Journal of Advanced Scientific Research

Available online through http://www.sciensage.info

ISSN
0976-9595
Research Article

A STUDY ON BIOSORPTIVE REMOVAL OF HEAVY METAL CHROMIUM FROM AQUEOUS CHROMIUM SOLUTION USING APONOGETON NATANS ROOT POWDER

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ABSTRACT

Pollution is the main problem due to heavy metal discharges from industries. In this study *Aponogeton natans* roots powder (Family: Aponogetonaceae), a biosorbent was selected to remove the heavy metal chromium ion from aqueous chromium solution. Various parameters like pH, biosorbent dose, equilibrium time and metal ion concentration were investigated using batch studies for optimization. A kinetic model study and isotherm model fitting study were studied using Langmuir and Freundlich isotherms. The results revealed that it follows pseudo first order kinetic model and also fit in the Langmuir and Freundlich isotherms. The thermodynamic parameters ΔG, ΔH and ΔS are investigated and reported. The results are very much encouraging. So, it can be used as low cost biosorbent in controlling the pollution.

Keywords: Biosorbent, *Aponogeton natans*, Chromium, Kinetics, Thermodyanamic study.

1. INTRODUCTION

The discharge of heavy metals into drain water through industrial actions has become a big issue for humans and aquatic lives. The most familiar toxic pollutants are chromium, lead, cadmium, copper, and mercury. Chromium as a heavy metal is one of the top 16 toxic metals that have destructive effects on human health [1]. Cr(VI) is a strong oxidizing agent and is extremely toxic than Cr(III) [2]. It defectively influences the human being by oxidizing the building block of DNA and some protein molecules. The toxicity of Cr(VI) has negative effects such as skin irritation, asthma, ulceration, and severe diarrhoea. It harms the kidney, circulatory tissues, liver, and nerve tissues. Disclosure to high chromium quantity causes cancer in the digestive tract and lungs [3-5]. Therefore, extensive discharge of Cr (VI) roughly into aquatic sources of potable water has to be regulated through the enactment of legal standards and strict environmental control mechanism [6]. The maximum permitted concentration limit for Cr(VI) for drinking waters that is recommended by the Environmental Protection Agency (EPA) is 0.05 mg/L. Several techniques, such as membrane process, electrochemical precipitation, electrodialysis, ultrafiltration, reverse osmosis, and ion exchange, are possible to remove harmful metals from the aquatic medium [7, 8]. But, these methods are inadequate or costly when Cr(VI) is present in the wastewater at a low concentration. The adsorption technique stays the most preferred procedure because of its efficiency, non-hazardous technique, and low-priced method [9]. The recent adsorbents supply an attractive material, especially if the adsorbent is cheap and ready for use. As a result, we should pay close consideration to the use of natural biomass feasible in large quantities. In recent times, many researchers have achieved the sufficient elimination of Cr(VI) from wastewater, applying natural biomasses such as rice straw [10], Sterculia guttata shell [11], fish scales and egg shells [12], activated carbon derived from *Leucaena leucocephala* [13], mangrove leaf powder [14], garlic stem and horse chestnut shell [15], *Juniperus procera* sawdust, avocado kernel seeds and papaya peels [16], *Cornus mas* kernel shell, *Rosa canina* seed shell and *Musa cavendishii* peel [17]. The economic price of these adsorbents is insignificantly correlated to the price of ion-exchange resins or activated carbon. Most of these biomaterials consist of functional groups combined with polysaccharides, proteins, lignin, cellulose, and hemicellulose as major components. Cr(VI) uptake process is united with these functional groups [18]. The search for substituted advanced, cheap, eco friendly and sufficient biomass to replace the economically available biomasses is continuing.

In the current study, the adsorption was carried out with inexpensive *Aponogeton natans* roots powder in the elimination of Cr(VI) from the liquid phase. The batch adsorption applications were implemented under different criterions like adsorbent quantity, influence time, initial Cr(VI) concentration and pH. Additionally, kinetic models, adsorption equilibrium isotherms, and thermodynamics were completed in this research.

2. MATERIAL AND METHODS

2.1. Preparation of biosorbent

Appanogeton natans (kottikilangu) biomass was obtained from ponds in Gandhrvakottai, Thanjavur Dt., Tamil Nadu. *Appanogeton natans* were washed using tap water followed by double distilled water, dried under sunlight for 72 hrs to remove moisture content. The dried biosorbent were washed with hot water (70°C) to remove any soluble matter present and dried in over at 85°C for 48 hours. The oven dried *Apponogeton natans* biosorbent were powdered at sieved through 100 mesh sieves and store air tight polythene bottles for adsorption experiments.

2.2. Preparation and analysis of Cr(VI) solutions

For biosorption experiments, stock chromium (VI) solution of 1000mg/L, was prepared by dissolving an appropriate amount of chromium (VI) salt in de-ionized distilled water. Cr(VI) solutions of different concentrations were prepared by adequate dilution of stock solution with deionized distilled water. Before and after the experiments Cr(VI) content in the solutions were determined by spectrophotometer.

2.3. Batch biosorption studies

The experiment was carried out by the batch adsorption method in the standard flasks for a predetermined period using orbital shaker. In the adsorption, parameters such as pH, biosorbent dose, equilibrium time fixation and metal ion concentration were studied for optimization. The kinetic studies and isotherm study were carried out at different metal ion concentrations, *i.e.* 20ppm, 40ppm, 60ppm, 80ppm, and 100ppm by keeping temperature as constant at 450rpm for 2 hours. The adsorption was investigated by pseudo first order, pseudo second order. The thermodynamics study carried out at three temperatures 310, 320, and 330K. The measurement of absorbance of colour was done spectrophotometically.

The equilibrium adsorption capacity was evaluated using the equation:

$$q_e = (C_i - C_e)V\,W^{-1} \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where, q_e is (mg/g) is the equilibrium adsorption capacity, C_i and C_e (mg/g) are the initial and equilibrium concentrations, V is the volume of solution in 'L' , W is the mass of adsorbent in 'g'.

3. RESULTS AND DISCUSSIONS

3.1. Effect of pH

pH is one of the important factors affecting the biosorption of metal ions in the solution. The effect of biosorption of Cr(VI) onto *Aponogeton natans* was studied at pH for initial metal ion concentration 20 ppm for biosorbent dose 1g/L at time 30 mins and temperature 310K.

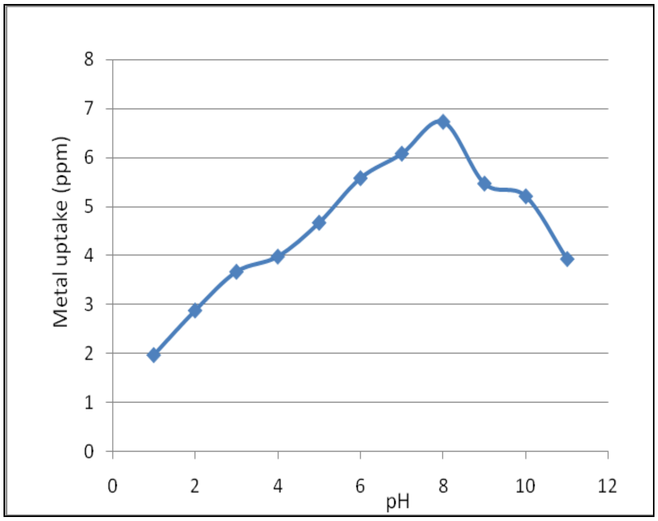


Fig. 1: Effect of pH on the metal ion uptake (Time: 30 min, Biosorbent dose: 1.0 g/L, Volume of the solution: 50ml, Temp. : 310K)

The metal ion uptake increases, as the pH of the solution increases from 1 to 8 and then decreases of pH up to 11. The maximum metal ion uptake was found to be at pH 8.

3.2. Effect of adsorbent dosage

The percentage of Cr(VI) metal ion adsorption increases with adsorbent dosage increases from 0.5g/L to 3.5 g/L. The maximum biosortption 66.25%, obtained at adsorbent dosage 2.5g/L. After that adsorbent dose 2.5g/L there is no increases in adsorption.

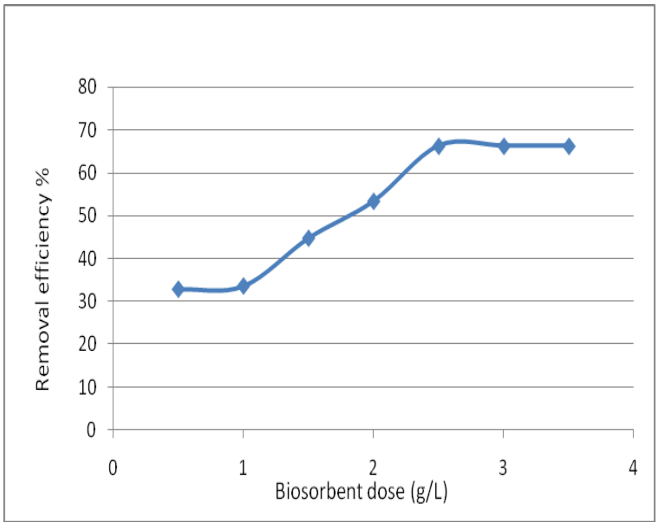


Fig. 2: Effect of adsorbent dose on removal efficiency (%) of Cr(VI) (Time:30min, pH:8, Volume of the solution:50mL, Initial metal ion concentration:20ppm, Temp.:310K)

3.3. Effect of contact time

The effect of contact time on removal of Cr (VI) ion is shown in Fig.3. According to results, an increase at contact time led to increase at surface adsorption rate to 40 min and then remains unchanged. Maximum adsorption occurred in the 40 min for pH 8, biosorbent dose 2.5g/L at Temp 310K for initial ion concentration 20ppm.

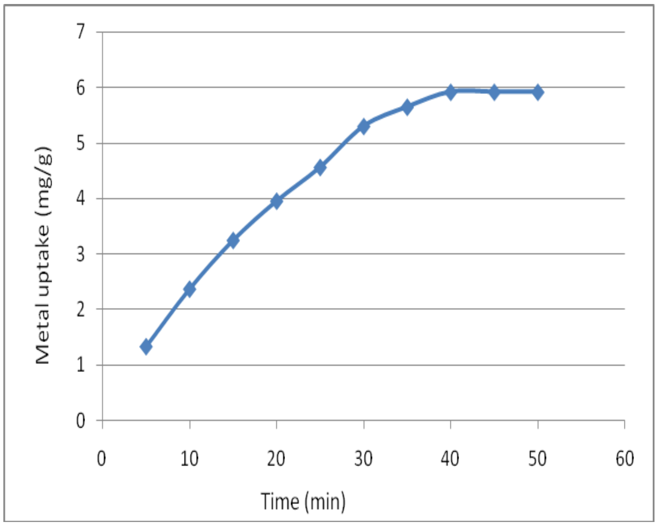
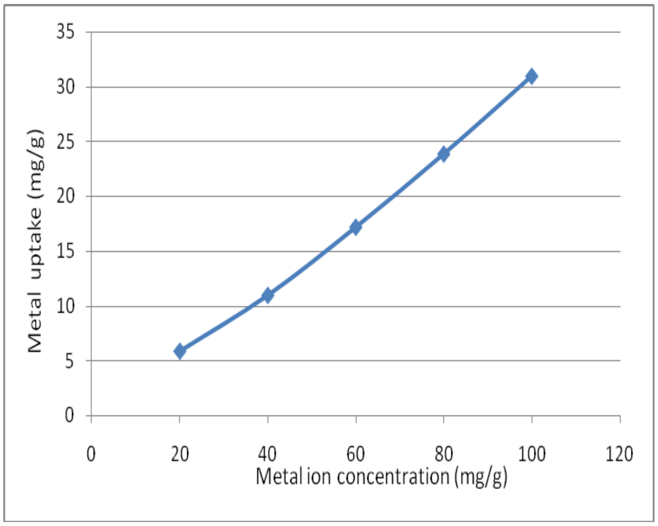


Fig. 3: Effect of contact time for Cr(VI) biosorption (Biosorbent dose: 2.5g/L; pH:8, Volume of the solution: 50mL, Initial metal ion concentration: 20ppm, Temp:310K)

3.4. Effect of initial concentration

From the Fig.4 it can be observed that optimised condition for biosorption at pH is 8, biosorbent dose 2.5g/L and equilibrium time is 40 mins.



Time: 40 min, pH 8, Volume of the solution50mL, Biosorbent dose: 2.5 g/L, Initial metal ion concentration: 20ppm to 100ppm. Temp:310K

Fig. 4: Effect of initial metal ion concentration on biosorption after adsorption of Cr(VI),

3.5. Kinetic study

The kinetics of Cr (VI) sorption on adsorbent was analyzed using two kinetic models. The pseudo first-order equation

$$\mathrm{Log}(q_e-q_t)=\log q_e-k_1t/2.303 \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Where, q_e is the mass of the material ion adsorbed (mg/g) at equilibrium time, q_t is the amount of the metal ion adsorbed at time‘t’ (min). For pseudo first order kinetic model, the sorption coefficient and equilibrium capacity q_e can be determined from the linear plot of log (q_e-q_t) versus time at different concentrations. The graph is shown in the Fig.5.

The pseudo second-order equation is given by

$$t/q_t= 1/ k_2q_e^2 + (1/q_e)t \ldots\ldots\ldots\ldots\ldots\ldots(3)$$

where k_1 and k_2 symbolize the pseudo first-order and pseudo second-order rate constants respectively. For pseudo second order kinetic model, the sorption coefficient and equilibrium capacity q_e can be determined from the linear plot of t/q_t versus time at different concentrations. The graph is shown in Fig.6.

From the kinetic study, the fact suggests the sorption of Cr (VI) ion follows pseudo- first order kinetic model than pseudo-second order kinetics. The result indicated that it doesn't follow pseudo second order kinetics because, its R^2 values are from 0.913 to 0.967 (Table 2). For the pseudo first order kinetics, R^2 values are from 0.999 to 1.0 (Table 1).

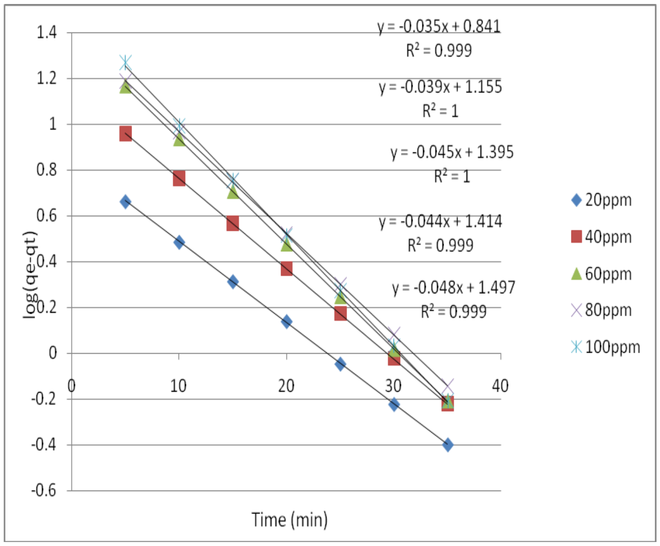


Fig. 5: Time Vs log (q_e-q_t) for pseudo first order kinetic model at 310K

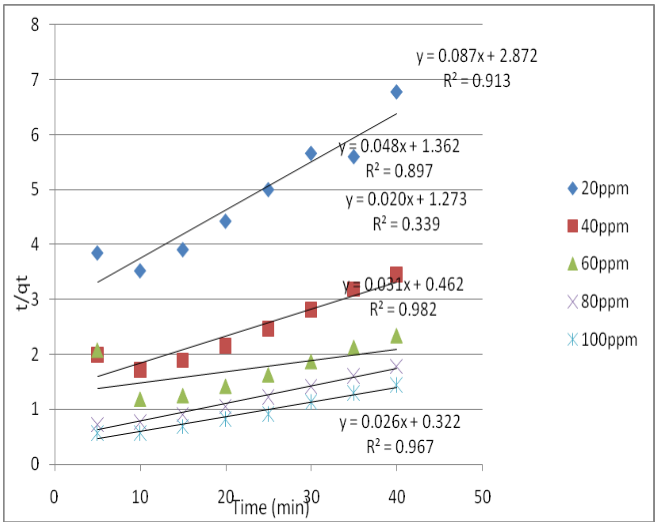


Fig. 6: Time Vs t/qt for pseudo second order kinetic model at 310K

Closure agreement between experimental and calculated kinetic constants and coefficient of correlation closure to unity indicated that the pseudo first order model better represents the experimental data. So, *Aponogeton natans* biosorbent follows pseudo first order kinetic model.

Table 1: Pseudo first order different values obtained from experimental of graph

Metal ion concentration (ppm)	Pseudo first order kinetic model from graph	Pseudo first order kinetic model graph	Pseudo first order kinetic model theoritical	Pseudo first order kinetic model graph	Pseudo first order kinetic model graph
	Log Qe(Exp) mg/g	Qe(Exp) mg/g	Qe(The) mg/g	R^2	K^1
20	0.841	6.93	5.9	0.999	-0.035
40	1.155	14.28	11.6	1	-0.039
60	1.395	24.83	17.11	1	-0.045
80	1.414	25.94	22.44	0.999	-0.044
100	1.497	31.40	27.6	0.999	-0.048

Table 2: Pseudo second order different values obtained from experimental of graph

Metal ion concentration (ppm)	Pseudo second order kinetic model from graph	Pseudo second order kinetic model graph	Pseudo second order kinetic model theoritical	Pseudo second order kinetic model from graph	Pseudo second order kinetic model graph
	Log Qe(Exp) mg/g	Qe(Exp) mg/g	Qe(The) mg/g	R^2	K^1
20	2.872	744	5.9	0.913	0.087
40	1.362	23.01	11.6	0.897	0.048
60	1.273	18.74	17.11	0.339	0.020
80	0.462	2.89	22.44	0.982	0.031
100	0.322	1.06	27.6	0.967	0.026

The theoretical and qe experimental values are very close for the pseudo first order kinetic model, for 20ppm q_e theoretical value is 5.9 and q_e experimental value is 6.93. whereas, the q_e theoretical and qe experimental values are not very close for the pseudo second order kinetic model, for 20ppm q_e theoretical value is 5.9 and q_e experimental value 744. So *Aponogeton natans* biosorbent follows pseudo first order kinetic model.

3.6. Adsorption Isotherms

The study of adsorption has been of great importance and significance in the treatment of water and waste water by adsorption principle in selecting an adsorbent for the removal of metal ions and colorants [19]. The adsorption data for the removal of Cr metal ion on biosorbent were used to fit the Freundlich and Langmuir isotherms

Freundlich isotherm: $\log q_e = \log k + (1/n) \log C_e$..............(5)

Langmuir isotherme : $(C_e/q_e) = (1/Q_o\ b) + (C_e/Q_o)$ ....(6)

Where, k and 1/n are the measures of adsorption capacity and intensity of adsorption, respectively. q_e is the amount Cr metal ion adsorbed per unit mass of adsorbent(in mgg^{-1}) and $C_e$is the equilibrium concentration of metal ion (in mg L^{-1}or ppm); Q_o and b are the adsorption capacity(in mg g^{-1}) and b is the Langmuir constant, which are the measures of monolayer adsorption capacity (in mgg^{-1}) and surface energy (in g L^{-1}), respectively. Further, the essential characteristics of the Langmuir isotherm can be described by a separation factor, R_L,which is defined by the following equation .

$R_L = [1 / (1 + bC_i)]$ ....(7)

Where, $R_L$is the separation factor, C_i and b are the initial concentration of metal ion (in mg L^{-1} or in ppm) and Langmuir constant (in g L^{-1}). The value of R_L, indicates the shape of the isotherm and nature of the adsorption process as given below:

R_L value	Nature of adsorption process
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

Table 3: Langmuir isotherm parameters, Temperature 310K

Q_{max}(mg/g)	111.11
R^2	0.998
K_L(L/mg)	0.0106
R_L	0.4854

Table 4: Freundlich isotherm parameters, Temperature 310 K

$1/n_f$	0.870
n_f	1.1494
R^2	0.999
K_f(L/mg)	1.4125

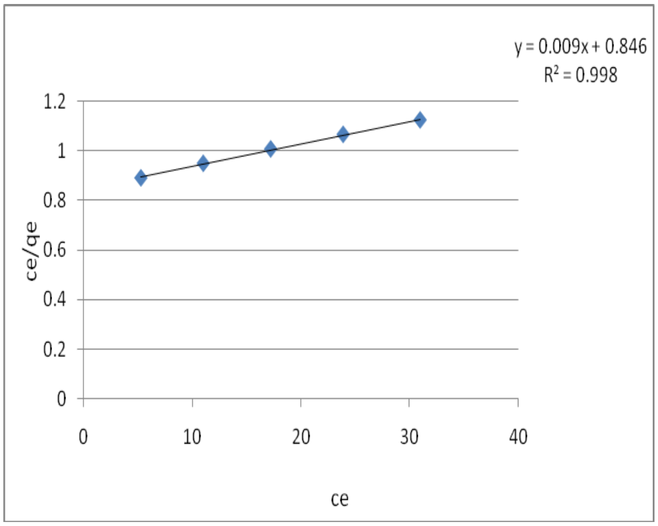


Fig.7: Langmuir adsorption isotherm plot

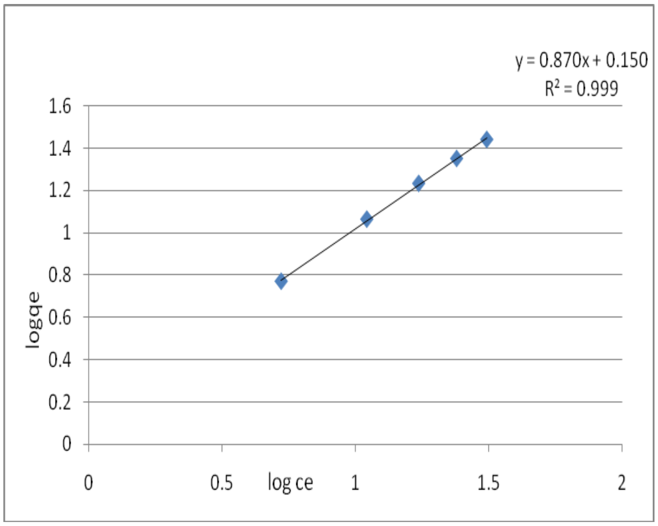


Fig.8: Freundlich adsorption isotherm plot

Langmuir and Freundlich plots are shown in the Fig. 7 and Fig 8. Even though both Langmuir and Freundlich model better fit the experimental results over the experimental range with good correlation co-efficient, the Freundlich isotherm model is best fitted due to best R^2 value. In Langmuir isotherm R_L value is below 1 i.e 0.4854. So, this is a favourable isotherm. Since it follows Freundlich isotherm, The value 'n_f' coefficient found in Freunlich isotherm is 1.1494 which indicate high tendency forward adsorbing the metal ion onto the adsorbate. The value coefficient ‘1/n’ in the Freundlich isotherm model is between 0 to 1 which represents adsorption intensity of adsorbate to adsorbent. In this study $1/n_f$ = 0.870 which indicates the favourable adsorption of the adsorbate.

Table 5: The adsorption distribution co-eficeient K_0 and $\ln K_0$ values for the adsorption of Cr(VI) at three temperatures.

Metal ion concentration (ppm)	310K		320K		330K	
	K_0	$\ln K_0$	K_0	$\ln K_0$	K_0	$\ln K_0$
20	2.8095	1.0330	3.7619	1.3249	5.4516	1.6959
40	2.6363	0.9693	3.5977	1.2802	5.2893	1.6656
60	2.4843	0.9099	3.4609	1.2415	5.1287	1.6348
80	2.3472	0.8532	3.3243	1.2012	4.9746	1.6043
100	2.2258	0.8001	3.1981	1.1625	4.8343	1.5757

Table 6: Thermodynamic parameters ΔGº, ΔSº and ΔHº values for the adsorption of Cr(VI) at three telmperatures.

Metal ion concentration (ppm)	310K	320K	330K	ΔSº	ΔHº
	ΔGº	ΔGº	ΔGº		
20	-2662	-3524	-4652	97	27
40	-2498	-3405	-4569	101	28
60	-2345	-3302	-4485	104	30
80	-2198	-3195	-4401	107	31
100	-2062	-3092	-4323	110	32

3.7. Thermodynamic studies

Using the following equations, the thermodynamic parameters, which are standard free energy change (G), enthalpy (H), and entropy (S), were obtained to examine the Cr(VI) adsorptions on biosorbent thermodynamically.

$\Delta G^0 = -RT \ln K_d$.............................. (8)

$\Delta G^0 = \Delta H^0 - T\Delta S^0$ .... (9)

$\ln K_d = (-\Delta H^0/R)1/T + (\Delta S^0/R)$ ....(10)

where, R is the universal gas constant (8.314 J/mol K), T is the absolute temperature in Kelvin, and K_d is the equilibrium constant obtained from Langmuir constant K_L. By drawing the van’t Hoff plot of $\ln K_d$ versus 1/T, the H and S values were found from the slope and intercept. Table 6 lists the H, S, and G values at various temperatures for Cr(VI) adsorption on biosorbent.

4. CONCLUSION

The effect of different factors on the sorption abilities of inexpensive wild plant *Aponogeton natans* root powder is studied for the removal Cr(VI) from aqueous solutions. The following conclusions are drawn from the present studies. *Aponogeton natans* root powder is a suitable material for Cr(VI) adsorption. pH, biosorbent dose, equilibrium time and initial metal ion concentration highly affect over all metal uptake capacity of biosorbent. The sorption is pH dependent and sorption capacity increased in pH value upto 8 after that there is a decrease in sorption. So, this indicates pH 8 is more suitable medium for adsorption of Cr(VI).The optimum time is observed to be 40min with sorption capacity of 14.80 mg/L for 20mg/L. The optimum dosage is 2.5 g/L and the percentage of removal is 66.25%. In the examined concentration range 20-100mg/L the results also reveals, it follows pseudo first order kinetic model than pseudo second order kinetic. Since R^2 value near 1 and also theoretical and experimental values of q_{max} are close to each other. Present result show that both Langmuir and Freundlich model fits perfectly from the adsorption equilibrium data. In Langmuir isotherm model R_L value is below 1($R_{L=}$0.4854). So it indicates favourable adsorption. For freundlich isotherm model $1/n_f$value is 0.870. It is between 0 to 1 which represents favourable adsorption of the adsorbent and also n_f value is 1.1494 which indicate high tendency forward adsorbing the metal ion onto the adsorbate. Thermodynamic parameters (ΔG, ΔH and ΔS) reveal that it is favourable endothermic spontaneous reaction. In the future *Aponogeton natans* root powder can be used to remove heavy metal from the effluent. Engineering technologies can be developed by using the results of isotherm model and thermodynamic parameters for removal of effluent in most efficient way.

Conflict of interest

The authors declare no conflict of interest.

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