

# Equilibrium, Kinetic and Thermodynamic Studies of Simultaneous Co-Adsorptive Removal of Phenol and Cyanide Using Chitosan

Bhumica Agarwal, Priya Sengupta, Chandrajit Balomajumder

**Abstract**—The present study analyses the potential of acid treated chitosan for simultaneous co-adsorptive removal of phenol and cyanide from a binary waste water solution. The effects of parameters like pH, temperature, initial concentration, adsorbent dose, and adsorbent size were studied. At an optimum pH of 8, temperature of 30°C, initial phenol and cyanide concentration of 200 mg/L and 20 mg/L respectively, adsorbent dose of 30 g/L and size between 0.4-0.6 mm the maximum percentage removal of phenol and cyanide was found to be 60.97% and 90.86% respectively. Amongst the adsorption isotherms applied extended Freundlich best depicted the adsorption of both phenol and cyanide based on lowest MPD value. The kinetics depicted that chemisorption was the adsorption mechanism and intraparticle diffusion is not the only rate controlling step of the reaction. Thermodynamic studies revealed that phenol adsorption was exothermic and spontaneous whereas that of cyanide was an endothermic process.

**Keywords**—Chitosan, Co-adsorption, Cyanide, Phenol.

## I. INTRODUCTION

WITH the rapid population growth and industrialization, the access to clean and fresh water resources has been greatly marginalized [1]. The contaminated waste of different industries is bringing down havoc to the civilization. Amidst of all the sources of contamination of water resources, the one considered in the present study is the waste water from the coke industries. The effluent from coke industries consist of a variety of toxic chemicals amongst which phenol and cyanide have higher devastating effects on both humans and aquatic life [2]-[5].

The MCL (Maximum Contaminant Level) of phenol and cyanide in industrial discharge is set to be 0.5mg/L and 0.2mg/L [2]. Phenol and cyanide derivatives are also listed in CERCLA priority list of hazardous substances [6]. Exposure to even small amounts of these can prove deadly therefore treatment of these effluents is necessary before their discharge [3], [4], [7]. A number of removal techniques have been suggested for phenol and cyanide [1], [8], but the most widely used method still remains adsorption as it is cost effective, safe at handling, eco-friendly and it has efficiency in

operational time [9]. Researchers have used a variety of adsorbents for the removal of phenol and cyanide separately. Generally the adsorbents like GAC, pressmud, flyash, bentonite [2], [9]-[11] etc. have been used for the treatment of phenol and activated carbon, metal impregnated activated carbon, pistachio hull waste etc have been used for cyanide removal [7], [8], [12]. From the previous studies it can be concluded that among the aforementioned adsorbents Granular activated Carbon (GAC) has the highest adsorption capacity for both phenol as well as cyanide. However search for economically fit alternative raw material is being carried out.

Chitosan, derived from the natural sources, is the exoskeleton of insects, crustaceans and fungi. It is a semi synthetically derived aminopolysaccharide which is biodegradable and has a wide range of applications in biomedical and other industries. A linear co-polymer of  $\beta$ -(1-4) linked 2-acetamido-2-deoxy- $\beta$ -D-glucopyranose and 2-amino-2-deoxy- $\beta$ -D-glucopyranose [13], chitosan has been used previously for the adsorptive removal of phenol [14] but to the best of our knowledge it has not been used for the co-adsorptive removal of phenol and cyanide.

The present study is focussed on the efficient co-adsorptive removal of phenol and cyanide from coke industry waste water. Co-adsorptive removal is a better option when a multicomponent mixture is taken into consideration as it is cost effective, saves time as compared to the separate removal of components, and brings out the effect of one pollutant on the adsorptive removal of other pollutants thereby bringing forth a more realistic picture of waste water treatment before discharging into main river stream. So the present study considers the potential of chitosan for simultaneous removal of cyanide and phenol by co-adsorption, along with applicability of various equilibrium and kinetic models.

## II. MATERIALS AND METHODS

### A. Chemicals and Adsorbents

All the chemicals used in this study were of analytical grade and obtained from Himedia Laboratories Pvt. Ltd. Mumbai India. 0.25g of KCN was dissolved in 1L of millipore water (Q-H<sub>2</sub>O, Millipore Corp. with resistivity of 18.2 MX-cm) to prepare a stock solution of cyanide concentration of 100mg/L. The pH of the cyanide stock solution was adjusted to 10 using 1N NaOH. The phenol stock solution, with the concentration of 1000mg/L, was prepared by adding 1g of pure phenol crystals to 1L of millipore water. To increase the surface area

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and pore volume of chitosan, the flakes were washed with millipore water and soaked in 0.5M H<sub>2</sub>SO<sub>4</sub> for 24h in 2:1 ratio of liquid to solid. After acid treatment the adsorbent was again washed with millipore water then dried overnight in the hot air oven at 60°C to completely remove moisture. It was then cooled to room temperature, grinded in a ball mill, sieved to various fractions (0.2-0.4mm, 0.4-0.6mm, 0.6-0.8mm, and 0.8-1mm) and stored in polybags until further use. Adsorbent's surface area (BET) which was 7.68 m<sup>2</sup>/g and total pore volume was determined using physisorption surface analysis on surface area analyzer (ASAP 2010 Micrometrics, USA). Composition of Chitosan used in present study was 0.24% ash, 11.54% moisture, 65.43% carbon, 6.06% hydrogen, 7.45% nitrogen and 0.073% sulfur as analyzed by proximate and ultimate analysis.

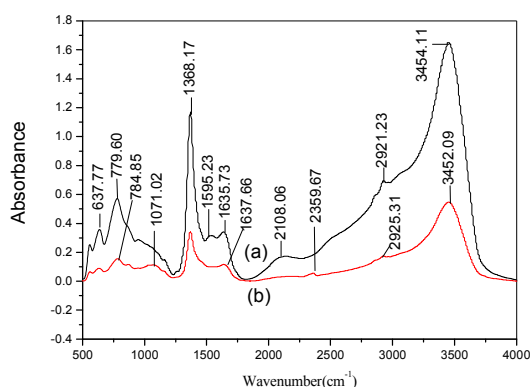


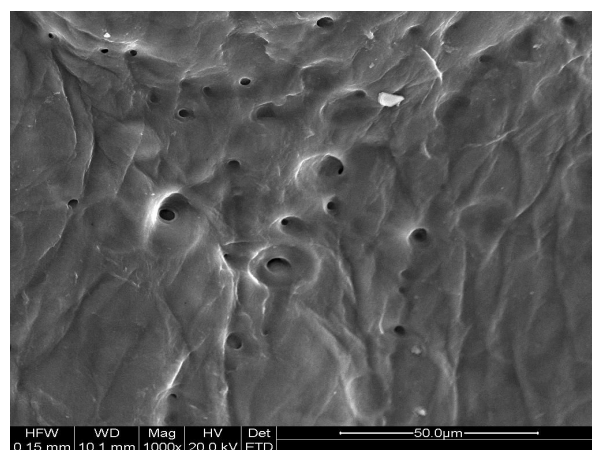
Fig. 1 FTIR spectrum of (a) Acid treated chitosan (b) Phenol and cyanide loaded chitosan.

The type of functional group present on adsorbent's surface before and after adsorption was determined by using Fourier Transform Infrared Spectroscopy FTIR (FTIR, Nicolet 6700, USA), as it influences the extent of adsorption. The results of FT-IR (Fig. 1) depicted the functional groups of the acid treated GAC involved in the adsorption of phenol and cyanide. As shown in Fig. 1 (a) the spectrum of chitosan displays following major distinct bands at wavenumbers 3454, 2921, 1635, 1595, 1368, and 637cm<sup>-1</sup>. A broad and strong band appeared at 3454cm<sup>-1</sup> which corresponds to the stretching and extension vibration of O-H and N-H and inter hydrogen bonds of polysaccharides. The bands located at 2921cm<sup>-1</sup> can be attributed to asymmetric and symmetric -CH<sub>2</sub> groups. The absorption band at 1635cm<sup>-1</sup> is characteristic of amine deformation. Peak at 1595cm<sup>-1</sup> is indicative of -CH stretching due to the presence of conjugated hydrocarbon groups, aromatic hydrocarbons, carboxylic groups and carboxyl and carbonate structures. The prominent band observed at 1368cm<sup>-1</sup> represents C-N stretching. The band at 637cm<sup>-1</sup> corresponds to -NH<sub>2</sub> wagging vibration band. From Fig. 1 (b) it could be observed that some peaks are shifted, appeared, depleted or broadened indicating that the functional groups present on the biosorbent is involved in adsorption of phenol and cyanide. SEM analysis was also carried out of loaded and

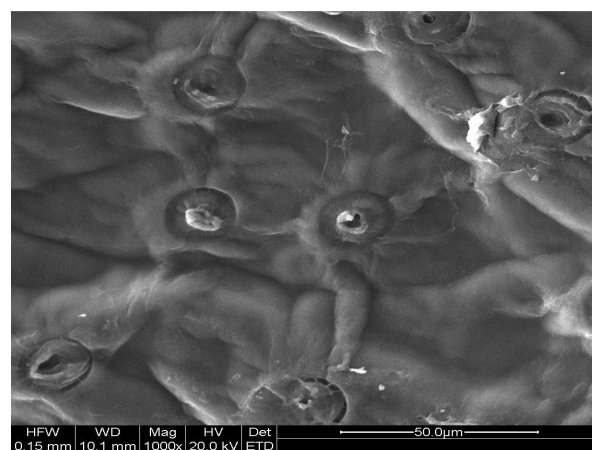
unloaded samples to visualize the changes in surface morphology due to adsorption of phenol and cyanide (Fig. 2).

### B. Batch Experiments

A 250mL round bottom flask with working volume of 100mL was taken for the experiments and kept at 125rpm in an incubator cum orbital shaker (Metrex MO-250, India). The concentration of phenol and cyanide was taken in the ratio 10:1 for the multi-component mixture [2]. The incubator was covered with black cardboard properly throughout the experiment to avoid photo-oxidation of phenol. All the experiments were carried out in triplicates and average results were used. Initial adsorbate concentrations were selected as 200mg/L for phenol and 20mg/L for cyanide.



(a)



(b)

Fig. 2 SEM analysis of acid treated chitosan (a) before adsorption and (b) after adsorption

The optimum pH and temperature were selected from the range of 4-11 and temperature 20-40°C. Chitosan dose was varied between the range of 5-40 g/L and the adsorbent dose at which the highest percentage removal of phenol and cyanide was witnessed was taken as the optimum dose. The experiments were carried out for 48h to provide sufficient time for equilibrium to be achieved. The initial pH of the solution

was maintained after every 2h with 1N NaOH or HCl as per requirements. For equilibrium studies, the initial concentrations of phenol and cyanide were taken in the range between 100-1000 mg/L and 10-100 mg/L respectively. At an interval of every 2 h, till the equilibrium was achieved, sample was withdrawn and filtered with standard Whatman filter paper Cat No. 1001 125. The filtrate was then analysed for phenol and cyanide using colorimetric method, 4-aminoantipyrene and picric acid method respectively. The amount of phenol and cyanide adsorbed per unit mass of the adsorbent was evaluated by the following mass balance equation:

$$q = (C_0 - C_t)V/M \quad (1)$$

where  $C_0$  is the initial pollutant concentration (mg/L),  $C_t$  is the pollutant concentration at any time  $t$ ,  $V$  is the volume of the solution (L) and  $M$  is the mass of adsorbent used (g).

### C. Equilibrium Isotherms

Equilibrium modeling of adsorption data is necessary for describing the interactive behavior of adsorbates and adsorbents. They help in studying the effect that one component has on the adsorption of the other component and their comparative affinity for binding sites [2]. The simple equilibrium models used for typical adsorption processes are Langmuir, Freundlich, Toth, Redlich-Peterson, Radke-Prausnitz model etc. Since the present study is based on the simultaneous removal of pollutants from multi-component system containing phenol and cyanide where components cause interference and competition for active sites which leads to a more complex mathematical formulation of the equilibrium therefore single component models cannot fully solve the purpose [15]. These complex multi-component systems can be modeled using variants of single isotherm models as discussed below:

Non-modified competitive Langmuir:

$$q_{e,i} = (Q_{0,i}b_iC_{e,i})/(1 + \sum_{j=1}^N b_jC_{e,j}) \quad (2)$$

Modified competitive Langmuir:

$$q_{e,i} = (Q_{0,i}b_iC_{e,i}/n_i)/(1 + \sum_{j=1}^N b_j(C_{e,j}/n_j)) \quad (3)$$

Extended Langmuir:

$$q_{e,i} = (Q_{0,i}b_iC_{e,i})/(1 + \sum_{j=1}^N b_jC_{e,j}) \quad (4)$$

Extended Freundlich:

$$q_{e,i} = (K_{F,i}C_{e,i}^{n_i+x_i})/(C_{e,i}^{x_i} + y_iC_{e,j}^{z_i}) \quad (5)$$

$$q_{e,j} = (K_{F,j}C_{e,j}^{n_j+x_{ij}})/(C_{e,j}^{x_{ij}} + y_{ij}C_{e,i}^{z_j}) \quad (6)$$

### D. Kinetic Studies

To investigate the mechanism of adsorption i.e. physisorption or chemisorption along with the time profile and rate constant of the adsorption kinetic studies were carried out. Different models used were pseudo first order (physisorption), pseudo second order (chemisorption) and Weber and Morris or intraparticle model for mass transfer effects. Equations describing the aforementioned models are given below:

Pseudo-first order:

$$q_t = q_e(1 - \exp(-k_1t)) \quad (7)$$

Pseudo-second order:

$$q_t = k_2q_e^2t/(1 + q_ek_2t) \quad (8)$$

Intraparticle:

$$q_t = k_{id}t^{0.5} \quad (9)$$

### E. Thermodynamic Studies

The thermodynamic parameters like  $\Delta S^0$  (Entropy),  $\Delta G^0$  (Gibbs free energy),  $\Delta H^0$  (Enthalpy) can be studied by Linearized Van't Hoff equations:

$$\log K_c = (\Delta S^0/2.303R) - (\Delta H^0/2.303RT) \quad (10)$$

$$\Delta G^0 = -RT \log K_c \quad (11)$$

where  $R$  is the gas constant =8.314 J/mol K,  $\Delta G^0$  is kJ/mol,  $T$  is the temperature in K,  $\Delta S^0$  is kJ/mol-K,  $\Delta H^0$  is kJ/mol and  $K_c$  is the equilibrium constant (amount of adsorbate on adsorbent/ amount of adsorbate in solution).

### F. Model Validation

The error function, namely, Marquardt's percent standard deviation (MPSD) was used for the validation of both equilibrium and kinetic models:

$$MPSD = 100 \times \sqrt{\frac{1}{N-P} \sum \left( \frac{q_{e,i}^{exp} - q_{e,i}^{cal}}{q_{e,i}^{exp}} \right)^2} \quad (12)$$

where  $q_{e,i}^{exp}$  = experimental specific uptake (mg/g),  $q_{e,i}^{cal}$  = calculated specific uptake (mg/g) for corresponding  $q_{e,i}^{exp}$ ,  $N$  is the number of observations in the experimental isotherm and  $P$  is the number of parameters in the regression model. The smaller MPSD value indicates more accurate estimation of  $q_e$ .

## III. RESULTS AND DISCUSSION

### A. Effect of pH

The study of the effect of pH is necessary as it affects the extent of ionisation, the speciation of pollutant along with the surface characteristics of adsorbent. pH greatly influences the adsorption capacity of the adsorbent as well as the ability of adsorbate to get adsorbed. The effect of pH on the co-adsorption of phenol and cyanide was studied in the pH range

of 4-11. Fig. 3 shows the change in percentage removal of phenol and cyanide with pH. In case of phenol, the percentage removal increases with pH between 4-8, shows a maximum removal of 61 % at a pH 8 and then decreases as the pH further reaches 11. This shows that phenol adsorption takes place mainly in its undissociated form adhering to the fact that phenol has a  $pK_a$  of 9.96 under which it remains undissociated. In case of cyanide the percentage removal increases in acidic pH, shows a maximum of 90.86 % at pH 8 and then becomes constant in alkaline conditions. In acidic pH cyanide is evolved as HCN gas which shows the increase in removal of free cyanide but is not a favorable condition as HCN is highly toxic and evolution of HCN does not account for cyanide removal but does account for a good deal of air pollution. Therefore the pH should not be reduced below 4 and the pressure should be so maintained that there is no evolution of HCN [16]. Since the  $pK_a$  of cyanide is 9.39 therefore cyanide also shows the behavior of getting adsorbed in its undissociated form [2].

#### B. Effect of Temperature

Fig. 4 depicts the effect of increasing temperature on the percentage removal of phenol and cyanide. The behavior of the graph shows that maximum removal of 67% phenol takes place at 20°C and then it decreases gradually with increasing temperature. The decrease in percentage removal of phenol with temperature could be due to the increased tendency of desorption of phenol at increased temperature resulting due to weakening of adsorptive forces between active sites of adsorbent and adsorbate as well as between the adjacent molecules of adsorbate [17]. In case of cyanide the percentage removal increases very slowly with increasing temperature and becomes almost constant after 30°C, showing a maximum removal of 92% at 40°C. The behavior shown can be attributed to the fact that with increase in temperature the number of active sites for adsorption increases due to breaking of some internal bonds [18]. The increase in temperature also increases the rate of diffusion of adsorbate molecules in the adsorption sites due to the decrease in viscosity of the solution [19].

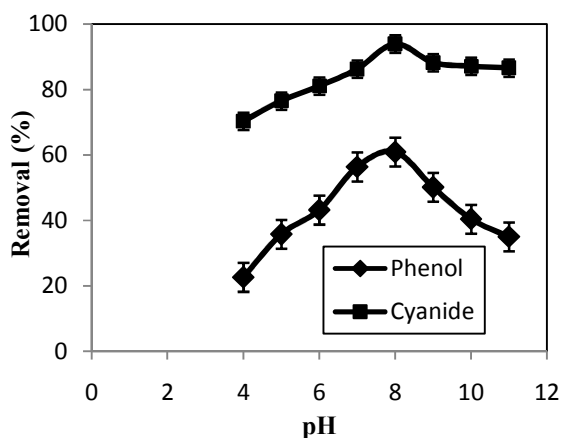


Fig. 3 Effect of pH on percentage removal of phenol and cyanide

#### C. Effect of Adsorbent Dose

The effect of adsorbent dose on the co-adsorptive removal of phenol and cyanide was studied between a chitosan dose of 5-40g/L. From Fig. 5 it is clearly visible that the percentage removal increases with adsorbent dose till 30g/L and then it becomes constant. The initial increase in percentage removal could be explained due to increase in active sites with increase in adsorbent dose. However above certain dose removal percentage assumes an asymptotic value [3]. The possible explanation for the behavior could be that there is an overlapping of active sites at high doses which decreases the surface area as was observed by [2] in the case of GAC for co-adsorptive removal of phenol and cyanide. Optimum removal of 61% phenol and 91% cyanide occurs at 30g/L therefore it has been taken as optimum adsorbent dose and is considered for further equilibrium and kinetic studies.

#### D. Effect of Contact Time

Analyzing the effect of contact time is essential for the adsorption study for kinetic studies as well as for further practical applications concerned with the design of continuous reactor. In case of phenol an increase in removal is witnessed till 18h (Fig. 6) where it shows the maximum removal and after that removal becomes constant. Similar study on cyanide revealed that cyanide showed a trend of increasing removal with time and reached a maximum in 26h. Initially the adsorption is fast attributing to weak Van der Waals forces only. However with increase in time there is a strong bond formation between adsorbate and adsorbent which slows down the percentage removal. The results are in accordance with the results obtained in the co-adsorption of phenol and cyanide on GAC [2].

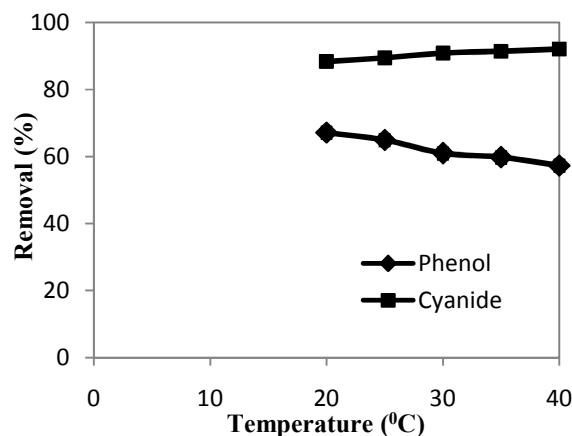


Fig. 4 Effect of temperature on percentage removal of phenol and cyanide

#### E. Effect of Initial Concentration

The initial adsorbate concentration provides a driving force to overcome mass transfer limitations between adsorbate and adsorbent. In the case of phenol (Fig. 7 (a)) a maximum percentage removal of about 69% takes place at an initial concentration of 100mg/L; on further increasing the concentration from 200-1000 mg/L the percentage removal

decreases. Similarly maximum cyanide removal is around 93% at a concentration of 10mg/L which decreases further with increasing concentration till 100mg/L (Fig. 7 (b)). The reason for this behavior could be that at low concentrations the active sites are easily occupied by the sorbent molecules which show a high percentage removal while a high concentration leads to saturation of binding capacity of adsorbents which decreases removal [15].

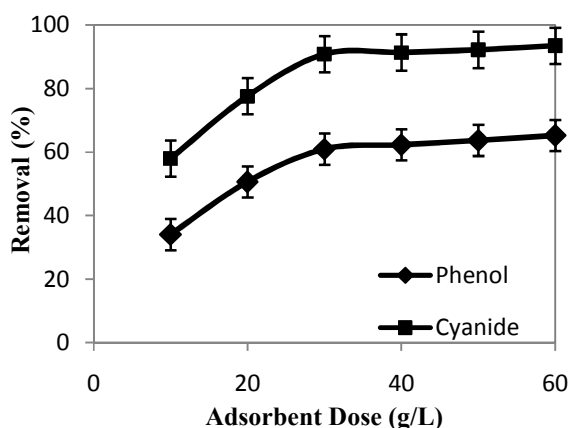


Fig. 5 Effect of adsorbent dose on percentage removal of phenol and cyanide

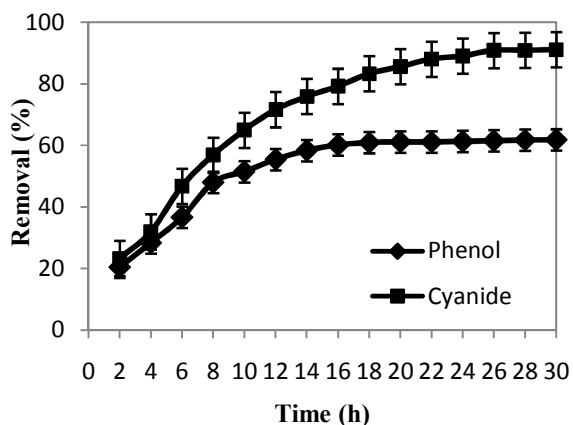


Fig. 6 Effect of contact time on percentage removal of phenol and cyanide

#### F. Effect of Adsorbent Size

The effect of size of adsorbent on percentage removal of phenol and cyanide has been studied and depicted in Fig. 8. The maximum removal of 65% phenol and 91% cyanide can be seen in the adsorbent size of 0.4-0.6mm. Keeping in view the economy of the process an adsorbent size of 0.4-0.6mm is selected to be optimum for further studies as achieving an even smaller size increases the operating cost of the process.

#### G. Equilibrium Modeling

The adsorption equilibrium data for phenol and cyanide on chitosan was analyzed using Solver function of Microsoft excel 2010. The data for multicomponent adsorption of phenol and cyanide onto chitosan were fitted to different

multicomponent isotherm models i.e. Non-modified Langmuir, Modified Langmuir, Extended Langmuir and Extended Freundlich. These multicomponent models use the constants from single component models. From Table I and Fig. 9 it could be concluded that Non-modified Langmuir as well as Modified Langmuir are not suitable to be used for prediction of  $q_{e,cal}$  for the multicomponent adsorption due to the high values of MPSD. Extended Langmuir provided reduced value of MPSD but better results were obtained by Extended Freundlich model with lowest MPSD's of 12.78 for phenol and 6.47 for cyanide. The maximum adsorption capacity of chitosan as calculated by extended Langmuir model was found to be 218.54 and 2.05 mg/g for phenol and cyanide respectively.

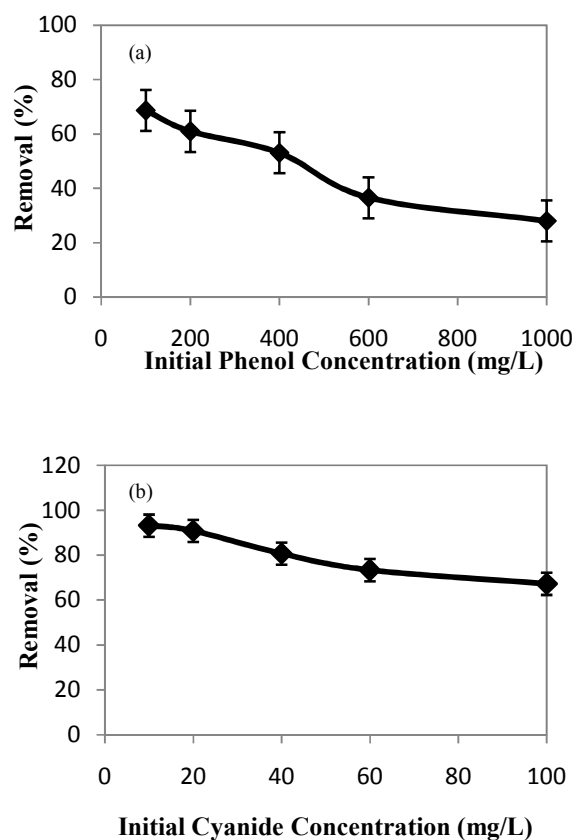


Fig. 7 Effect of initial concentration on percentage removal of (a) phenol and (b) cyanide.

#### H. Kinetic Modeling

The adsorption takes place either by physisorption (pseudo-first order) or by chemisorption (pseudo-second order) which could be determined by kinetic modelling. From the data presented in Table II and Fig. 10, following inferences could be drawn: both phenol and cyanide shows better kinetic data prediction by pseudo-second order model owing to lower MPSD values. Hence both phenol and cyanide are adsorbed by chemisorption. Further the nature of diffusion is determined by graph of  $q_t$  vs  $t^{0.5}$ . According to [3] the plot should be linear for intraparticle diffusion to be involved.

Since the plot is non-linear (Fig. 11) and it does not pass through origin, intraparticle diffusion is not the rate controlling step and other kinetic models also control the rate of adsorption [3], [8].

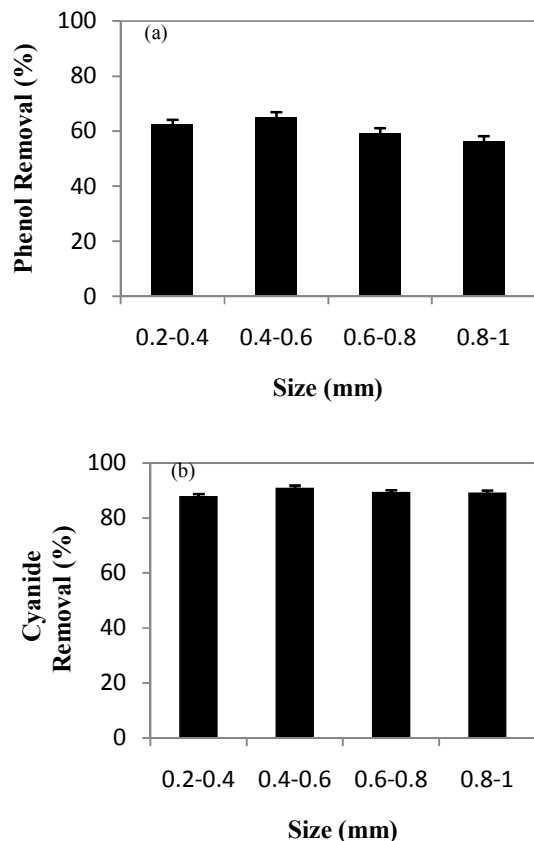


Fig. 8 Effect of particle size on percentage removal of (a) phenol and (b) cyanide

TABLE I  
STUDY OF DIFFERENT MULTI-COMPONENT ISOTHERMS FOR ADSORPTION OF PHENOL AND CYANIDE

Isotherm	Parameter	Phenol	Cyanide
Non-modified Langmuir	MPSD	65.28	36.71
	$n_i$	0.669631	1.00696
Modified Langmuir	$Q_{0i}$	9.567028	1.641725
	MPSD	35.89	18.33
Extended Langmuir	$b_i$	0.000315	0.228854
	MPSD	12.78	6.47
Extended Freundlich	$x_i$	1.28736	-0.51077
	$y_i$	7.552561	23.48165
	$z_i$	-3.07299	-1.14092

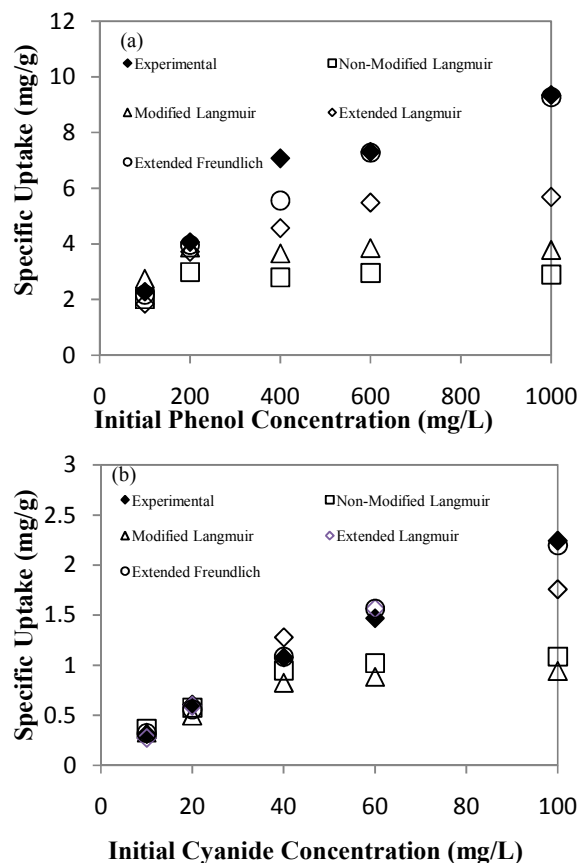


Fig. 9 Equilibrium adsorption isotherms for (a) phenol and (b) cyanide at 30 °C and 200 mg/L phenol and 20 mg/L cyanide

### I. Thermodynamic Modeling

From the graph plotted between  $\log k_c$  vs  $1/T$ , the values of  $\Delta H^0$  and  $\Delta S^0$  were calculated from slope and intercept respectively and the results are summarized in Table III. In the case of phenol  $\Delta G^0$ ,  $\Delta H^0$  and  $\Delta S^0$  emerge as negative which shows the process to be feasible, exothermic and spontaneous in nature, whereas for cyanide the values of  $\Delta H^0$  and  $\Delta S^0$  emerge as positive values which shows an endothermic process along with increased randomness at the surface of solute-solution interface during adsorption. The value of  $\Delta S^0$  comes out to be less than 1 which shows that the adsorption process is reversible for both phenol and cyanide [2].

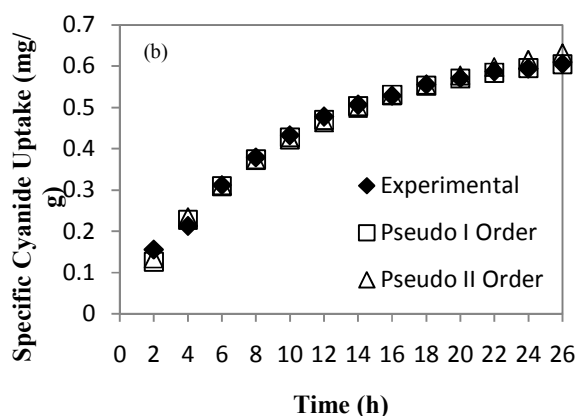
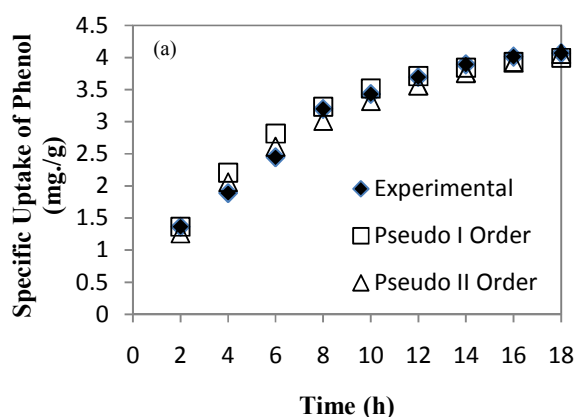


Fig. 10 Kinetic modelling of adsorption of (a) phenol and (b) cyanide at reaction conditions

#### IV. CONCLUSION

Simultaneous co-adsorption of phenol and cyanide was studied at different pH, temperature, sizes and doses of adsorbents. The optimum parameters at which a maximum phenol removal of 60.97% and cyanide removal of 90.86% from a binary solution containing phenol 200 mg/L and cyanide 20mg/L was attained at pH 8, temperature 30°C and adsorbent dose of 30g/L at an optimum size of 0.4-0.6mm. Equilibrium, kinetic and thermodynamic studies were also carried out at optimized parameters. Phenol and cyanide co-adsorption in multicomponent system was expressed by extended Freundlich isotherm. As per the kinetic studies pertaining to phenol and cyanide co-adsorption, chemisorption was revealed to be the mechanism of the process. Further evaluation showed that intraparticle diffusion is not the rate controlling step; other phenomenon may also be involved. Adsorption of phenol onto acid treated chitosan was found to be exothermic and spontaneous while that of cyanide was an endothermic process. The study revealed that chitosan can be used as a promising adsorbent for simultaneous co-adsorptive phenol and cyanide removal.

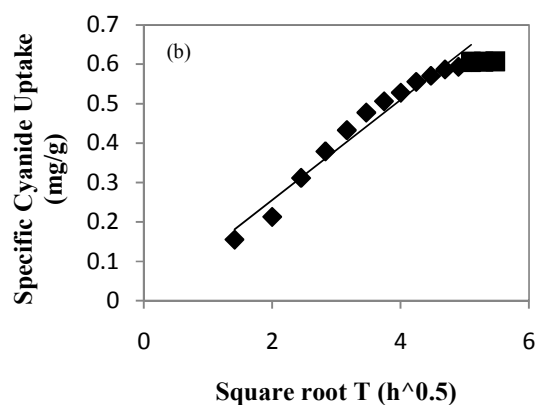
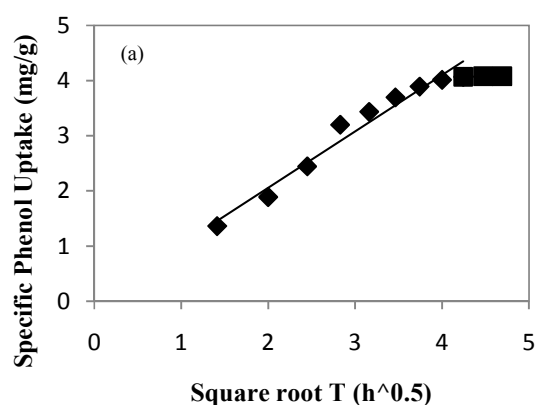


Fig. 11 Intraparticle plot of (a) phenol and (b) cyanide adsorption

TABLE II  
EVALUATION OF PARAMETERS OF KINETIC MODELS

Component	Parameter	Phenol	Cyanide
Pseudo-first order	$q_{e,cal}$	4.124	0.642
	$k_1$	0.201	0.109
	MPSD	7.670	5.59
Pseudo-second order	$q_{e,cal}$	5.612	0.914
	$k_2$	0.025	0.094
	MPSD	5.096	5.282
Intraparticle	$k_1$	1.022	0.127
	$k_2$	0.027	0.004
	ARE	1.616	1.827

TABLE III  
THERMODYNAMIC PARAMETERS OF PHENOL AND CYANIDE ADSORPTION

Adsorbate	Temp (°C)	$\Delta G^0$ (KJ/mol)	$\Delta H^0$ (KJ/mol)	$\Delta S^0$ (KJ/mol-k)
Phenol	20	-1.745	-16.079	-0.049
	30	-1.124		
	40	-0.769		
Cyanide	20	-4.936	16.281	0.073
	30	-5.788		
	40	-6.381		

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