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Investigation of Cadmium (II) Ions Biosorption onto Pretreated Dried Activated Sludge

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Abstract: Problem statement: Heavy metals have been one of hazardous components in industrial effluents that can be damaged on the environment by discharging uncontrolled wastewater. The aims of this investigation were biosorption of Cd (II) ions onto pretreated dried activated sludge and determination of kinetic and isotherm of biosorption. **Approach:** Activated sludge was obtained from Tehran municipal wastewater treatment plant. Activated Sludge was dried and used for biosorbtion of Cd (II) ions from aqueous solution. Dried Activated Sluge (DAS) was pretreated with three different solutions (H_2O_2, NaOH and ethanol). Biosorption capacity of different types of DAS to remove Cd (II) ions was investigated as a function of Cd (II) concentrations at variable initial Cd (II) concentrations between 10 and 500 mg L^{-1} with a DAS particle size 0.2-0.3 mm using batch biosorption experiments. **Results:** Biosorption of Cd (II) by Dried Activated Sludge (DAS) was found to perform better than the others after pretreatment with H_2O_2. The maximum biosorption capacity was given 256.41, 217.39, 212.77 and 204.08 mg g^{-1} for the H_2O_2, NaOH; Ethanol pretreated and untreated DAS, respectively. The pseudo-second order kinetic model was found to be more suitable than the pseudo-first order kinetic model to correlate the experimental data for all types of DAS (R^2>0.9). The Freundlich isotherm was found to fit the experimental data slightly better than the Langmuir isotherm model for all pretreated and untreated DAS (R^2>0.99). **Conclusion:** It can be concluded that pretreatment DAS yield higher Cd (II) biosorption capacity, especially DAS that pretreated with H_2O_2.

Key words: Wastewater, chrome, sorbtion, isotherm, kinetic

INTRODUCTION

Heavy metal ions present in some industrial effluents have detrimental effects on the environments such as water and soil[1-5]. Conventional methods for removal of heavy metals from industrial wastewater such as: chemical precipitation, ion-exchange, adsorption, solvent extraction were found to be ineffective or expensive and require high capital and operating costs, also may result large volumes of sludge causing disposal problems[1,5-10]. Therefore, recent researches have been focused on use of non-conventional alternative including different biomaterials such as: waste sludge, algae, yeast and fungal biomass[1,5,6]. Biomaterials are environmental-friendly, cost-effective, highly selective, high biosorption capacity and high efficiency in detoxifying dilute wastewater[1,5,7-9]. Biosorption of metal ions is the passive binding of heavy metal ions to biopolymers on the cell wall of organisms. On the other hand, passive binding of heavy metal ions was defined as biosorption and active binding on the cell wall of live organisms defined as bioaccumulation[1,5,10]. Dead biomaterial is more applicable than living biomaterial, because living system requires nutrients and maintenance of living biomass is very difficult in high toxicity environment. In addition, dead biomaterials can be easily regenerated and reuse[7,8,10]. Waste activated sludge as a biomaterial, for removal of heavy metal ions can be used because of low cost and its availability[1,11-15]. Activated sludge consists of microbial population such as bacteria and protozoa[1]. Bacterial biomass in activated sludge is a natural biosorbent for heavy metal ions because of its negative cell wall charge. Cell wall of bacteria consists of polymeric substances that contain negatively charged functional groups, such as carboxyl, phosphate and

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sulfate[1,13,16,17]. In a few literatures, biosorption of heavy metal ions onto pretreated activated sludge was studied[2]. In this study, dried activated sludge was pretreated with different solutions and the kinetic and isotherm models of the biosorption were investigated.

MATERIALS AND METHODS

Experimental system: Batch system was performed using 250 mL erlenmayer flask and shaker at 150 rpm at room temperature (25°C) for 240 min to achieve sorption equilibrium time for experiments. Cadmium (II) ions (in form of Cd $(NO_3)_2$) and Dried Activated Sludge (DAS) were added to the flasks to obtain desired concentrations of Cd (II) (10-500 mg L^{-1}) and DAS (1 gL^{-1}) in the solution. In selection experiments the DAS and Cd (II) concentrations were 1 gL^{-1} and 50 mg L^{-1}, respectively. The pH was adjusted to 4 in all selective experiments. After shaking, Samples were collected from the erlenmayer flasks for analysis. A control flask, without biosorbent (DAS) with 50 mg L^{-1} Cd (II) ions, was used to determine Cd (II) removal in the absence of the biosorbent. The pH values were adjusted by using NaOH or H_2SO_4 solutions in all experiments. All biosorption experiments were carried out in triplicates to check the precision of results[18-21].

Experimental procedure: Activated sludge was obtained from a municipal wastewater treatment plant in Tehran, Iran. The sludge was ground and pretreated using three different solutions including H_2O_2, NaOH and ethanol in order to activate the functional groups for binding heavy metal ions[2]. Two hundred milliliters of pretreatment solution were mixed with 2 g of DAS in a 250 mL erlenmeyer flask and placed on a shaker at 150 rpm for 6 h for pretreatment[1]. Activated sludge was washed with deionized water after pretreatment. Washed activated sludge was dried at 60°C until constant weight, reground and sieved by using standard sieve (particle size between 0.2-0.3 mm).

Analytical methods: The withdrawn samples from the erlenmeyer flasks were filtered. Samples were analyzed for Cd (II) ions concentration by an atomic adsorption spectroscopy (BRAIC-WFX-130) according to method no.3111B from standard methods for the examination of water and wastewater[22].

Adsorption equilibrium: The equilibrium established between adsorbed metal ions on the biosorbent and unabsorbed metal ions in solution can be described by adsorption isotherm models[10]. Two different isotherms, the Langmuir and Freundlich were used for describing adsorption equilibrium. The well known equation of the Langmuir isotherm is:

$$q_{eq} = q_m\left(\frac{C_{eq}}{K_d + C_{eq}}\right) \quad (1)$$

Where:

q_{eq} (mg g^{-1}) = The amount of biosorbed metal ions per unit weight of biosorbent

C_{eq} (mg L^{-1}) = Unbiosorbed metal ions concentration in solution

Q_m (mg g^{-1}) = The maximum amount of the biosorbent per unit weight of biosorbent to form a monolayer on the surface of biosorbent

b (Lm g^{-1}) = Related to the affinity of the binding sites

The Freundlich equation is:

$$q_e = K_F C_e^{1/n} \quad (2)$$

Where, n and K_F are the Freundlich constants that n and K_F are indicators of sorption intensity and sorption capacity, respectively[11,23]. The Freundlich model provides a more realistic description of biosorption by organic matter because of different binding sites. However, in most cases, both equations were fitted the experimental data reasonably well[10].The pseudo-first order and pseudo-second order kinetic models have been used In order to evaluate the mechanism of biosorption. The pseudo-first order kinetic equation is:

$$\frac{dq}{dt} = k_{1ads}(q_e - q) \quad (3)$$

Where:

q (mg g^{-1}) = The amount of adsorbed metal ions on the biosorbent at time t

k_{1ads} (min^{-1}) = The rate constant

The linear form of Eq. 4 is:

$$\log(q_e - q) = \log q_e \frac{k_{1ads}}{2.303} t \quad (4)$$

A straight line of log (q_e-q) versus time suggests the suitability of pseudo-first order kinetic model. The second-order kinetic equation is:

$$\frac{dq}{dt} = k_{2ads}(q_e - q)^2 \quad (5)$$

where, k_{2ads}(gm g^{-1} min^{-1}) is the rate constant. The linear form of Eq. 5 is:

$$\frac{t}{q} = \frac{1}{k_{2ads}q_e^{\ 2}} + \frac{1}{q_e}t \quad (6)$$

If the second-order kinetics be suitable, the plot of t/q against t of Eq. 6 should give a linear form[2,23,24].

RESULTS

Effect of Cd (II) concentration: Three different types of pretreated DAS were used in this set of experiments. Cadmium (II) ion concentration was 50 mg L^{-1} in this experiment while the DAS concentration and pH were constant at $1gl^{-1}$ and 4, respectively. Variations of the Cd concentration against time are shown in Fig. 1 for different pretreated DAS. Figure 1 shows that biosorbtion of Cd (II) ion concentrations increased with time and reached equilibrium after 60 min for different pretreated and untreated DAS. Hence, sorption equilibrium time was given 60 min, approximately. To investigate initial effects of Cd (II) ion concentration a set of experiments was designed with varied ion concentrations between 10 and 500 mg L^{-1} while the different pretreated DAS concentration and pH were constant at 1 gL^{-1} and pH 4, respectively. Figure 2 shows that rate of biosorption (as mg g^{-1}) was increased with increasing concentration of Cd (II). The equilibrium biosorbed Cd (II) concentration was given 211.63, 131.905, 115.52 and 114.02 mg g^{-1} for H_2O_2, NaOH, Ethanol pretreated and untreated DAS, respectively.

Kinetic studies: Pseudo-first and Pseudo-second order kinetic models were used to correlate the experimental data (Eq. 3 and 4). Experimental data were plotted in form of log (qe-q) against time in Fig. 3 to evaluate the suitability of the pseudo-first order model and were plotted in form of t/q versus time to show the suitability of the Pseudo-second order kinetic model in Fig. 4.

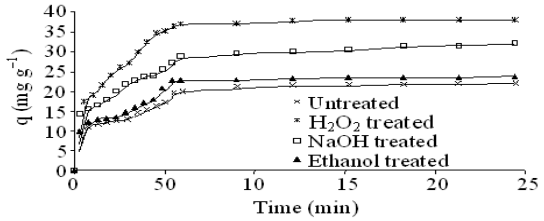

Fig. 1: Variation of biosorbed Cd (II) concentration with time using different types of DAS. pH = 4, mixing speed = 150 rpm, biosorbent mass = 1 g L^{-1}, contact time = 4 h, metal concentration = 50 mg L^{-1}.

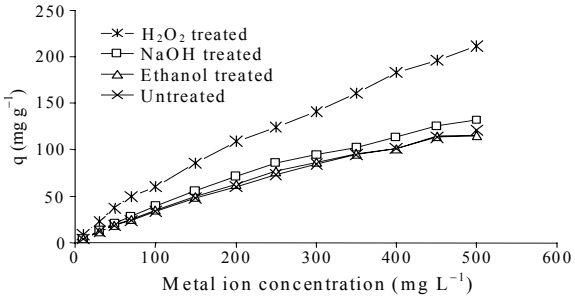

Fig. 2: Variation of biosorbed Cd (II) concentration with initial Cd (II) ion concentration using different types of DAS. pH = 4, mixing speed = 150 rpm, biosorbent mass = 1 g L^{-1}, contact time= 60 min

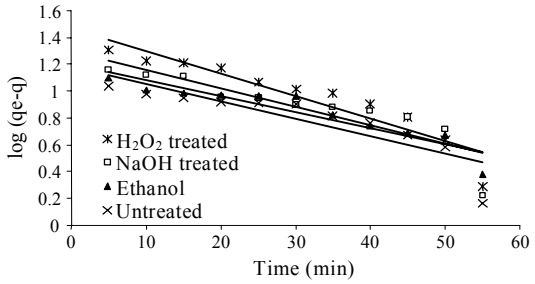

Fig. 3: Pseudo -first order biosorption kinetic of Cd(II) onto different types of DAS. pH = 4, mixing speed = 150 rpm, biosorbent mass = 1 g L^{-1}, contact time = 60 min

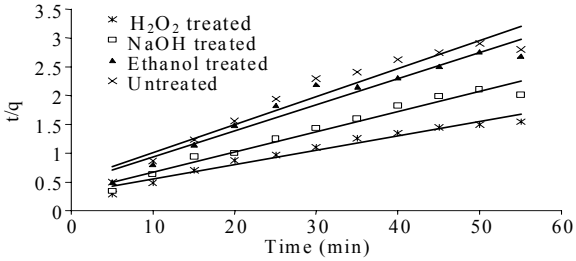

Fig. 4: Pseudo-second order biosorption kinetic of Cd (II) onto different types of DAS. pH = 4, mixing speed = 150 rpm, biosorbent mass = 1 g L^{-1}, contact time = 60 min

Correlation coefficients of the pseudo-first and pseudo-second order were shown in Table 1.

Adsorption isotherm analysis: The adsorption isotherms were studied with different types of pretreated DAS. Figure 5 and 6 show a plot of linear

Table 1: Correlation coefficients of Pseudo -first and Pseudo -second order kinetic models

order kinetic models

Ion	Type of sludge	Pseudo-first order R^2	Pseudo-second order R^2
Cd(II)	untreated	0.7581	0.9358
	H_2O_2 treated	0.8736	0.9657
	NaOH treated	0.7635	0.9672
	Ethanol treated	0.8606	0.9446

Langmuir equation as C_e/q_e versus C_e and linear Freundlich equation as log q_e versus log C_e, respectively.

The values of isotherm constants and maximum biosorption capacity (q_{max}) were given in Table 2. The maximum biosorption capacity, q_{max}, were determined as 256.41, 217.39, 212.77 and 204.08 mg g^{-1} for Cd(II) removal with H_2O_2, NaOH, ethanol pretreated and untreated DAS, respectively.

Table 2: Langmuir and Freundlich parameters for biosorption of Cd (II) ion onto different types of DAS.

		Langmuir parameters			Freundlich parameters		
Ion	Type of sludge	Q_{max}	R^2	b	K_F	n	R^2
Cd(II)	untreated	204.082	0.9589	0.00320	1.148	1.262	0.9930
	H_2O_2 treated	256.410	0.9139	0.01000	7.290	1.680	0.9960
	NaOH treated	217.390	0.9820	0.00390	1.623	1.312	0.9943
	Ethanol treated	212.766	0.9796	0.00321	1.239	1.273	0.9946

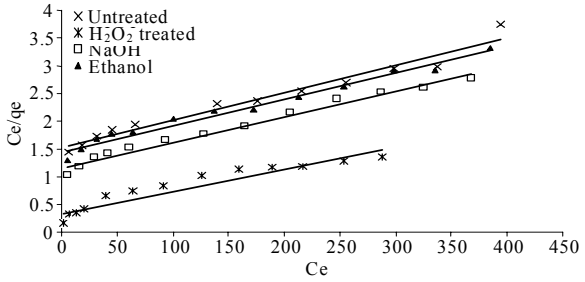

Fig. 5: Langmuir isotherm plot of the biosorption of Cd (II) onto different types of DAS and untreated DAS. pH = 4, mixing speed = 150 rpm, variations of Cd (II) concentration (5-500), biosorbent mass = 1 g L^{-1}, contact time = 60 min

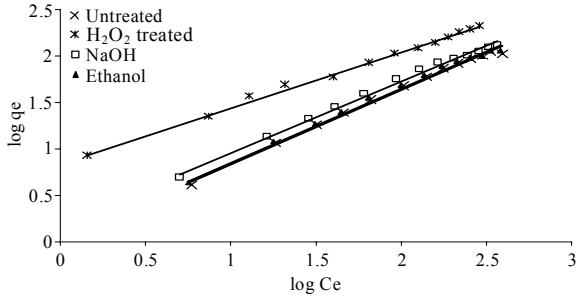

Fig. 6: Freundlich isotherm plot of the biosorption of Cd (II) onto different types of DAS. pH = 4, mixing speed = 150 rpm, variations of Cd (II) concentration (5-500), biosorbent mass = 1 g L^{-1}, contact time = 60 min

DISCUSSION

In the present study, biosorption of Cd(II) ions has been evaluated as a treatment technology for cadmium removal from industrial effluents. Cadmium removal efficiency at different types of pretreated DAS and in various times was evaluated. The finding shows that duration of time is important to reach equilibrium in reactor which is agreed with some literatures that report indicating higher sorption equilibrium time[1,2,18]. For example, Yuncu et al. were shown that biosorped heavy metal ions concentrations increased with time and reached equilibrium after 90 min[17].

Variations of Cd(II) ion concentration from 10-500 mg L^{-1} show that biosorption of Cd(II) ions increased with increasing concentration of ions. In agreement with this study, Xuejiang *et al.*[11] and also other researchers have shown that the equilibrium biosorption capacities increased with increase of initial metal ion concentration[1,3,11].

Pseudo-second order kinetic model was found to be more suitable for biosorption of Cd (II) onto all types of pretreated and untreated DAS because of larger correlation coefficients as compared to the other model. Wang *et al.*[14] were reported that Pseudo-second order kinetic model represented the data better than the Pseudo-first order model for biosorption of dye by anaerobic sludge. Also in the other studies were shown that Pseudo-second order kinetic model correlated the data better than the Pseudo-first order model for biosorption of different metal ions[5,11,14].

The Langmuir and Freundlich Eq. 1 and 2 were used to model biosorbed metal ions on the biosorbent and unbiosorbed metal ions in solution[10].

The data in Table 2 show that the Freundlich equation provides a suitable description of the experimental data because of high values of the correlation coefficients. Present investigation indicates that maximum biosorption capacity (q_{max}) is belong to the treated DAS with H_2O_2. Yunus Pamukoglu and Fikret Kargi showed that H_2O_2 pretreatment solution to be more suitable than the other pretreatment solution because of higher capacity improved for biosorption[2].

The Freundlich model physically provides a more realistic description of adsorption by organic matter because it accounts for different binding sites. But, in most cases, both equations fit the data set reasonably well for the experimental data[10]. The other investigators showed that the equilibrium data fitted very well to both Langmuir and Freundlich models for Biosorption of different metal ions[4,11,23,25]. In the other researches were shown that biosorption of different metal ions onto biosorbents was fitted by Langmuir[2,5].

CONCLUSION

The capability of using untreated and pretreated DAS for biosorption of Cd (II) were examined, including equilibration time, effect of initial Cd (II) concentration, kinetic and isotherm studies. Experimental data was shown that most of the Cd (II) ions were sequestered from solution within 60 min and no considerable increase in biosorbed Cd (II) ions after 60 min occurred. Initial Cd (II) ion concentration affected the biosorption as mg g^{-1} at constant DAS concentration. The equilibrium adsorption capacities increase with increasing of initial metal ion concentration for all types of DAS. As the Cd (II) ion concentration increased, more binding sites on DAS were occupied by Cd(II) ions yielding larger biosorbed Cd(II) as mg g^{-1}[1,11]. Pseudo-first and Pseudo-second order kinetic models for the biosorption of Cd (II) onto untreated and pretreated DAS were discussed. Pseudo-second order kinetic model correlated the data better than the Pseudo-first order model for biosorption of Cd (II) ions onto pretreated and untreated DAS. The Freundlich isotherm was found to fit the experimental data slightly better than the Langmuir isotherm. Although the Langmuir isotherm model correlated obtained experimental data reasonably well. Among the three different pretreatment solutions, H_2O_2 was found to be more suitable than untreated DAS and the other pretreated DAS (NaOH and ethanol) that yielding higher Cd (II) biosorption capacity. The maximum biosorption capacity of pretreated DAS for the Cd (II) ions was found 256.41 mg g^{-1} for H_2O_2 pretreated DAS. It can be concluded that pretreatment of DAS yielding higher Cd (II) biosorption capacity, especially in the case of H_2O_2 pretreated DAS.

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