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Adsorption of Cd(II) by Dried Activated Sludge

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Abstract

The biosorption of Cd(II) ions from aqueous solutions by dried activated sludge was investigated as a function of initial pH, initial cadmium ion concentration, adsorbent mass, adsorbent particle size and temperature. Biosorption experiments were performed using activated sludge of the systems of wastewater refining of milk factory. The results showed that increasing the initial pH from 2 to 5.5 and the adsorbent mass from 0.5g to 2g increased the removal efficiency from 11% to 68% and 68% to 79% respectively. Increasing the adsorbent particle sizes from smaller than 0.063mm to greater than 0.5mm and the initial cadmium ion concentration from 15ppm to 120ppm decreased the removal efficiency from 77% to 67% and 80% to 54% respectively. The equilibrium data fitted both the Langmuir and Freundlich adsorption models, but the Freundlich isotherm was found to fit the experimental data slightly better than the Langmuir isotherm. The characteristic parameters for each isotherm have been determined. Maximum adsorption capacity (q_0) was calculated at different temperatures (303, 318, and 333 K) 1.283, 1.581 and 1.726 mg/g, respectively. The dimensionless separation factor (R_L) showed that the activated sludge of milk factory can be used for the removal of cadmium ions from aqueous solutions. The results (n, R_L) represented good and favorable adsorption. Therefore, the activated sludge could remove Cd(II) ions effectively from aqueous solution.

Keywords: *Biosorption, Adsorption Isotherm, Heavy Metal, Activated Sludge, Industrial Wastewater*

1- Introduction

Industrialisation has caused an increase in the disposal of various contaminants into the environment. Among the various contaminants, heavy metals have received special attention, since some of them are extremely toxic for a large variety of organisms, even at very low concentrations (in the order of milligrams or microgams per liter). In addition, these ions are nondegradable and thus persistent, leading to both ecological and health problems [1]. For these reasons, the presence of heavy metal ions in the environment at concentrations above critical values is unacceptable and their removal from the wastewater is of primary importance [2–4].

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As a heavy metal, cadmium is prevalent in industrial and agricultural fields. Cadmium contamination mainly comes from mining and metallurgical processes, electroplating, stabilizing plastics, batteries, alloy manufacturing, pigment and high-phosphate fertilizers [5]. Cadmium is a non-essential element and highly toxic to organisms even at very low dosages. Cadmium is the most dangerous metal ion characterized by high stability and toxicity. It is not degradable in nature and will thus, once released to the environment, stay in circulation. Cadmium is known to bind with essential respiratory enzymes [6] causing oxidative stress and cancer [7].

There are various methods for the removal of heavy metals from the environment. These methods can be grouped into biotic and abiotic. Biotic methods are based on the accumulation of the heavy metal by plants or microorganisms, abiotic methods include physicochemical processes such as chemical precipitation, like sulfides and hydroxides, coprecipitation, chemical oxidation or reduction processes, electrochemical treatment, ion exchange evaporative recovery, parametric pumping with a variation of pH, adsorption of the heavy metal by a suitable adsorbent and membrane processes (such as ultrafiltration, electrodialysis and reverse osmosis) [8-11].

Most Physicochemical processes were found to be expensive and generate new products or simply transfer the metal from one medium to another, not propitiatory, the definitive solution of the problem [8]. In addition, most of these processes are not eco-friendly, because of the production of sludge causing a solid disposal problem [12].

Recently, bioadsorbents have emerged as an eco-friendly, effective and low cost material option [13-14]. Microorganisms such as bacteria, fungi, mosses, macrophytes, higher plants, yeast and algae can remove heavy metals from aqueous solutions in substantial quantities [15-19].

It has been found that both living and dead microbial cells adsorb metal ions [20-21]. However, living cells are subject to toxic effects of heavy metals, resulting in cell death [22]. Moreover, living cells often require the addition of nutrients and hence increase the BOD and COD in the effluent [23]. For these reasons, the use of nonliving biomaterials or dead cells as metal binding compounds has been gaining advantage because they are not affected by toxic ions. In addition, dead cells require less care, maintenance and they are cheaper [24]. Furthermore, dead biomass can be easily regenerated and reused [25].

The treatment of cadmium contaminated water is similar to that of many metal contaminated effluents. There are several methods to treat the metal contaminated effluent such as chemical precipitation, ion-exchange, reverse osmosis, adsorption etc. [26], but the selection of the treatment method is based on the concentration of waste and the cost of treatment [27-30].

Consequently, interest is growing in the use of sorbents made from low-cost renewable materials [31-34]. Several natural adsorbents, including algal biomass [35-37], peat moss [38-39] bark and juniper fiber [40-43], and sugar beet pulp [44], have been investigated for their ability to sequester Cd from water.

In another study, Cd-resistant bacteria were

isolated and used to sequester Cd from water and wastewater[45- 48].

The activated sludge process is a biological method of wastewater treatment that is performed by a variable and mixed community of microorganisms in an aerobic aquatic environment. Bactria, fungi, protozoa, and rotifers constitute the biological component or biological mass of activated sludge.

Activated sludge produced in the biological treatment facilities of the treatment plant is considered a good bioadsorbent for the removal of heavy metal ions from industrial wastewater.

The purpose of this investigation is to study the bioadsorption characteristics of the Cd^{+2} ion from synthetic water using activated sludge obtained from a treatment unit of a factory. The influence of the initial Cadmium ion concentration, initial pH, adsorbent mass, adsorbent particle size and temperature on the capacity of the adsorbent has been investigated.

2- Materials & methods

2.1- Bioadsorbent

Waste activated sludge samples were collected from the system of wastewater refining, milk factory. The collected samples were filtered and oven dried at 90ºC for 24 h. The dried biomass was ground in a mortar and sieved into several fractions, greater than 0.5 (>0.5), 0.250-0.5, 0.125-0.250, 0.063-0.125 and smaller than 0.063mm (<0.063) size.

The organic matter content in the activated sludge was measured by burning in an electrical furnace about 90min at 300ºC.

FT-IR analysis of dried activated sludge was determined by Bruker, Tensor 27 FT-IR system.

Activated sludge pH was measured using 691 Metrohm pH meter. 1g of biomass was suspended in 250 ml of double distilled water, the mixture was stirred for 2 hours, giving ample time for equilibrium to be reached, then the pH was measured.

The density was measured by weighing a certain volume of the adsorbent.

2.2- Adsorbate

Stock solution of l000 ppm concentration of Cd^{+2} was prepared by using analytical grade $3CdSO_4.8H_2O$ provided by Merck company and stored at room temperature. This stock solution was used to prepare dilute solutions of Cadmium ion by dilution with double distilled water.

2.3- Analysis

Cadmium ion concentration in the solutions before and after equilibrium were determined with a pu9100x Philips atomic absorption spectrophotometer. Solution pH was measured with a 691 Metrohm pH meter using a combination glass electrode. A known quantity of suspension was taken. This sample was centrifuged and supernatant was separated. Cadmium ion concentration was measured in this solution.

2.4- Adsorbent capacity studies

The adsorbent capacity experiments were carried out in a 0.5L beaker equipped with stirrer. The mixing speed was maintained at 100 rpm. The needed mass of the adsorbent according to the experiment was added to the mixed vessel containing 250 ml of the Cadmium ion solution. The total volume of

the reaction mixture was kept at 250 ml. A 1ml sample of the solution was withdrawn different times from the vessel by a suitable syringe and Cadmium ion concentration was measured by atomic absorption spectrophotometer. Each experiment continued until equilibrium conditions were reached when no further decrease in the ion concentration was observed. The time needed to reach this point of equilibrium was about 3h. This procedure was repeated to study the influence of the adsorbent mass, adsorbent particle size, initial concentration of Cd^{+2}, temperature and initial pH on the value of the concentration of the Cd^{+2} in contact with the activated sludge in order to estimate the adsorbent capacity of biomass in each condition. Solution pH was maintained at a desired value by adding 0.1M H_2SO_4 or NaOH solution. All experiments were performed in duplicate.

The cadmium concentration retained in adsorbent phase (activated sludge) was calculated using the mass balance equation:

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (1)$$

where q_e is the amount of Cd adsorbed (mg adsorbate/g dsorbent) at equilibrium time; V is the solution volume in the vessel (L); C_o and C_e are the initial and equilibrium concentrations of the cadmium ion in solution (mg/L), respectively; m is dry mass of the adsorbent (g).

The removal efficiency, E_r, of the adsorbent on the metal ion is defined as:

$$E_r = \frac{C_0 - C_e}{C_0} * 100 \quad (2)$$

and

$$E_r = \frac{C_0 - C}{C_0} * 100 \quad (3)$$

where C is the t time concentration of the metal ion (mg/L).

2.5- Adsorption isotherm study

Adsorption isotherm experiments were performed by adding 1 g of the dried activated sludge to 250 ml of metal ion solution in a glass bottle with screw cap. The initial concentration of cadmium ion varied from 15 to 120 ppm. The mixtures were placed in a shaker bath at constant temperature for 3 h. The solutions were then centrifuged and the filtrate was analyzed. The filtrate samples were analyzed by atomic absorption spectrophotometer. This procedure was repeated at three different temperatures of 30, 45 and 60ºC.

3- Results and discussion

3.1- Adsorbent properties

Table 1 shows some properties of the activated sludge used in this investigation.

The organic matter in sludge contains many types of functional groups such as the amino and the carboxyl groups and many others. These groups are expected to play an important role in the adsorption process of the ion. In addition, the low density of the sludge indicates the ease of suspending the sludge in the solution. The pH value indicates that this sludge can be considered as a weak acid material.

The FT-IR spectra of dried activated sludge was given in Fig. 1.

Table 1. some properties of the activated sludge

Organic matter	pH	C_{Cd}^{+2}(ppm)	Density(g.ml^{-1})	ash
40%	5.5±0.2	0	1.38	59.79

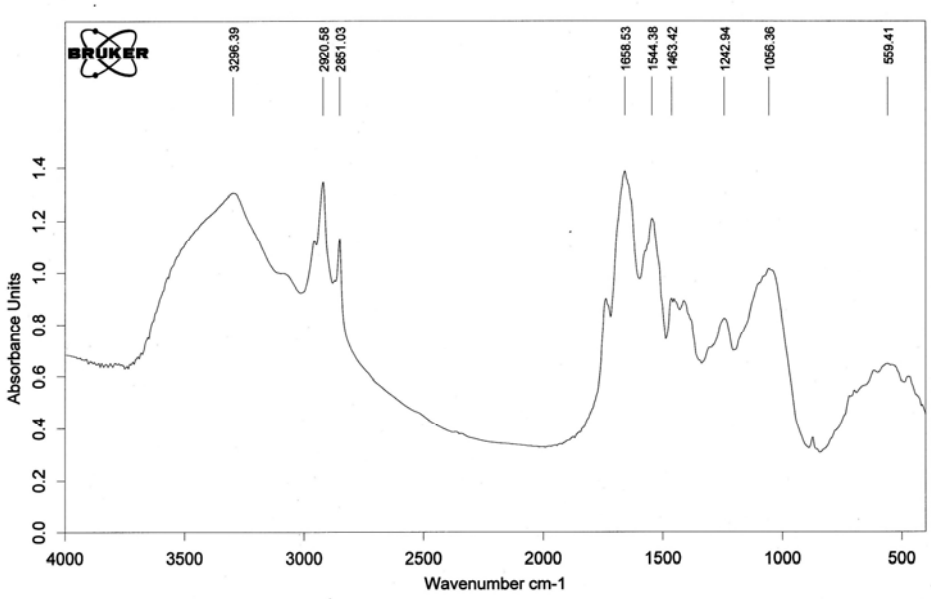

Figure 1. FT-IR spectra of dried activated sludge

Spectra analysis of FT-IR spectrum showed the groups of –OH, and C-O-C at 1463 and 1056cm^{-1}, and amide I group at 1658 and 1544cm^{-1}. These groups play an extremely important role in binding of Cadmium ion.

3.2- Effect of adsorbent particle size

Removal efficiency was measured at contact times from 0 to 180 minutes for different adsorbent particle size. All tests were carried out at room temperature, with 0.5g of biomass and 60 mg.L^{-1} of Cadmium ion concentration. Initial pH was 5.5 ± 0.2.

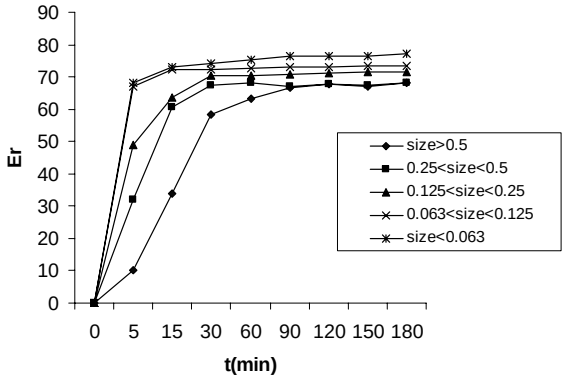

Figure 2. Removal efficiency of the activated sludge at different contact times in different adsorbent particle size

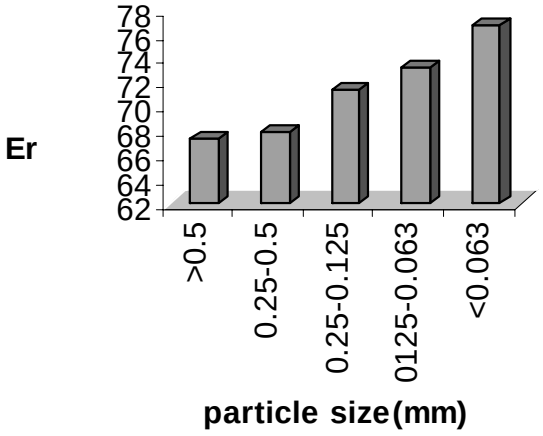

Figure 3. The influence of the adsorbent particle size on the removal efficiency

Figure 2 shows the removal efficiency (calculated from equation (3)) of the activated sludge increased with contact time at all adsorbent particle sizes. It was also observed that Cadmium uptake is rapid for the first 15 min and thereafter it proceeds at a slower rate and finally is constant. This is probably due to a larger surface area of the activated sludge being available at the beginning for the adsorption of cadmium. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles. The increasing contact time increased the cadmium adsorption and it remained constant after equilibrium was reached in about 20 to 30 min for different adsorbent particle sizes. At this time, cadmium concentration in solution is equilibrium concentration. These observations show that the adsorbent particle size has little effect on equilibrium time, but this parameter does effect removal efficiency.

Fig. 3 shows the role played by the adsorbent particle size on the adsorptive properties of activated sludge. In this figure, Er was calculated from equation (2). The removal efficiency of the activated sludge is increased as the adsorbent particle sizes are decreased. This is due to a larger surface area of the activated sludge being available at the small particle sizes for the adsorption of cadmium. It can be seen from the figure that the removal efficiency increased from 67% to 77% as the particle size decreased from greater than 0.5mm to smaller than 0.063mm size.

3.3- Effect of pH

The influence of initial pH on the removal efficiency of the activated sludge is shown in Fig.4 and 5. All tests were carried out at room temperature, by 0.5g of biomass of the 0.25- 0.5mm adsorbent particle size and 60 $mg.L^{-1}$ of Cadmium ion concentration. Initial pH was adjusted at values below the metal precipitation and was controlled in experimental time. It has been calculated that the precipitation of cadmium starts at pH=8.5. Therefore, at higher pH values, the precipitation is dominant or both ion exchange and aqueous metal hydroxide formation (not necessarily precipitation) may become significant mechanisms in the metal removal process. This condition is often not desirable as the metal precipitation could lead to incorrect values of the adsorption capacity.

Cadmium adsorption was measured at the different contact times from 0 to 180 minutes and the different initial pH from 2 to 5.5 (Fig.4). Figure 4 shows, at very low initial pH value (pH=2) metal uptake is negligible,

therefore removal efficiency of the activated sludge is negligible too. There is also little change in the removal efficiency at different contact times. At high initial pH values, the removal efficiency initially increases with time and finally is constant. At this time, cadmium concentration in solution is equilibrium concentration. In this figure (Fig. 4), Er was calculated from equation (3). These observations show that the initial pH has an effect on the removal efficiency. Equilibrium concentrations in every pH were used for calculating Er (equation (2)) in Fig. 5. The removal efficiency of the activated sludge increases as the pH increases (Fig. 5). It is evident from Fig. 5 that increasing the initial pH from 2 to 5.5 increased the removal efficiency from 11% to 68%.

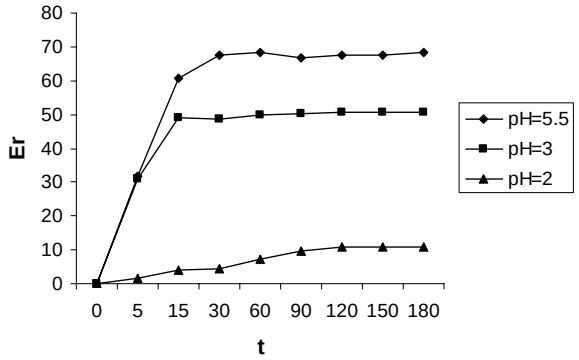

Figure 4. Removal efficiency of the activated sludge at different contact times in different initial pH

Adsorption of cadmium on the adsorbent depends upon the nature of the adsorbent surface and the species distribution of the metal cation. Surface distribution mainly depends upon the pH of the system. The primary metal ion species in the pH range studied are Cd^{+2} and $CdOH^{+}$ [49]. The percent adsorption of metal ion decreased with the decrease in pH, because protons compete with metal ions for sorption sites on the adsorbent surface and because the contaminant decreases the negative charge of the same surface.

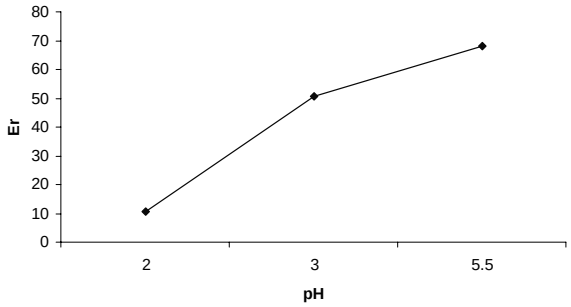

Figure 5. The influence of initial pH on removal efficiency

Experimental results showed that as cadmium uptake is by sludge, the solution pH is changed. Fig. 6 shows the pH evolution versus time for different initial pH. At low initial pH value (pH=2), pH remained constant during the experiment time. For initial pH values 3 and 5.5, the trend is to reach, within the first 15 min, and remain constant for the rest of the biosorption process. According to Fig. 4, after this time, cadmium uptake is almost constant and does not change either.

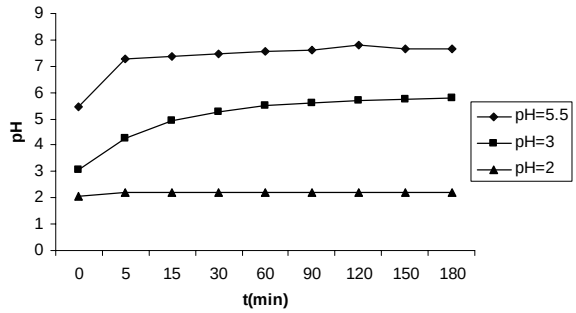

Figure 6. The pH evolution versus time for different pH

3.4- Effect of adsorbent mass

Effect of adsorbent mass on the removal efficiency was studied by different amounts of adsorbent. 0.5, 1, 1.5 and 2 g of biomass were tested with 250ml 60 $mg.L^{-1}$ of Cadmium ion concentration at room temperature and initial $pH=5.5\pm0.2$, in order to obtain the optimum biomass concentration corresponding to a maximum binding capacity.

Removal efficiency at different contact times for different amounts of adsorbent is shown in Fig. 7.

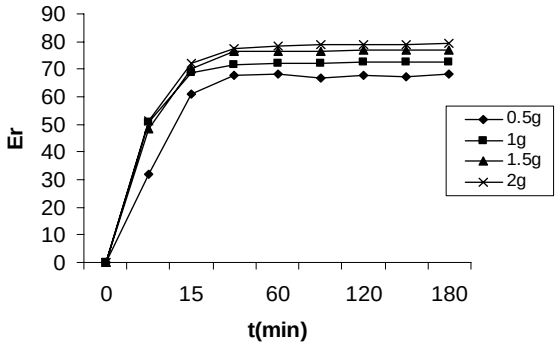

Figure 7. Removal efficiency of the activated sludge at different contact times in different adsorbent mass

Figure. 7 shows that removal efficiency initially increases rapidly with contact time and finally is constant at all biomass masses. At this time, no significant change in Er is observed. In this figure, E_r was calculated from equation (3). Therefore, biomass mass has little effect on equilibrium time but this parameter does have an effect on the removal efficiency. Equilibrium concentrations in every adsorbent mass were used for calculating E_r (equation (2)) in Fig. 8. Figure 8 shows that removal efficiency increases with an increase in the amount of activated sludge. This is due to greater availability of the suface area at higher concentrations of the adsorbent. The maximum removal efficiencies when 0.5,1,1.5 and 2 g of the activated sludge used are: 68, 73, 77 and 79%.

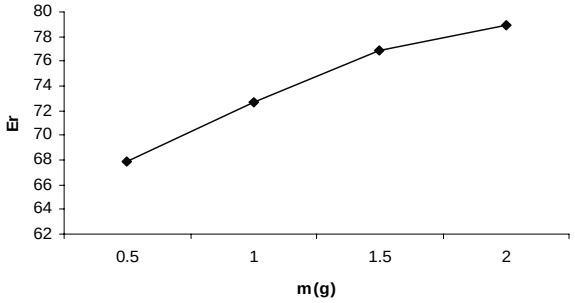

Figure 8. The influence of adsorbent mass on removal efficiency

3.5- Effect of initial Cadmium concentration

The effect of initial Cadmium concentration in the range of 15-20 mg/L on adsorption was investigated and is shown in Figs. 9 and 10. All tests were carried out at room temperature, by 0.5g of biomass of the 0.25-0.5mm particle size. Initial pH was 5.5 ± 0.2. Fig. 9 shows removal efficiency at contact times for the different initial Cadmium concentration. It is evident from this Figure that the removal efficiency initially increased with time and finally was constant at all initial Cadmium concentrations. At this time, the cadmium concentration in the solution is the equilibrium concentration. In this figure, E_r was calculated from equation (3). Therefore, initial Cadmium concentration has little effect on equilibrium time, but this parameter does have an effect on the removal efficiency. Equilibrium concentrations in every adsorbate concentration were used for calculating the E_r (equation (2)) in Fig. 10. Figure. 10 shows that the removal efficiency

decreases with the increase in the initial concentration of Cadmium.

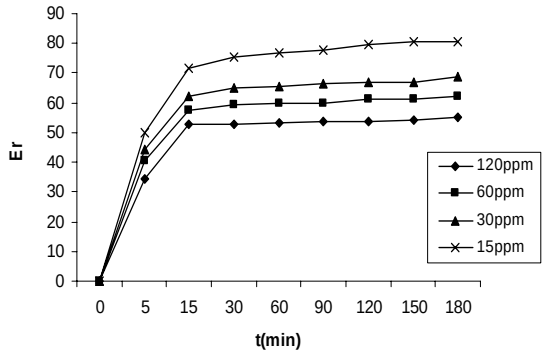

Figure 9. Removal efficiency of the activated sludge in different initial Cadmium concentration at different times

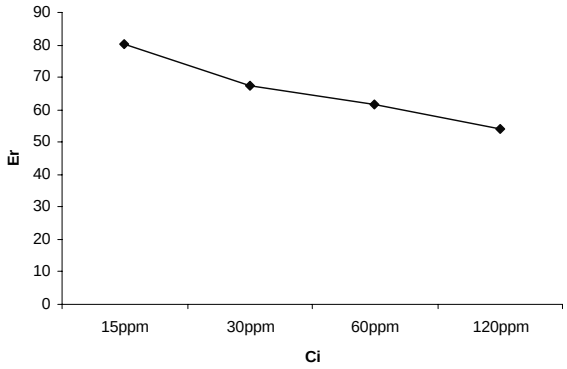

Figure 10. The influence of initial Cadmium concentration on the removal efficiency

The initial cadmium concentration provides the necessary driving force to overcome the resistances to the mass transfer of cadmium between the aqueous phase and the solid phase. The increase in initial cadmium concentration also enhances the interaction between cadmium and the activated sludge. Therefore, an increase in initial concentration of cadmium enhances the adsorption uptake of cadmium. This is due to the increase in the driving force of the concentration gradient produced by the increase in the initial cadmium concentration. This results in higher adsorption [50-52].While the removal efficiency was found to be 80% for a 15 mg/L initial concentration, this value was 54% for 120 mg/L.

3.6- Effect of temperature

The adsorption of cadmium on activated sludge was investigated as a function of temperature in the different initial concentrations of Cadmium and maximum uptake was obtained. Experiments were performed at temperatures of 303, 318 and 333 K for the initial cadmium concentrations of 15, 30, 60 and 120mg/L (Fig. 11). All tests were carried out by 1g of adsorbent of the 0.25- 0.5mm adsorbent particle size and initial pH of 5.5 ± 0.2.

As seen in Fig. 11, the adsorption ability for the uptake of the Cd^{+2} ion increases with increasing temperature for the same initial Cadmium concentration. The removal efficiency increased from 54.27 to 61.15 for the initial cadmium concentration of 120mg/L, from 61.57 to 66.33 for the initial cadmium concentration of 60 mg/L, from 67.60 to 75.48 for the initial cadmium concentration of 30 mg/L, from 80.20 to 82.29 for the initial cadmium concentration of 15 mg/L, with an increase in temperature from 303 to 333K (Fig. 11). This means that the increase in the adsorption rate was more significant than that of the desorption rate as the temperature increases, which implies that the adsorption affinity increases.

Equilibrium concentration was obtained at every initial concentration and temperature. Figure. 12 shows the amount of Cd adsorbed (mg adsorbate/g dsorbent) at equilibrium time (q_e) at different temperatures.

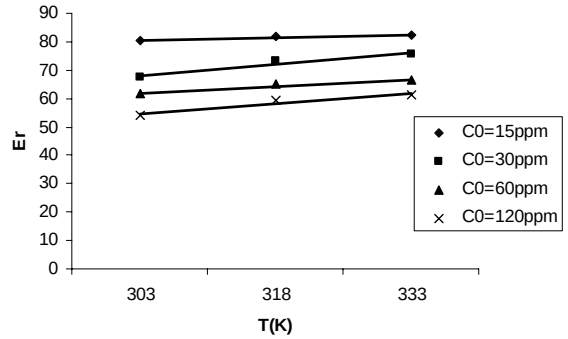

Figure 11. Removal efficiency of the activated sludge in different initial Cadmium concentrations and temperatures

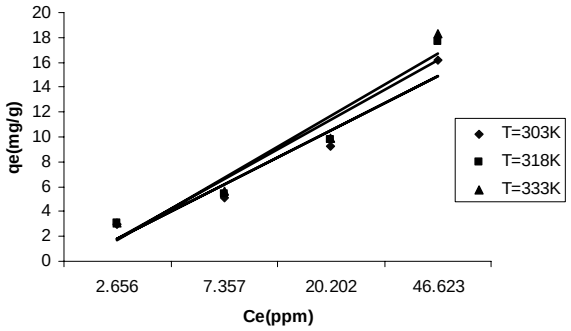

Figure 12. Adsorption isotherms at different temperatures

4- Adsorption isotherms

The equilibrium established between adsorbed metal ions on the biosorbent and unadsorbed metal ions in solution can be described by adsorption isotherm models[53]. In general, the adsorption isotherm describes how adsorbates interact with adsorbents, and thus is critical in optimizing the use of adsorbents. The analysis of the isotherm data, by fitting them to different isotherm models is an important step in finding a suitable model that can be used for design purposes.

Several isotherm equations are available, and two important isotherms were selected for this study: the Langmuir and Freundlich isotherms. The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogeneous sites within the adsorbent, and it has been used successfully for many adsorption processes of monolayer adsorption[54]. The well-known equation of the Langmuir isotherm is:

$$q_e = \frac{q_0 K_L C_e}{1 + K_L C_e}$$

where q_0 is the maximum metal uptake under the given conditions, K_L is a constant related to the affinity between the adsorbent and the adsorbate.The linear form of the Langmuir model is:

$$\frac{C_e}{q_e} = \frac{1}{q_0 K_L} + \frac{C_e}{q_0}$$

The second model is the Freundlich model which is an emprical equation used to describe heterogeneous systems. The Freundlich isotherm assumes that the adsorption occurs on heterogeneous surface at sites with different energies of adsorption and with non-identical adsorption sites that are not always available[54].

This model can be written as:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (4)$$

where K_F and n are Freundlich constants, which are correlated to the maximum adsorption capacity and adsorption intensity, respectively. The linear form of this model takes the form:

$$\log q_e = \log K_F + (\frac{1}{n}) \log C_e \quad (5)$$

It is generally stated that the values of *n* in the range of 1 to 10 represent good adsorption [55].

The adsorption isotherms were studied at different temperatures. Figure 13 and 14 show a plot of linear Langmuir equation as C_e/q_e versus C_e and linear Freundlich equation as log q_e versus log C_e, respectively.

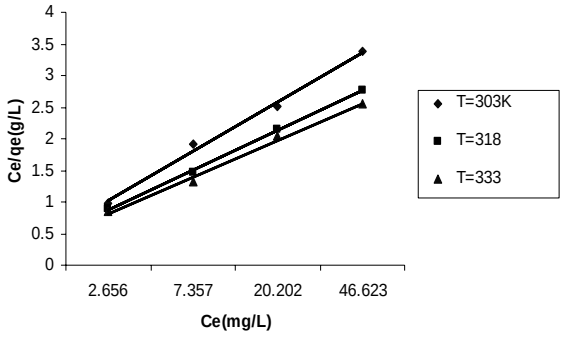

Figure 13. Langmuir plot of the bioadsorption of Cd^{2+}

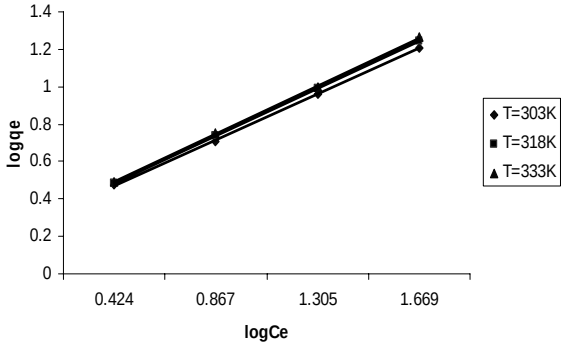

Figure 14. Freundlich plot of the bioadsorption of Cd^{2+}

Table 2 shows the values of the two models parameters at the three different temperatures. It is evident from the high values of R^2 that the data continue to fit the linear regression of both models. But, the Freundlich isotherm is obeyed better than the Langmuir isotherm, as is evident from the values of the regression coefficients. In addition, the data presented in Table 2 revealed that the values of q0 indicate that increasing the temperature will increase the maximum adsorptive capacity. The maximum adsorption capacities, q0, for Cadmium ion onto activated sludge at 303, 318, and 333 K were found to be 1.283, 1.581 and 1.726 mg/g, respectively.

The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor (R_L), which is defined by the following relationship [55]:

$$R_L = \frac{1}{1 + K_L C_0} \tag{6}$$

The parameter R_L indicates the shape of the isotherm accordingly. According to the value of R_L, the isotherm shape may be interpreted as follows:

$R_L > 1.0$	Unfavorable
$R_L = 1.0$	Linear
$1 > R_L > 0$	Favorable
$R_L = 0$	Irreversible

The results given in Table 2 show that the values of *n* are in the range of 1 to 10. The values of *n* in the range of 1 to 10 represent good adsorption. The values of R_L in this table show that the adsorption of Cadmium by activated sludge is favorable.

Based on the above results, activated sludge, an inexpensive and easily available material, can be an alternative for more costly adsorbents used for the removal of Cadmium ions in wastewater treatment processes.

5- Conclusions

In this study, the capability of the use of dried activated sludge was collected from the system of wastewater refining of a milk factory for removing Cd(II) was examined. Based on the experimental results the following conclusions can be drawn.

Activated sludge collected from the system of wastewater refining of a milk factory, can be easily applied as a cheap bioadsorbent for heavy metal ion Cd^{2+}. The removal of cadmium ions by adsorption on activated sludge was found to be rapid at the initial period of contact time and then slows down with increasing contact time.

The FT-IR analysis showed that the amide I group, –OH, and C-O-C groups play an extremely important role in the binding of Cd(II).

The isotherm experiments conducted at constant temperature showed that the biosorptive capacity of activated sludge was highly dependent on temperature, initial pH, initial cadmium ion concentration, adsorbent mass and adsorbent particle sizes.

The removal efficiency of the activated sludge for the same initial Cadmium concentration was found to increase as the temperature increased.

Initial pH plays a major role in the adsorption process. The optimum pH for the removal of Cd^{2+} from the aqueous solution under the experimental conditions used in this work was 5.5 ± 0.2.

Increasing the initial cadmium ion concentration and adsorbent particle sizes decreased the removal efficiency.

The removal efficiency of the activated sludge increases as the biomass mass increases.

The Langmuir and Freundlich Eq. were used to model biosorbed metal ions on the biosorbent and unbiosorbed metal ions in solution. The data show that the Freundlich equation provides a suitable description of the experimental data because of higher values of the correlation coefficients. Furthermore, the corresponding parameters indicate favourable and good adsorption in all cases.

The present investigation indicates that maximum biosorption capacity (q_{max}) is at 333K.

We can use the activated sludge that was collected from the system of wastewater refining of a milk factory to eliminate cadmium ions from waste water and their refinement, considering the low cost of the sludge substrast and also its availability.

6- Acknowledgment

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