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Studies of Kinetic and Equilibrium isotherm models for the Sorption of Cyanide ion on to Almond shell

Dwivedi Naveen[1*], Balomajumder Chandrajit[2] and Mondal Prasenjit[2]
[1]Uttarakhand Technical University, Dehradun
[*]Department of Biotechnology, S. D. College of Engineering and Technology, Muzaffarnagar-251001, UP, INDIA
[2]Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee 247667, Uttarakhand, INDIA

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Abstract

Bioadsorption of cyanide by almond shell in batch reactor has been carried out. The optimum bioadsorbent dose is 20g/L for an optimum agitation time 90 minute. The % removal of cyanide decreased with increased initial concentration of cyanide. The experimental data have been analyzed using the Freundlich (R^2 = 0.995), Langmuir (R^2 = 0.946) and Temkin (R^2 = 0.919) isotherm models. These models are well represented by indicating favorable isotherm. Adsorption of cyanide onto almond shell obeyed the pseudo second order rate equation.

Keywords: Cyanide, isotherm, biosorption, *almond shell*, kinetic.

Introduction

Free and metal-complexed cyanides are extremely harmful to humans and aquatic organisms. Water is contaminated by cyanides i.e. released into the environment through the effluents of industrial activities such as electroplating, mining, photography, coal coking, plastics, chemical fertilizer and metals milling operations and/or accidental spills[1-3]. The toxicity of cyanide is dependent upon the form of cyanide in which it occurs; the toxicity of free cyanide increases with decreasing pH; in fact, the acid form, HCN, is 2.3 times more toxic than the anionic form (CN^-)[4,5]. To protect the water resources and environment, cyanide containing wastewaters must be treated before being discharged into the environment. Hence, environmental regulations require reducing the cyanide concentration in wastewater to below 0.2 mg/L prior to discharge into the environment[6]. Several treatment processes based on natural degradation, physical, chemical and biological oxidation, complexing/ precipitation and recovery/ recycling have been exploited for the reduction of cyanide levels in waste solutions/ slurries in compliance with environmental regulations[7]. Chemical processes of cyanide removal are not appropriate for environmental and economic perspectives; due to its elevated demand of chemicals/ regents and secondary pollutants are created; furthermore it also needs some additional treatment prior to its disposal. Adsorption is a simple and attractive method for the removal of toxic compounds from the effluents due to its high efficiency, easy handling and economic feasibility. Biosorption of cyanide from aqueous solutions is quite a new process that has confirmed very promising in the removal of contaminants from aqueous effluents. Various agro based adsorbents have been reported for cyanide removal from wastewater due to their abundant availability and low cost[6]. Further, almond shell has hardly been investigated for cyanide removal from water. Therefore, in this work the potential of almond shell, an agro- based biomass, has been explored for the removal of cyanide from water. The effects of contact time and initial cyanide concentration on the removal of cyanide have been studied and kinetic and equilibrium parameters have been estimated.

Models: To understand adsorption phenomena two types of models are generally developed. The first type is on the basis of contact time (kinetics model), and the second type is on the basis of initial cyanide concentration (equilibrium model) are shown in table 1.

Material and Methods

Materials: The raw material almond shell *(Prunus amygdalus)* was obtained from the local market of Muzaffarnagar, UP, India. The shells were cut into small pieces and, after drying and crushing, washed thoroughly with double-distilled water to remove adhering dirt. Then, they were dried in oven at 100°C for 24 h and were sieved[8]. After screen analysis of the grinded product the fraction having average particle size of ~ 600µm was used. A 1-L stock solution of cyanide was prepared by dissolving 1.885 g NaCN in distilled water with NaOH pellet. All chemicals used were analytical grade and purchased from Merck Co and Qualigens Fine Chemical Company (Glaxo Smithkline).

Procedure: Batch experiments were carried out in a 250 ml conical flask at 30^0C in an incubator shaker at 125 rpm using 100 ml of cyanide solution of known concentration and adsorbent doses. The solutions pH were maintained by measuring it intermittently each hour and controlled by drop wise addition of N/10 HCL or NaOH solutions. Ranges of operating parameters for various experiments are shown in table 2.

Table-1
Various kinetic and equilibrium models normally used to explain adsorption phenomena

Name of Model	Model Expression	Model parameter
Kinetic models		
Pseudo first order model	$\log(q_e - q_t) = \log(q_e) - k_1 t/2.303$ (Lagergren, 1898),	q_e and q_t are sorption capacities (mg/g) of adsorbent at equilibrium and at a given time "*t*,". k_1 is the pseudo-first order adsorption rate constant (s^{-1})
Pseudo second order model	$t/q_t = 1/ K_2 q_e^2 + t / q_e$	k_2 is the pseudo-second-order adsorption rate constant (g/mg s)
Intra particle diffusion model	$q_t = K_{id} \sqrt{t} + C$ (Weber and Morris (1963)	q_t is sorbed concentration at time t; K_{id} is rate constant of intra particle transport (mg/g/time $^{1/2}$) C (mg/g) is the intercept that gives an idea about the thickness of the boundary layer.
Elovich model	$q_t = \beta \ln (\alpha \beta) + \beta \ln t$ (Zeldowitsch 1934)	q_t is the sorption capacity at time t (mg/g), α is the initial sorption rate (mg/g/min) β is the desorption constant (g/mg).
Equilibrium model		
Freundlich model	$\log q_e = \log K_f + 1/n \log C_e$	K_f ((mg/g)/(mg/L), 1/*n*) and n are the constant
Langmuir model	$C_e/q_e = 1/Q^0 b + C_e/Q^0$	Q^0 is q_{max} (mg/g), and *b* (L/mg) is the Langmuir constants related to the capacity and energy of adsorption.
Temkin model	$q_e = B \ln A + B \ln Ce$	*A* and *B* are the temkin constant

Table-2
Ranges of operating parameters for time and initial cyanide concentration

Objective of experiment	Operating parameters
To study the effect of contact time on cyanide removal	AD: 20 g/L, ICC: 100 mg/l; Temp.: 30^{0}C; solution pH 7; time: 15, 30, 45, 60, 75, 90, 105, 120 min;
To study the effect of Initial cyanide concentration on cyanide removal	AD: 20 g/L; Time.: 90 min; solution pH:7; Temp: 30^{0}C; ICC: 100-800 mg/l;

AD: adsorbent dose, ICC: initial cyanide concentration

All experiments were performed in triplicate and the results average was reported. In each case sample was filtered through a 0.45 µm membrane filter. Filtrate was analyzed for total cyanide ion concentration using picric acid method.

The cyanide adsorption efficiency was calculated as using following formula:

$$\% \text{ Removal} = \frac{(C_i - C_f) \times 100}{C_i}$$

Where, C_i and C_f are the initial and residual concentration at equilibrium (mg/L) respectively of cyanide in solution.

The cyanide concentration retained in the adsorbent phase, q_e (mg/g), was calculated according to following formula[9],

$$q_e = (C_i - C_f) \times V/ W \quad (1)$$

Where q_e is the amount of cyanide adsorbed (mg/g); C_i and C_f are the initial and residual concentration at equilibrium (mg/L), respectively, of cyanide in solution; *W* is the weight (g) of the adsorbent and V is the volume (L) of solution.

Analytical measurements: Analysis of cyanide was done by using picric acid methods[10] at 520 nm wavelength using double beam UV/visible spectrophotometer (Microprocessor UV/VIS EI Spectrophotometer model 1371).

Free cyanide and weak acid cyanide reacts with the picric acid reagent to produce an orange color that can be measured colorimetrically at a wavelength of 520nm. The dissolved alkali metal picrate was converted by cyanide to the colored salt of *iso*-purpuric acid and its concentration was measured.

Results and Discussion

Effect of contact time and initial cyanide concentration on the removal of cyanide by almond shell along with kinetic and equilibrium study is discussed in the following sections.

Effect of contact time on percentage removal of cyanide and adsorption kinetics: The effect of contact time on adsorption was investigated under the conditions given in table 2. Figure 1 depicts at least 84.7% cyanide removal was achieved for concentrations as 100 mg/L cyanide a very short contact time of 15 min. Overall, the rate of cyanide removal was higher within 30-60 min contact time. The equilibrium removal efficiencies of cyanide were 91.5% at 90 min. This result implies high affinity and thus favourability of almond shell for adsorbing cyanide from industrial wastewaters.

To find out a suitable kinetic model for explaining the adsorption process pseudo first order model, pseudo second order model, intra particle diffusion model and Elovich model are tested. For this purpose the nonlinear models are first linearized as described in table 1 and are presented through figure 2 to figure 5.

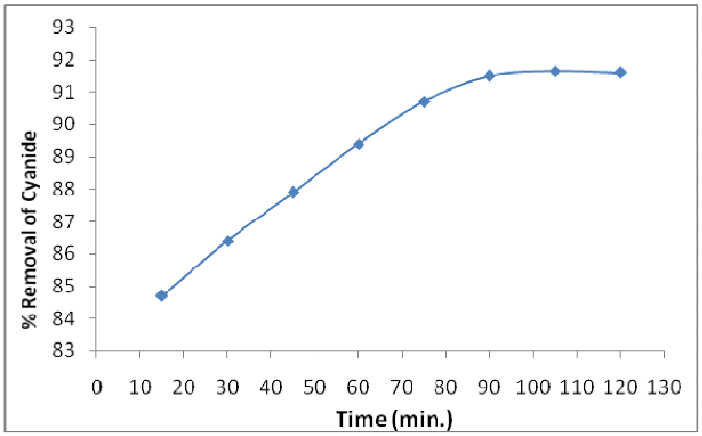

Figure-1

Effect of contact time (15-120 min.) on cyanide removal by almond shell. (Process conditions: pH: 7; temp: 30 ^{0}C; Adsorbent dose: 20 g/L; initial concentration of cyanide: 100 mg/l; rpm: 125.)

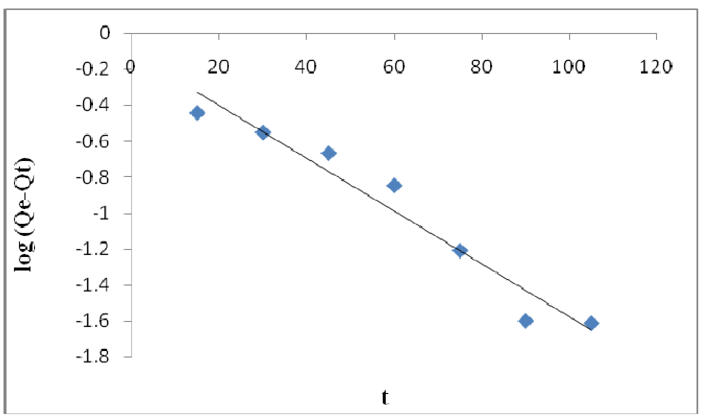

Figure-2

Pseudo first order model for adsorption of cyanide removal by almond shell. (Process conditions: pH: 7; temp: 30 ^{0}C; adsorbent dose: 20 g/L; initial concentration of cyanide: 100 mg/l; rpm: 125.)

Kinetic parameters for the above model equations are computed from the slope and intercept of the respective figure as stated above and are reported in table 3 along with the values of correlation coefficients (R^2). From table 3 it is clear that pseudo-first order model, pseudo-second order model, intra particle diffusion model and Elovich model shows R^2 value of 0.948, 0.999, 0.964 and 0.965 respectively. Thus it seems that the kinetics of cyanide adsorption is well explained by pseudo-second order model, which also has maximum R^2 value of 0.999.

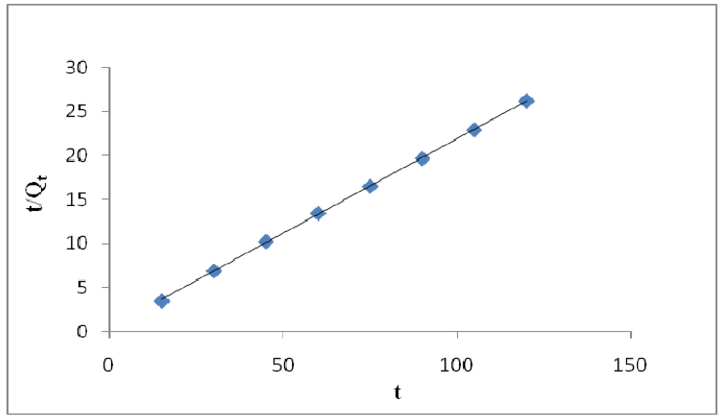

Figure-3

Pseudo second order model for adsorption of cyanide removal by almond shell. (Process conditions: pH: 7; temp: 30 ^{0}C; adsorbent dose: 20 g/L; initial concentration of cyanide: 100 mg/l; rpm: 125.)

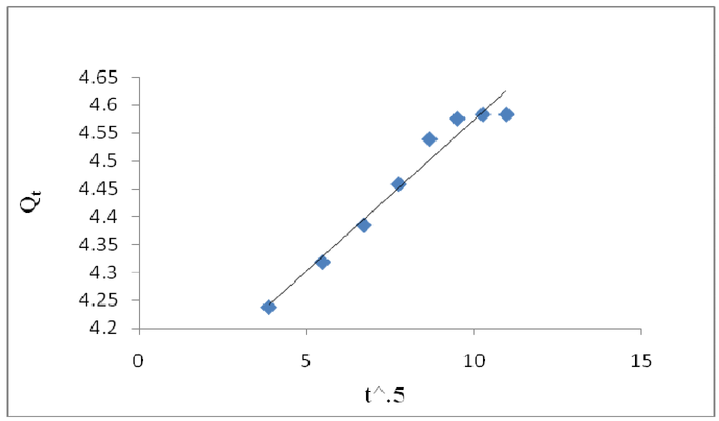

Figure-4

Intra particle diffusion model for adsorption of cyanide removal by almond shell. (Process conditions: pH: 7; temp: 30 ^{0}C; adsorbent dose: 20 g/L; initial concentration of cyanide: 100 mg/l; rpm: 125.)

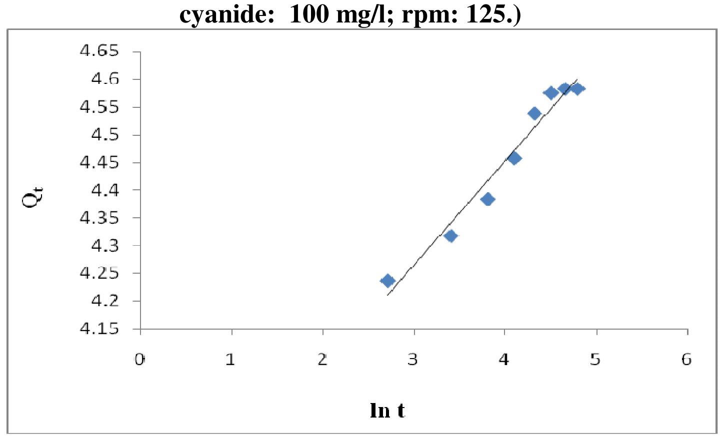

Figure-5

Elovich model for adsorption of cyanide removal by almond shell. (Process conditions: pH: 7; temp: 30 ^{0}C; adsorbent dose: 20 g/L; initial concentration of cyanide: 100 mg/l; rpm: 125.)

Table-3
Kinetic models for almond shell

Pseudo- first order model			
$[C]_{0\ mg/l}$	K_1	Q_e	R^2
100	0.034	0.781	0.948
Pseudo- 2nd order model			
$[C]_{0\ mg/l}$	K_2	Q_e	R^2
100	0.093	4.67	0.999
Intra particle diffusion model			
$[C]_{0\ mg/l}$	K_{id}	C	R^2
100	0.054	4.033	0.964
Elovich model			
$[C]_{0\ mg/l}$	α	β	R^2
100	1.16×10^9	0.1868	0.965

$[C]_0$: initial cyanide concentration (mg/L)

Effect of initial cyanide concentration: The influence of varying initial cyanide concentration from 100 to 800 mg/L on adsorption was investigated under the conditions given in table 2. Figure 6 depicts the results of influence of varying initial cyanide concentration on almond shell. Based on data plotted in figure 6, at least 91.5% cyanide removal was achieved for concentrations as lower as 100 mg/L cyanide and 63.6% cyanide removal was achieved for concentrations as high as 800 mg/L. The reduction of cyanide removal as an efficacy of its concentration can be explained by the restriction of available free sites for adsorption of cyanide with increased cyanide concentration in bulk solution for a fixed mass of adsorbent, as well as by the increase in intraparticle diffusion[11].

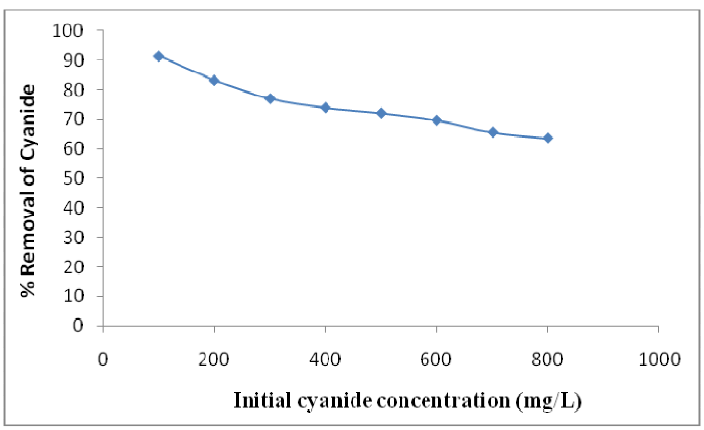

Figure-6
Effect of initial cyanide concentration. (Process conditions: pH: 7; temp: 30 ^{0}C; Contact time: 90 min; adsorbent dose 20 g/L; rpm: 125.)

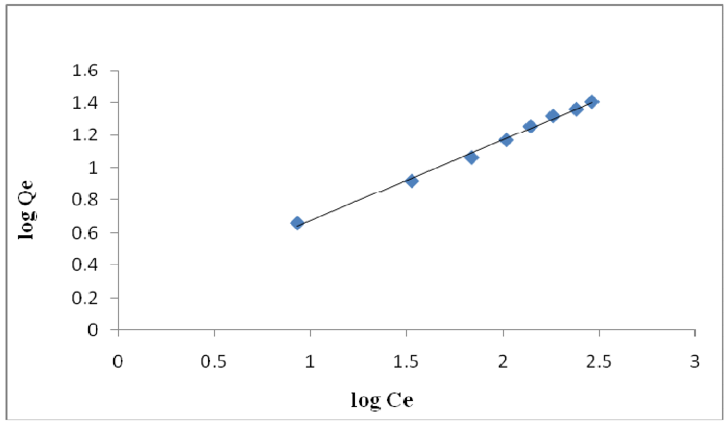

Figure-7
Freundlich isotherm model for adsorption of cyanide removal by almond shell. (Process conditions: pH: 7; temp: 30 ^{0}C; Contact time: 90 min; adsorbent dose 20 g/L; rpm: 125.)

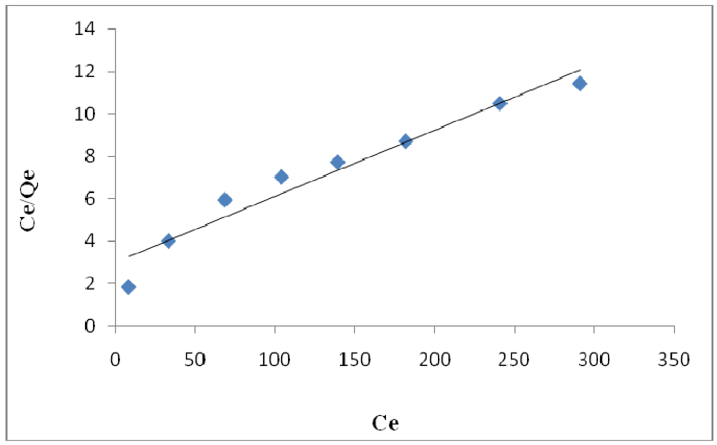

Figure-8
Langmuir Isotherm model for adsorption of cyanide removal by almond shell. (Process conditions: pH: 7; temp: 30 ^{0}C; Contact time: 90 min; adsorbent dose 20 g/L; rpm: 125.)

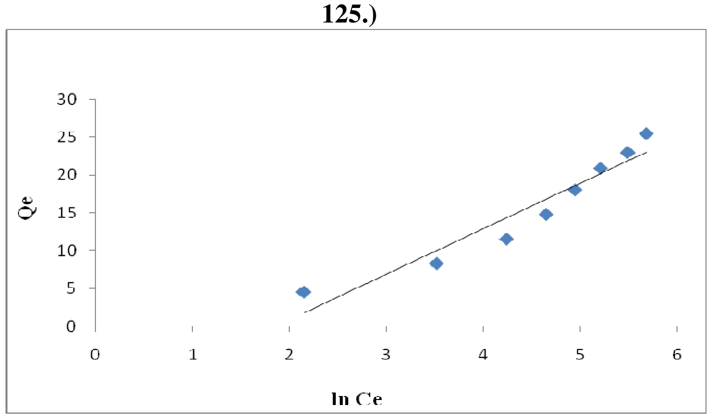

Figure-9
Temkin isotherm for adsorption of cyanide removal by almond shell. (Process conditions: pH: 7; temp: 30 ^{0}C; Contact time: 90 min; adsorbent dose 20 g/L; rpm: 125.)

To find out a suitable model equation for predicting equilibrium adsorption of cyanide from water Freundlich, Langmuir and Temkin isotherm models have been tested. To find out the isotherm constants the nonlinear models were linearized as described in table 1. The isotherm constants for the above equilibrium model are shown in table 4 along with their respective R^2 values. A very important characteristic of Langmuir isotherm is a dimensionless separation factor R_L which is defined by Weber and Chakravorti in 1974[12].

Table-4
Different parameters and their values of adsorption isotherms

Isotherms	Parameters	Values
Freundlich	R^2	0.995
	n	2.016
	1/n	0.496
	K_f	1.510
Langmuir	R^2	0.946
	Q^0	32.05
	b	0.010
	R_L	0.5
Temkin	R^2	0.919
	B	5.986
	A	0.159

According to them;

$$R_L = \frac{1}{1 + b\, C_0}$$

Where C_0 and *b* are the initial cyanide concentration and Langmuir constant respectively. By using the separation factor value, the shape of isotherm can be assessed whether it is in linear, favorable or unfavorable as in following way.

$R_L > 1$: unfavorable, $R_L = 1$: linear, $R_L < 0$: irreversible, $0 < R_L < 1$: favorable

In the present work, the R_L values calculated as per given formula in the studied range of cyanide concentration are found to be 0.5 which falls in the range of 0–1, which suggests the favorable sorption of cyanide onto the studied almond shell, under the conditions used for the experiments. For almond shell, the 1/n value is ~ 0.496 (<1), which indicates a favorable sorption. The present data fit the Freundlich, Langmuir, and Temkin isotherm models for almond shell, in the following order Freundlich (0.995) > Langmuir (0.946) > Temkin (0.919).

Conclusion

From the present work the subsequent conclusions have been made: i. Under the experimental conditions, agitation period required to reach adsorption equilibrium for the adsorption of cyanide on almond shell is 90 minutes. ii. Prediction of the non-equilibrium stage adsorption by pseudo second order kinetic model is more accurate for the cyanide. iii. Amongst the conventional isotherms, Freundlich isotherm provides better prediction for equilibrium specific uptake for the cyanide. iv. The specific uptake increases from 4.57 mg/g to 25.45mg/g with the increase in initial cyanide concentration from 100 mg/L to 800 mg/L. v. Maximum specific uptake obtained from Langmuir isotherm is found to be 32.05 mg/g.

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