Simultaneous Removal of Phenol and Cyanide from Aqueous Solution Using Low Cost Adsorbent: Optimization of Process Parameters and Isotherm Modeling

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Abstract—*In the present investigation Rice husk was used as low cost adsorbent for simultaneous removal of phenol and cyanide from aqueous solution by adsorption. Langmuir, Freundlich and Redlich-Peterson adsorption models and model parameters were estimated by the non-linear regression method. The effect of various process parameters such as pH, adsorbent dose, contact time and initial concentrations of phenol and cyanide on adsorption behavior was investigated. At an optimum pH 8, temperature 30^0C and adsorbent dose of 40 g/L, 53.45% of 300mg/l Phenol and 66.33 % of 30mg/l Cyanide were removed.*

Keywords: *Phenol, Cyanide, Rice husk, Isotherm Modeling.*

1. INTRODUCTION

The importance of removal of pollutants from waste water has received serious consideration of researchers across the world. Phenol and cyanide and their derivatives are very harmful compound due to their extreme toxicity [1]-[3]. Phenol and cyanide contamination is one of the most outdare environmental problem .Various industries discharge and produce waste water effluent containing phenol, cyanide, thiocyanides, thiosulphates, ammonium, chlorides, etc such as coke plant, electroplating industries explosive manufacturing, petrochemicals industries, pesticides industries, synthetic fiber and resin manufacture etc.[4]-[5]. Phenol and cyanide compounds give an abominable taste and odor to drinking water. The permissible limit for portable water according to indian standered and Environmental Protection Agency (USEPA), disposal standard in Mexico is 0.001 and 0.5 for phenol and 0.05and 0.2 for cyanide respectively[5]-[7]. Phenol and cyanide produce harmful health effects such as nausea; vomiting; diarrhea and abdominal pain, affects kidney, skin, and eyes irritation, headache lever damage etc even at low concentration.

There are various method available in literature for removal of phenol and cyanide and other industrial effluent from waste water such as membrane filtration, coagulation, adsorption, oxidation, ion exchange, and Simultaneous adsorption and biodegradation etc .However among these waste water treatment technologies ,adsorption has acquire much prominence owing to its high efficiency and low cost. Adsorption using GAC was highly accomplished for the removal of phenol and cyanide [8]-[9]. But due to its high cost and difficulty in its regeneration have led to investigation of non-conventional low cost adsorbents.

In last few decades, agricultural and industrial by products have been widely used for removal of phenol and cyanide from waste water. These adsorbents include saw dust, vegetable and fruit peels, peat, fly ash, bentonite, prawn waste, leaves [10]-[13] etc. As a low cost adsorbent Rice husk attractive, feasible and inexpensive option for the bio sorption removal of phenol and cyanide from industrial waste water. The use of rice husk would solve disposal problem and no need to regeneration because of their low production cost. Rice husk contain silica and carbon in sufficient amount which is responsible for adsorption. Rice husk has been utilized as bioadsorbent for removal of metal like Pb, Cd, Zn, Ni and As etc, phenol and cyanide from waste water.[14]-[20].

The main purpose of this present study is to analyze the effectiveness of Rice husk for the simultaneous removal of phenol and cyanide from aqueous solution in batch reactor. The effect of various process parameters like pH, contact time, adsorbent dose, and initial concentration has been studied.

2. MATERIALS AND METHODS

All the chemical employed in this study were of AR grade or better ,and obtained from Himedia Laboratories Pvt. Ltd. Mumbai India. A stock solution of phenol (1000mg/l) and cyanide (100mg/l) were prepared by dissolving appropriate quantities of pure phenol crystal and sodium cyanide. All solutions were prepared by using millipore water (Q-H2O, Millipore Corp. with resistivity of 18.2 MX-cm).

2.1 Preparation and characterization of adsorbent

Rice husk was purchased/collected from the local market of Institute of Technology Roorkee, India. The rice husk was cleaned with millipore water to remove dirt and air dried at room temperature. And then acid treated with 0.5 M H_2SO_4 for 24 hr in 2:1 liquid to solid ratio to increase surface area and pore volume of rice husk. After that the adsorbent washed with millipore water several times and dried at temperature of 80 ^{0}C, for overnight. The types of functional groups present on the surface of adsorbent was analyzed before and after adsorption by using Fourier Transform Infrared Spectroscopy (FTIR, Nicolet 6700, USA).Surface Morphology of rice husk changes due to adsorption of phenol and cyanide was determined using scanning electron microscopy (SEM) Quanta 200F, FEI, Netherlands). Brunauer–Emmett–Teller (BET) surface area and porosity of the adsorbent was evaluated by using surface area analyzer (ASAP 2020,Micromeritics).

2.2. Batch adsorption experiments

Synthetic stock solutions of phenol and cyanide were prepared in the ratio (10:1) with millipore water. Batch experiments for optimization of process parameters were carried out in 250 mL round bottom flasks with working volume of 100 mL at 125 rpm in an incubator cum orbital shaker (Metrex, MO-250, India) at room temperature (293 ± 1 K). The concentrations of phenol and cyanide were chosen to be in the range of 100–1000 mg/l and 10-100mg/l. In every flask a certain adsorbent dose in the range (5-60 g/l) was added. The pH of samples was readjusted to predefined value in the range of 4–12by adding HCl or NaOH as per requirement. All the batch experiments were carried out in duplicate and average results were used. The samples were withdrawn after equilibrium condition were achieved filtered with standard Whatman filter paper (Cat No 1001 125) and the filtrate was analyzed for phenol and cyanide by 4-aminoantipyrene and colorimetric picric acid methods, respectively [21].

The adsorptive uptake Q_e of phenol and cyanide by rice husk were calculated according to equ (1)

$$Q_e = \frac{(C_o - C_e) \times V}{W} \quad (1)$$

And adsorption efficiency η of phenol and cyanide were calculated as equ (2)

$$\eta = \frac{(C_o - C_e) \times 100}{C_o} \quad (2)$$

where, C_0 and Ce is the initial and equilibrium concentration (mg/l) of pollutants. V is the volume of the solution (l) and W is the weight of the adsorbent (gm).

2.3 Adsorption isotherms and modeling

Various types of isotherm models used to describe the experimental adsorption isotherms present in the literature. Langmuir equation is the most widely used isotherm equation for modeling equilibrium which is valid for monolayer sorption on to a surface a limited number of similar sites. The Freundlich isotherm equation is an empirical equation based on adsorption on a heterogeneous surface suggesting that binding sites are not continually. Langmuir and Freundlich models were evolved for a single layer adsorption and two parameter model whereas Redlich-Peterson isotherm is three parameter model.[22]-[24].

Langmuir:

$$Q_e = (Q_0 b C_e)/(1 + bC_e) \quad (3)$$

Freundlich :

$$Q_e = K_F C_e^{1/n} \quad (4)$$

Redlich-Peterson

$$Q_e = \frac{K_{RP} . C_e}{1 + a_{RP} . C_e^{\beta}} \quad (5)$$

The best isotherm model to fit the experimental data is selected on the basis of bias factor (BF) closer to unity and at the same time low values of statistical indices such as normalized standard deviation (NSD), root mean square error (RMSE), standard error of prediction (SEP) and Marquardt's percent standard deviation (MPSD) [23][26].

2.4 Model validation

To evaluate the best isotherm model to fit the experimental data. The following statistical indices are used in this study.

$$B_{Fac} = 10^{\left(\sum \log_{10}(Q_{e,cal} / Q_{e,\exp}) / N\right)} \quad (6)$$

$$RMSE = \sqrt{\frac{\sum \left(Q_{e,\exp} - Q_{e,cal}\right)^2}{N}} \quad (7)$$

$$NSD = \sqrt{\frac{\sum \left(1 - Q_{e,cal} / Q_{e,\exp}\right)^2}{N}} \times 100 \quad (8)$$

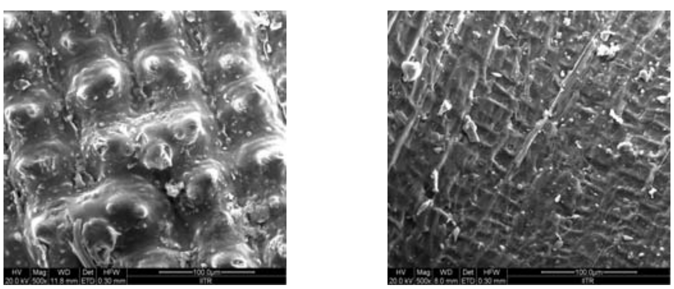
$$SEP = \frac{RMSE}{\sum Q_{e,i}^{\exp} / N} \times 100 \quad (9)$$

$$MPSD = 100 \sqrt{\frac{1}{n-p} \sum_{i=1}^{p} \left(\frac{Q_{e,i}^{\exp} - Q_{e,i}^{cal}}{Q_{e,i}^{\exp}} \right)^2} \quad (10)$$

3. RESULTS AND DISCUSSION

3.1. Characterization of Adsorbent

The characteristics of Rice husk are as follows: Moisture content 9.96, ash content 17.36, surface area 430.05m^2/g, bulk density 0.316 g/cm^3 and porosity 0.35 by fraction. Fig. 1(a) and (b) indicates the surface morphology of before adsorption and after adsorption as seen through scanning electron microscopy (SEM).The change in surface morphology indicates adsorption of phenol and cyanide onto surface of rice husk. Further adsorption of phenol and cyanide on to rice husk is observed from reduce in peak area of FTIR spectrum around wave number 2496.23 and 1245.22 and increased in peak area around wave number 3274.28,2919.94,1654.78,1508.74, 1339.40,1033.30,558.48 and 420.22cm^{-1} (Fig.2). The shifting of the peaks indicates that the functional groups at these wavenumbers participated in the adsorption of phenol and cyanide.



(a) (b)

Fig. 1: SEM photographs of Acid Treated Rice Husk (a) Before adsorption (b) After adsorption at 500 magnification.

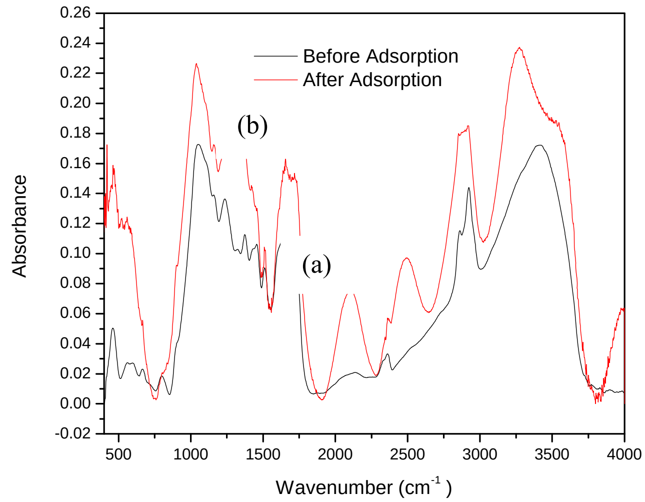


Fig. 2: FTIR Spectrum of Acid Treated Rice Husk (a) Before adsorption and (b) After adsorption

3.2. Effect of pH, adsorbent Dose, time and Initial Concentration

According to [25] the pH can highly influence the adsorbate and cell walls of adsorbents. The effect of pH on the adsorption of phenol and cyanide onto rice husk was shown in Fig.3.It is observed from Fig 3 that percent removal of phenol increase with the increase pH upto 8 and after that % removal start decreases with increase in pH from 9-12.Whereas for cyanide the % removal increases upto pH 9 after which the %removal start to decrease with the increase in Ph [4] . Hence, pH 9 was considered as optimum pH value for adsorption of phenol and cyanide in all further experiments. The effect of adsorbent dose on % removal of phenol and cyanide onto Rice husk are shown in Fig 4.It is evident from fig % removal of phenol and cyanide increases with the increase in adsorbent dose upto 40 g/l after which the removal became constant with increases in the adsorbent dose. The % removal increases initially due to increase in surface area available for adsorption and availability of more active sites. Hence, adsorbent dose of 40 g/l for both phenol and cyanide are considered as optimum dose for the further studies. Fig 5 shows the effect of contact time on %removal of phenol and cyanide onto Rice Husk .It is evident from fig that the adsorption of phenol and cyanide onto rice husk in binary mixture reached at equilibrium within 30hr and 26 hr respectively. A further increase in time had a negligible effect on the %removal. Fig. 6and 7 shows the effect of increasing phenol and cyanide initial concentration on their % removal respectively. It could be observed that percentage removal decreases with increases initial concentration. The % removal decreases from 58.21% to 20.31% and from 79.06% to 37.13% in case of phenol and cyanide respectively on increasing initial concentration of phenol from 100 to 1000 mg/L and initial concentration of cyanide from 10 to 100 mg/L.

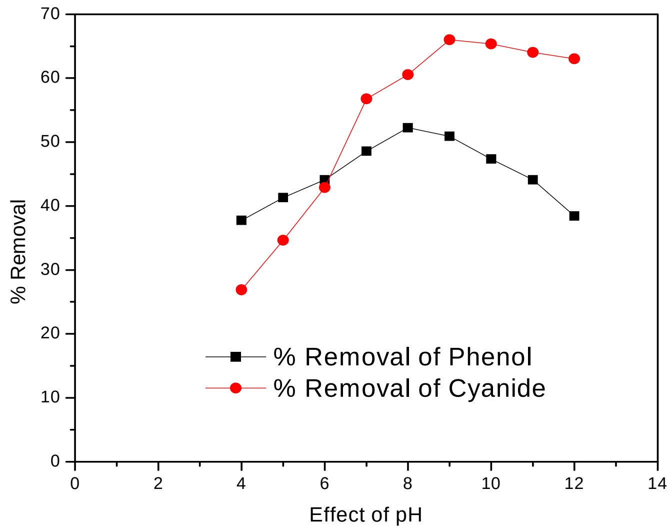


Fig. 3: Effect of pH on percentage removal of phenol and cyanide.

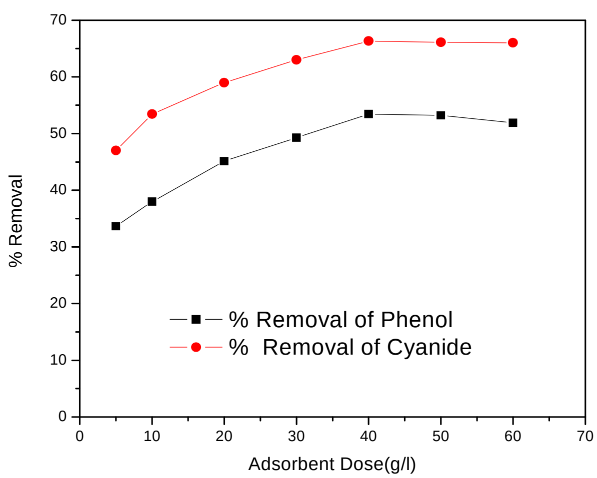


Fig. 4: Effect of Adsorbent Dose on percentage removal of phenol and cyanide

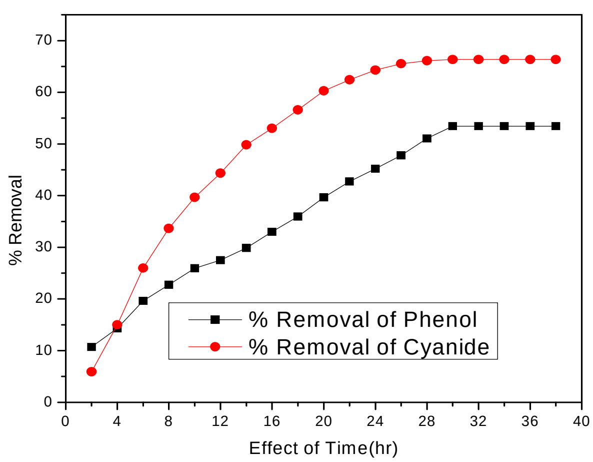


Fig. 5: Effect of contact Time on percentage removal of phenol and cyanide

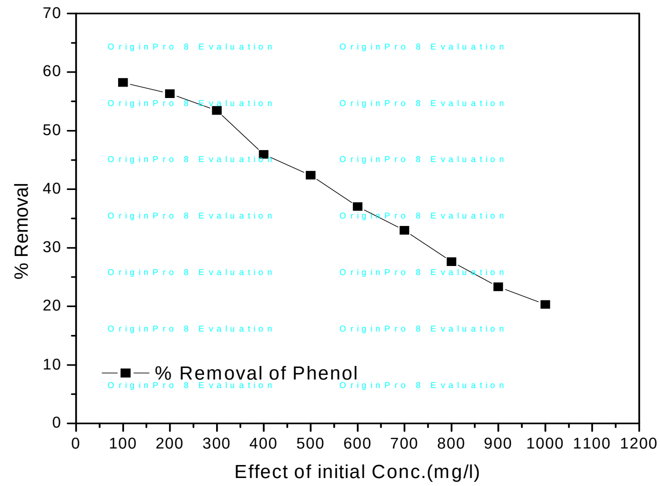


Fig. 6: Effect of initial concentration on percentage removal of phenol

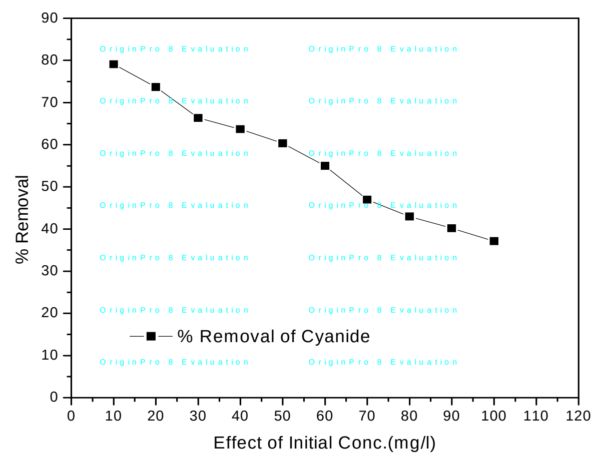


Fig. 7: Effect of initial concentration on percentage removal of cyanide

Table 1: Isotherm Models parameters of phenol and cyanide on Rice Husk

Component	Parameters	Values
Phenol	Q_0	63.5349
	b	0.000339
Cyanide	Q_0	41.89482
	b	0.00114
Phenol	K_f	2.5038
	n	2.910
Cyanide	K_f	0.33937

	n	8.453
Phenol	K_{rp}	0.5107
	a	847.534
	β	0.6991
Cyanide	K_{rp}	0.47063
	a	21.909
	β	0.3671

3.3 Adsorption isotherm model parameters estimation

Adsorption isotherms explain how adsorbate interacts with adsorbents and equilibrium isotherms are measured to determine the efficiency of the adsorbents for adsorbate. The most common types of models explaining this type of system are the Langmuir ,Freundlich and Redlich Peterson isotherms. The adsorption equilibrium data for phenol and cyanide onto Rice Husk were examined by non-linear curve fitting procedure to minimize the deviation between calculated and experimental data, using Microsoft Excel 2010 to fit the isotherm models. The isotherm parameters values are tabulated in Table-I and statistical indices of phenol and cyanide for the isotherm models are given in Table-2.

Table 2: Statistical indices values of phenol and cyanide on Rice Husk

S. No.	statistical indices	Langmuir Model		Freundlich Model		Redlich –Peterson Model	
		Phenol	Cyanide	Phenol	Cyanide	Phenol	Cyanide
1.	MPSD	37.59	23.3327	55.2194	57.0458	30.0255	17.1259
2.	Bf	0.844	0.93883	0.7050	0.7356	0.89613	0.96088
3.	NSD	33.622	20.8694	9.3898	51.0234	26.855	15.3179
4.	RMSE	1.2328	0.10711	2.02464	0.3111	1.08744	0.1018
5.	SEP	2.7185	1.5765	4.464	4.57941	2.3979	1.4983

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According to results listed in Table-2 best isotherm models for phenol and cyanide followed the increasing trend of models: (Redlich-Peterson<Langmuir <Freundlich). The MPSD values of isotherm models were tested. It was noticed that MPSD value of Langmuir was smaller as compared to that of Freundlich model. So, it can be concluded that Langmuir model was best fitted for the experimental data. The Langmuir model is represents monolayer coverage .

A dimensionless separation factor (R_L) can be represented as:

$$R_L = \frac{1}{(1+bC_0)}$$

where b (L/mg) is the Langmuir constant and C_0 is denoted to the initial concentration of adsorbate (mg/L). The value of R_L value indicates the nature of adsorption as unfavourable (RL > 1), linear (RL = 1), favourable (0 < RL < 1) or irreversible (RL = 0). It could be observed from Table I that the values of b are more for cyanide than that of phenol, thereby indicating more stable cyanide in comparison to phenol [27]. The value of constant n in freundlich isotherm gives an information about the favourability of adsorption. The values of n in the range 2–10 represent good, 1– 2 moderately difficult, and less than 1 poor adsorption characteristics.

The values of R_L for phenol and cyanide lies between 0 and 1 for all initial concentration indicating adsorption of phenol and cyanide on to Rice husk is very much favorable. And from Table-I it could be observed that the value of n for both phenol and cyanide was lie between 1 and 10 indicating favorable adsorption of phenol and cyanide Onto Rice husk[28][29]. The constant β in Redlich-Peterson isotherm lies between 0 and 1.

The maximum uptake capacity of phenol and cyanide were 63.53 mg/g and 41.89 mg/g respectively, it is observed that Rice Husk has a feasible to be a good adsorbent for removal of phenol and cyanide from wastewater due to its high sorption capacity and availability.

4. CONCLUSIONS

In the present investigation it was evident that Rice husk can be used as an economically feasible adsorbent for the removal of phenol and cyanide from waste water. It was observed that maximum percentage removal of 53.45% phenol and 66.33 % cyanide were found from binary component system containing 300 mg/L of phenol and 30mg/L of cyanide. Equilibrium isotherm study was also carried out at optimized parameters. The equilibrium sorption data was better fitted by Langmuir isotherm and Redlich Peterson isotherm model than that for Freundlich isotherm. The optimum pH was found 8 ,optimum adsorbent dose was estimated as 40 g/L with reaction temperature of 30 ^{0}C. Equilibrium adsorption time for phenol and cyanide are 30 h and 26 h respectively.

5. ACKNOWLEDGMENT

The authors are thankful to Department of Chemical Engineering, Indian Institute of Technology Roorkee, India for providing technical support and facilities. The authors would also like to thank to Ministry of Human Resource Development (MHRD, New Delhi), Government of India for funding this research work.

6. NOMENCLATURE

Q_e	Adsorptive uptake
C_0	Initial concentration (mg/l) of pollutants
C_e	Equilibrium concentration (mg/l) of pollutants
η	Adsorption efficiency
$Q_{e,cal}$	Experimental specific uptake (mg/g^{-1})
$Q_{e,\exp}$	Calculated specific uptake (mg/g^{-1})
R_L	Separation factor
K_F	Constant in Freundlich model
n	Constant in Freundlich model
K_{RP}	Redlich-Peterson Constant
a_{RP}	Constant Redlich-Peterson Constant
β	Constant of Redlich–Peterson isotherm (0 < b < 1)
B_F	Bias Factor
MPSD	Marquardt's percent standard deviation
RSME	Root mean square error
NSD	Normalized standard deviation
SEP	Standard error of prediction
V	Volume of the solution (L)
W	Mass of the adsorbent used (gm)
N	Number of observations in the experimental isotherm
P	Number of parameters in the regression model

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