Kinetics and Thermodynamics of Co(II) Adsorption on *Moringa Olifera* Bark From Aqueous Solutions

V.H. WAGHMARE, U.E. CHAUDHARI

Department of Chemistry, Mahatma Fule Arts, Commerce and Sitaramji Chaudhari Science Mahavidyalaya Warud, Dist:-Amravati, India, Corresponding author:- uechaudhari@gmail.com

Abstract

Presence of heavy metal in the aquatic system is posing serious problem. The aim of this study was to utilize the locally available material for scavenging the heavy metal. Adsorption is one of the effective method of removing heavy metals from aqueous solution. Conventional methods for the removal of Co(II) from wastewaters include chemical precipitation, chemical reduction, flocculation, filtration, evaporation, solvent extraction, biosorption, adsorption, ion-exchange, reverse osmosis, electro dialysis, membrane separation processes, etc. Adsorption is the most widely used method for removal of Co(II) from wastewater and is the most cost effective method for very dilute samples.In this investigation an attempt has been made to remove Co(II) from aqueous solution by using Moringa Olifera bark as an inexpensive adsorbent. Various parameters such as adsorbent dosages, pH, contact time and impact of adsorption efficiency were studied. Equilibrium contact time was found to be 360 minutes for Co(II). The removal efficiency for Cobalt at these contact time was 85.33%. The adsorption data were modeled by using both Langmuir and Freundlich adsorption isotherm.

Keywords: Adsorption, *Moringa Olifera* Bark, Kinetics and Thermodynamics, Cobalt removal, Adsorption isotherm.

Introduction:

Development of modern industry causes increasingly serious pollution in the environment. Treatment of water and wastewater needs serious attention all over the world especially in countries withdry climate. The most important pollutants in water and wastewater are heavy metals.[1]Environmental contamination with metal ions represents a potential threat to human, animals and plants.The metal ions do not undergo biodegradation and many of them are soluble in aqueous solutions, therefore becomemore available for living systems and accumulate in the environment. In recent years, considerable attention has been received the utilization of adsorption technique, in which the adsorbents are natural material or industrial andagricultural wastes, to passively remove of metal ions from aqueous effluents.[2] Cobalt, a natural element present in certain ores of the Earth's crust, is essential to life in trace amounts Cobalt has both beneficial and harmful effects on health. Important natural sources of cobalt in the environment are soil, dust and sea water. Cobalt and its salts are used in nuclear medicine, enamels and semiconductors, grinding wheels, painting on glass and porcelain, hygrometers and electroplating; as a foam stabilizer in beer, in vitamin B12 manufacture, as a drier for lacquers, varnishes and paints, and as a catalyst for organic chemical reactions.[3] Low cost adsorbent materials used by various investigators include saw dust, slurry, biomass and cellulose, peat, chitin, orange waste, rice husk and wheat bran and the technical feasibility of these various low-cost adsorbents for heavy metal removal from contaminated water has been reviewed.[4] In this study, the batch experiments were conducted in order to investigate the removal of Cobalt (II) ions from aqueous solutions using locally prepared granular bark from *Moringa Olifera* bark.[5] It is important to remove Cobalt from wastewater due to its known toxicity. The effects of acute Cobalt poisoning in humans are very serious; among them are asthma-like allergy, damage to the heart, causing heart failure, damage to the thyroid and liver. Cobalt may also cause mutations in living cells.[6-7]

Materials and Methods:

Preparation of Adsorbent

Moringa Olifera bark was collected from a local farm. It was cut in to small segment and dried in sunlight until almost all the moisture evaporated. Then it was ground to get desired particle size of 100 to 200 micron. It was then soaked 2 hours in 0.1M NaOH solution to remove the lignin content. Excess alkalinity was then removed by neutralizing with 0.1 N HCl. The *Moringa Olifera bark* was then washed several times with distilled water till the washings are free from color and turbidity. The washed bark was oven dried at 200^0C for 24 hrs and stored in desicator for the further study.

Preparation of solutions

The stock solution of Co(II) were prepared by dissolving $Co(NO_3)_2.6H_2O$ in double distilled water. The analytical grade salts used for analysis. The desired solutions were obtained by diluting the stock solution in double distilled water.

Results and Discussion

Effect of pH

The pH of the metal solution was key parameter for adsorption of Co(II). Optimization of pH was done at pH range 2-6.According to Fig.1 with increasing pH in the range of 4.0 to 6.0 metal uptake on adsorbent also increases. At higher pH the effect of competition from H^+ ions deceases and metal ions get adsorbed on the surface of adsorbent, resultings an increase in the metal uptake. The optimum pH was chosen for adsorption of Co(II) 4.0 shown in fig-I

Effect of Contact Time

The effect on contact time on the uptake of the studied cations on to the adsorbent is shown in Fig.2.this was achieved by varying the contact time from 30 to 360 minutes. Equilibrium contact time was found to be 360 minutes for Co(II). The removal efficiency for Co(II) at these contact time was 85.33%. Result shown in Fig-II

Effect of Adsorbent Dosages

The effect of adsorbent dosages on removal of Co(II) has been presented in Fig 3. The experiments were carried out by varying the adsorbent dosages from 200mg to 1gm/L. The adsorption capacity of adsorbent increases with increasing the adsorbent dosage. This is due to availability of more functional groups and surface area at higher dosages. In case of Co(II) maximum removal was attained at 1.0g/L of adsorbent weight. Result shown in fig-III.

Adsorption Isotherms Models

Freundlich Isotherm

The Freundlich isotherm may be written as-

$$\log qe = \log Kf + 1/n \log Ce \quad (1)$$

Where, *qe* is the amount of metal ion adsorbed per gram of adsorbent (mg/g).

Ce is the equilibrium concentration of metal ion in solution (mg/L).

Kf and *1/n* are Freundlich constants, indicating the Adsorption Capacity and Adsorption Intensity respectively.

The parameters are represented in Table-1. Results show that the adsorption of Co(II) are best explained by Freundlich and Langmuir model as the value of correlation R^2 for Cobalt metal are 0.996.

Langmuir Isotherm

The Langmuir isotherm is represented by the following equation-

$$1 / qe = 1/ b\, Q_0 \ \text{X} \ 1/Ce + 1/Q_0$$

Q_0 and *b is* Langmuir constants related to the adsorption capacity and energy of sorption respectively. A plot of *qe* versus *C*e should indicate a straight line of slope 1/ b Q_0 and an intercept of 1/ Q_0. The values of *Qo* and b and Correlation coefficient obtained from the Langmuir model are shown in Table 1.

Table 1- Isotherm Constants

Elements	Freundlich Constants			Langmuir Constants		
	K	1/n	R^2	Q_0	b	R^2
Cobalt (II)	6.213	0.712	0.996	9.323	0.057	1

First order kinetics: - The rate of adsorption of Cobalt(II) metal ions on Moringa Olifera bark was studied by using the first order rate equation proposed by Lagergren. The first-order kinetics model was considered initially which gave r^2 value (0.995). It is found that as initial Cobalt(II) metal ions concentration increases, Lagergren rate constant decrease. This indicates that, adsorption does not follow the 1st order kinetics.

Pseudo Second order Model: Pseudo second order model showed that, Rate constant k_2 is almost constant at different initial concentration which is shown in Table 1. This indicates that adsorption of Cobalt(II) metal ions on Moringa Olifera bark obey the 2nd order kinetics.

Elovich Model: - Adsorption of Cobalt(II) metal ions on Moringa Olifera bark System are shown a linear relationship is obtained between the amount of Cobalt(II) metal ions adsorbed qt and lnt. From the Table-II Shows that value and varied as a function of Cobalt(II) metal ions concentration. As the concentration of Cobalt(II) increases from 25mg/L to 75mg/L. value of α increase and β decreases. This favored the adsorption phenomenon

Table-II- Kinetic Model Value for Adsorption of Co(II) on Moringa Olifera bark

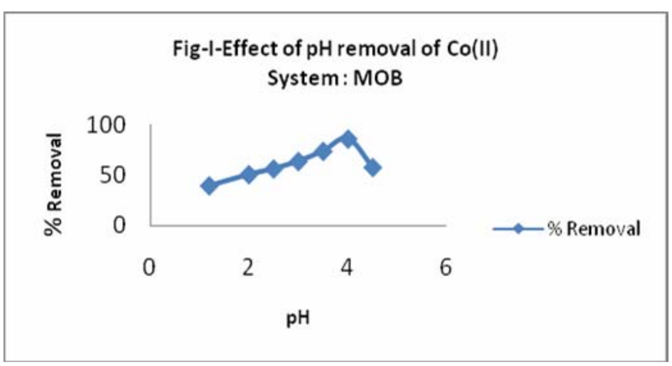
Concentration	1st Order			Pseudo Order			Elovich		
	K_L	q_e	r^2	q_e	k_2	r^2	α	β	r^2
25mg/L	0.0918	6.12	0.995	7.047	0.0374	0.992	0.5723	0.1574	0.9995
50mg/L	0.0772	11.56	0.984	12.734	0.0351	0.885	1.732	0.0928	0.9632
75mg/L	0.0412	13.27	0.977	20.347	0.0298	0.897	2.483	0.0674	0.9425

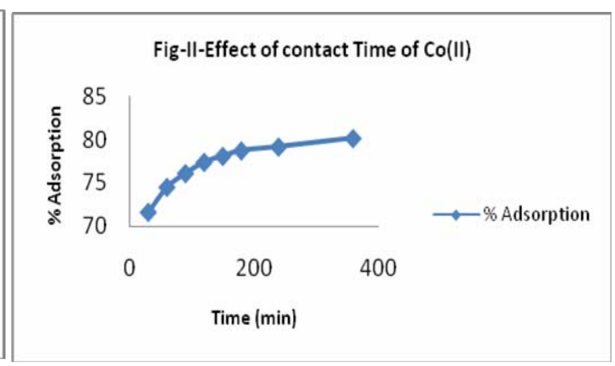
Thermodynamics Parameters

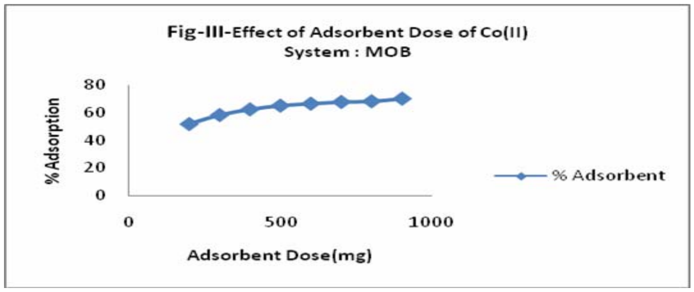
The negative value of free energy change ΔG indicates feasibility and spontaneous nature of adsorption of Cobal(II). ΔH value suggested endothermic nature of Cobalt(II) on Moringa Olifera bark. Positive value of ΔS is due to increase randomness during adsorption of Cobalt(II).

Table-III- Thermodynamics Parameters

Temperature	ΔH	ΔS	ΔG
20^{O}C			-0.5723
25^{O}C	0.3183	0.0753	-70.876
30^{O}C			-228.765







Conclusion

i) The current investigation shows that *Moringa Olifera* bark is very effective adsorbent in removal of Co(II) ions.

ii) The adsorption of Co(II) ions are dependent on pH, adsorbent dosages, contact time.

iii) In adsorption isotherm analysis Freundlich and Langmuir isotherm model well described the adsorption of Co(II).

iv) Hence, this adsorbent can be used as a low cost adsorbent in the treatment of wastewater containing Co(II) ions.

v) The result shows that in very less time, a good amount of the metal can be taken up by the *Moringa Olifera* bark.

Acknowledgements

The authors are thankful to Dr. D. V. Atkare Principal Mahatma Fule Mahavidhyalay Warud for providing the necessary facilities for this investigation.

References

[1]. Shaymaa H. Khazaal , “The study of typical conditions to remove Co(II) from water by adsorption by using Activated Carbon”, *Eng. &Tech.Journal*, Vol.29,No.9,(2011).

[2]. C. Caramalău, L. Bulgariu, M. Macoveanu, ‘Cobalt (II) Removal from Aqueous Solutions by Adsorption on Modified Peat Moss”.*Chem. Bull. "Politehnica" Univ.* Vol. 54(68), 1, (2009).

[3]. S. Rengaraj, Seung-Hyeo Moon, “Kinetics of adsorption of Co(II) removal from water and wastewater by ion exchange resins.”*Water Research*, 36,1783–1793, (2002).

[4]. W. K. Mekhemera, J. A. Hefneb, N. M. Alandisa*, O. A. Aldayel, S. Al-Raddadi, “Thermodynamics and Kinetics of Co (II) Adsorption onto Naturaland Treated Bentonite”.*Jordan Journal of Chemistry* Vol. 3 No.4, 2008, pp. 409-423

[5]. R.Prabakaran, S.Arivoli**, “**Removal of Cobalt (II) from Aqueous Solutions by Adsorption onLow cost activated carbon”.*International Journal of Science, Engineering and Technology Research,*Vol. 2, Issue 2, (2013).

[6]. Evans T. Musapatika, Ruella Singh, Krishnie Moodley, Charles N zila, Maurice S. Onyango and Aoyi O chieng "Cobalt removal from wastewater using pine sawdust."*African Journal of Biotechnology*, Vol. 11, 39, 9407-9415, (2012).

[7]. Jean Jacques Anguile, Joseph Ketcha M badcam, Divine Dingka'aNdaghu and Saustin Dongmo**,** **"**Effect of Solution parameters on the Adsorption of Cobalt (II) ions on Smectite from Cameroon: Equilibrium studies*". Journal of Academia and Industrial Research*Vol. 2, Issue 4,(2013).