacity of Cd(II) between pH values from 2 to 6. At pH value 6 maximum removal of 85.43% and uptake 71.19 mg/g were observed. Such behavior is due to the high concentration of H⁺ protons at low pH which competes with Cd(II) cation and decreases the adsorption of positively charged Cd(II) ion [20,21] but as pH increases the ionization of the adsorbent surface functional groups take place and thus, the total negative charge increased which further increases adsorption [17].

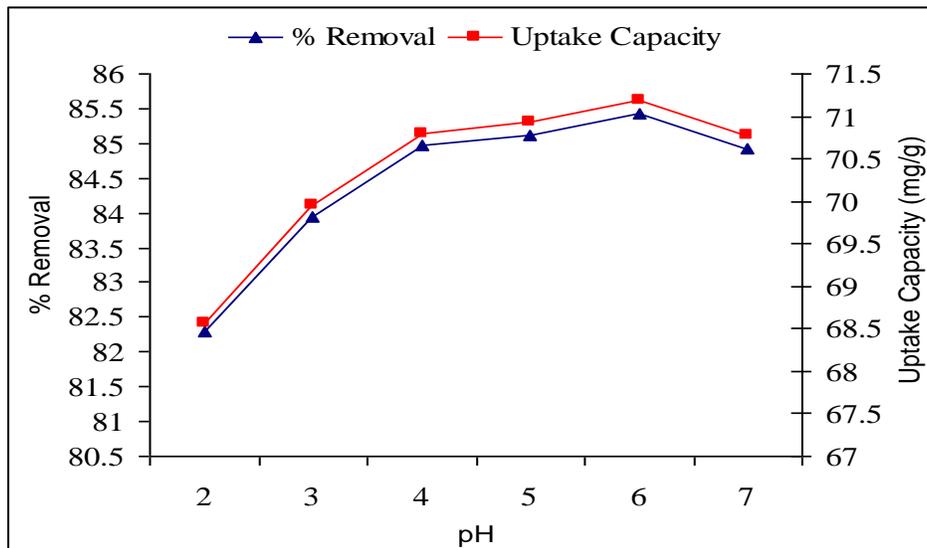


Fig. 1: Effect of pH On Removal of Cd (II) By DSBA at Initial Cd (II) Concentration 100 mg/L, Contact Time 3 Hr and Adsorbent Dose 1.2 g/L.

B. Effect of Contact Time and Adsorbent Dose:

Cd(II) adsorption as a function of contact time at different dose of DSBA is depicted in Fig. 2.

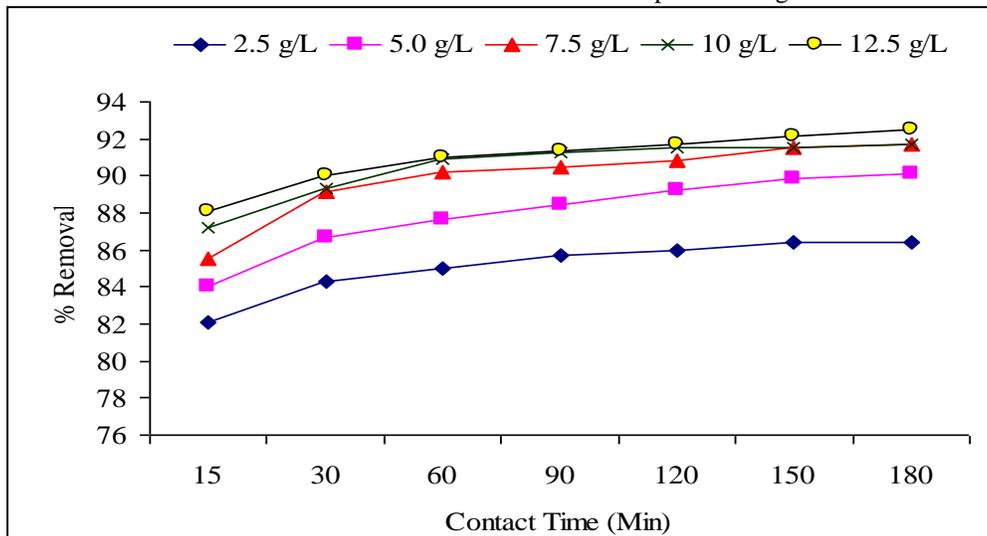


Fig. 2: Effect of Contact Time and Adsorbent Dose on Cd (II) Removal By DSBA At Initial Cd (II) Concentration 100 mg/L And Optimum pH 6.0.

The experiments was conducted with 100 mg/L Cd(II) concentration at optimum pH 6 with varying adsorbent dose range from 2.5 g/L to 12.5 g/L and the contact time was varied from 15 min to 180 min. The results revealed that Cd(II) removal increased with increase in contact time up to 180 min. There was no appreciable increase in Cd(II) removal after 60 min (Fig. 2) because initially for adsorption, large number of vacant surface sites were available and after optimum contact time, adsorption slower down due to exhaustion of remaining surface sites and repulsive force between solute molecule and bulk phase [22, 23]. Similarly Cd(II) removal also increased with increase in adsorbent dose up to some extent, thereafter no significant removal was observed as compare to increasing adsorbent dose. Optimum adsorbent dose was found to be 7.5 g/L. However, a possible reason is that initially more surface is available for the adsorption of Cd(II) and drop in removal beyond optimum dose may be attributed to the attainment of equilibrium between adsorbent and adsorbate at provided optimum conditions [24, 25].

C. Effect of Initial Cd(II) Concentration:

The behavior of Cd(II) removal with varying initial Cd(II) concentration from 20 mg/L to 200 mg/L at pH 6 and adsorbent dose of 7.5 g/L is shown in Fig. 3. It was observed that there is continuous decrease in percent removal and increase in uptake capacity for Cd(II) with increasing initial Cd(II) concentration. The result revealed that the rate of binding of Cd(II) with DSBA is initially high due to availability of more binding site and less competition. After that it gradually decreases as number of Cd(II) competition for the available binding site increased and also lack of binding sites for the complexation at higher metal ion concentration [26].

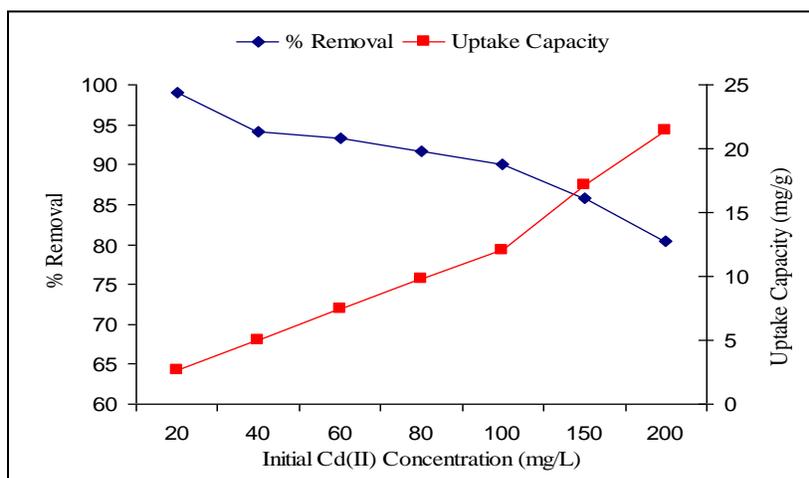


Fig. 3: Effect of Initial Cd (II) Concentration on Cd (II) Removal by DSBA at Adsorbent Dose 7.5 g/L and Optimum pH 6.0.

D. Cd (II) Desorption Study:

The desorption efficiency of studied desorbing agent in this study were found in following order $HCl > HNO_3 > EDTA > H_2SO_4$ (Fig. 4). The result indicated that HCl act as best desorbing agent for the Cd(II) desorption from the DSBA, whereas H_2SO_4 comes out as poor desorbing agent but the difference is not so significant among all the used desorbing agents for the Cd(II) desorption. In the literature also, Cd(II) is reported to be well eluted by HCl followed by HNO_3 [17].

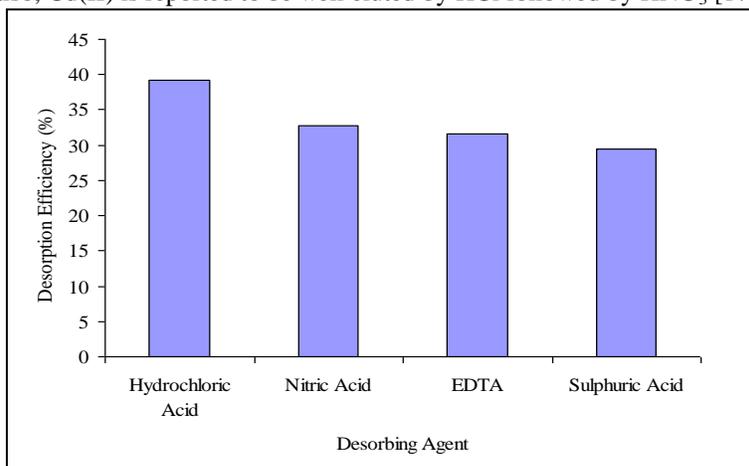


Fig. 4: Desorption Efficiency Of DSBA by Various Desorbing Agent For Cd (II).

E. Adsorption Isotherms:

Langmuir isotherm assumes that there are finite numbers of binding sites for adsorbate which are distributed homogeneously over the entire surface of the adsorbent and has energetically equivalent and there are no interaction between the adsorbed species on neighboring sites [27, 28]. The linearized form Langmuir models which allow the calculations of adsorption capacities and the Langmuir constants refer to (4) [29].

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (4)$$

Where C_e is the residual Cd(II) concentration (mg/L), q_e is amount of Cd(II) adsorbed (mg/g), Q_0 (mg/g) and b (L/mg) are Langmuir constants showing the adsorption capacity and energy of adsorption, respectively [29]. The values of Q_0 and b were calculated from the slope and intercept of the Langmuir plot of C_e/q_e versus C_{eq} (Fig. 5) are presented in the Table I. The adsorption capacity was found to be 24.75 mg/g (Table I).

Separation factor, dimensionless constant an essential feature of Langmuir model denoted by R_L and for formula refer to (5) [30].

$$R_L = \frac{1}{1 + b.C_0} \quad (5)$$

Where, C_0 is initial Cd(II) concentration (mg/L) and b is Langmuir constant. The value of R_L explain the adsorption nature to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The shape of the curve (Fig. 6) plotted between separation factor and initial Cd(II) concentration and the values of R_L (Table II) confirm the favourable uptake of the Cd(II) on DSBA .

Freundlich isotherm assumes that the surface of adsorbent support sites of varied affinities and adsorption take place first on site have strong affinity. The Freundlich isotherm support surface heterogeneity by multilayer adsorption [31]. Equation (6) represents the logarithmic form of Freundlich equation [32].

$$\log q_e = \log K_f + (1/n) \log C_e \quad (6)$$

The values k_f and n can be obtained from the intercept and slope of the plot of $\log q_e$ versus $\log C_{eq}$ (Fig. 7). Higher value of correlation coefficient shows the more suitability of this isotherm for the DSBA. The value of K_f (4.58) and n (2.47) (table I) indicating the high feasibility of the Cd(II) adsorption on the DSBA.

Temkin isotherm assumes that decreased in the heat of adsorption of all molecules is linear rather than logarithmic, as implied in the Freundlich equation [33]. Equation (7) expresses the Temkin isotherm equation [34].

$$q_e = \frac{RT}{b} + \ln(aC_e) \quad (7)$$

Where b is the Temkin constant related to heat of sorption (kJ/mol), R is the gas constant (0.0083kJ/molK), a is the Temkin isotherm constant (L/g) and T the absolute temperature (K). The value of both constant a and b (table I) were calculated from equation obtained from the curve plotted between q_e and $\ln C_e$ (Fig. 8). For the ion-exchange mechanism the reported typical bonding energy range should be between of 8–16 kJ/mol and for physisorption processes it should be less than -40 kJ/mol [35]. The low values of b (0.31 kJ/mol) obtained in the present study indicates physisorption process involve in the Cd(II) removal. Keeping in view the higher value of correlation coefficients revealed that adsorption data are best fitted in both Freundlich model and Langmuir model.

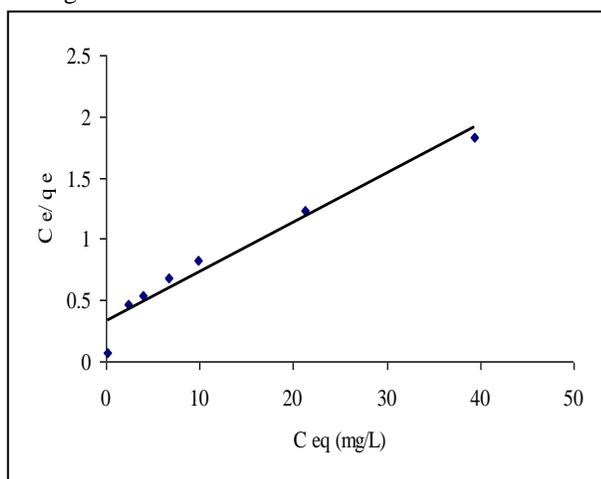


Fig. 5: Langmuir Isotherm Plot.

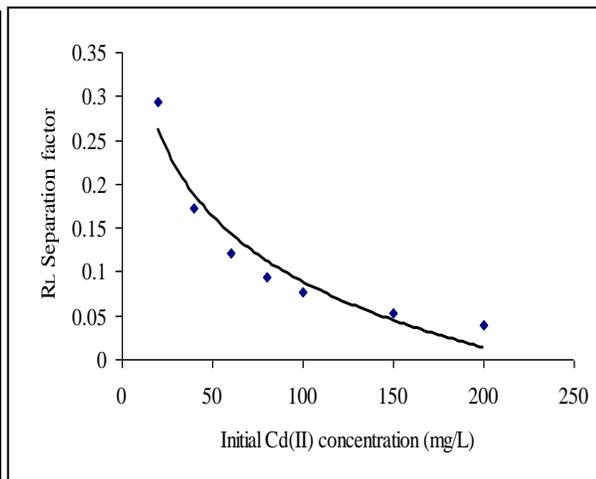


Fig. 6: Separation Factor Curve.

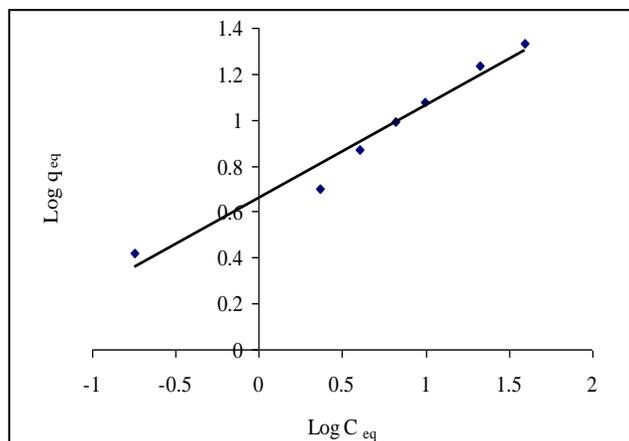


Fig. 7: Freundlich Isotherm Plot.

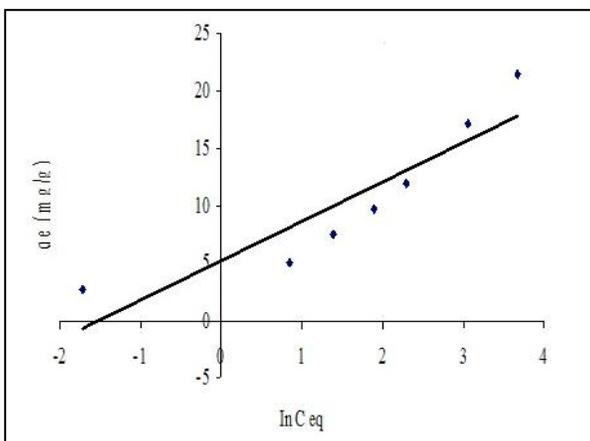


Fig. 8: Temkin Isotherm Plot.

Table - I
Langmuir, Freundlich and Temkin Constants for Cd(II) Adsorption on DSBA

Langmuir			Freundlich			Temkin		
Q_{max} (mg/g)	b (L/mg)	R^2	K_f (mg/g)	n (L/mg)	R^2	a (L/g)	b (kJ/mol)	R^2
24.75	0.12	0.95	4.58	2.47	0.96	1.64	0.31	0.82

Table - II
Separation Factor (R_L) of DSBA At Different Initial Cd(II) Concentration

Initial Cd(II) concentration (mg/L)	20	40	60	80	100	150	200
R_L	0.29	0.17	0.12	0.09	0.07	0.05	0.04

IV. CONCLUSION

The dairy sludge obtained from local milk processing plant is environment friendly and inexpensive adsorption for the Cd(II) removal from wastewater. The maximum Cd(II) adsorption was obtained at pH 6. The experimental adsorption data fit very well to both Langmuir model and Freundlich. Temkin study indicate the physical sorption of Cd(II) on the DSBA. The maximum adsorption capacity was found to be 24.75 mg/g. The results of the present study showed that dairy sludge as a solid waste can be used for the removal of Cd(II) from dilute wastewater.

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