International Journal of Environmental Engineering and Management.
ISSN 2231-1319, Volume 4, Number 3 (2013), pp. 233-238

http://www.ripublication.com/ ijeem.htm

Simultaneous Adsorption and Biodegradation of Phenol and Cyanide in Multicomponent System

B. Agarwal[1] and C. Balomajumdar[2]

[1]Department of Chemical Engineering, IIT Roorkee, Roorkee, Uttrakhand, INDIA.
[2]Department of Chemical Engineering, IIT Roorkee, Roorkee, Uttrakhand, INDIA.

Abstract

The present study deals with the equilibrium and kinetic modeling of SAB of phenol and cyanide from multicomponent solution using an isolated strain of Serratia sp. and Iron impregnated-Granular Activated Carbon (Fe-GAC). The effect of process parameters like pH, temperature and contact time on the removal efficiency has been evaluated. A pH of 8 and temperature of 30 ^{0}C were found to yield best results. At an adsorbent dose of Fe-GAC of 10 g/L, pH 8 and temperature 30 ^{0}C, over 99 % removal of 200 mg/L phenol and 20 mg/L cyanide was achieved. Four multicomponent isotherms viz., Non-modified Langmuir, Modified Langmuir, Extended Langmuir and Extended Freundlich model were applied to the experimental data conducted at an initial concentration range of 100–1000 mg/L of phenol and 10-100 mg/L of cyanide. Single component isotherms viz. Langmuir and Freundlich were applied to determine the multicomponent isotherm parameters. It was found that both phenol and cyanide adsorption followed Extended Freundlich isotherm in multicomponent system. The monolayer biosorption capacity was found to be 943.80 and 4.43 mg/g for phenol and cyanide, respectively as calculated by Extended Langmuir isotherm. The experimental kinetic data was well defined by both pseudo-first order and pseudo-second order kinetics. Intraparticle modeling revealed that intraparticle diffusion was not the only rate limiting step of the process.

Keywords: SAB; Multi-component; Equilibrium Modeling; Kinetic Modeling.

1. Introduction

Wastewater treatment has been the topic of research for decades. With ever evolving technology, attention is being focused on the use of biological treatment, owing to the advantages offered, either alone or in combination with physico-chemical treatment methods. An emerging technique is the use of simultaneous adsorption and biodegradation (SAB) of toxic pollutants in wastewater. SAB is expected to produce more stable and effective results since adsorption reduces the inhibitory effect of the toxic compounds for the microorganisms and biodegradation works by freeing adsorption sites (Dash et al., 2009). Remediation of wastewater from coke industries is of prime importance in today's scenario as it contains a number of pollutants like phenols, cyanides, thiocyanides, thiosulphates, ammoniacal nitrogen, chlorides etc. in extremely high concentration. Among them phenol and cyanide have been found to be extremely toxic to both human and aquatic life. The MCL (Maximum Contaminant Limit) of phenol and cyanide in industrial discharge has been set as 0.5 mg/L and 0.2 mg/L, respectively by USEPA, WHO and CPCB, India (Busca et al., 2008; Dash et al., 2009). Exposure to even low concentrations of cyanide can cause coma, heart pains, breathing disorders, thyroid gland enlargement, headaches and even death. On the other hand, phenol exposure can lead to skin and eyes injuries, headache, vomiting, gastrointestinal disorders, central nervous system depression, lung, kidney, liver and heart damage ultimately leading to death.

Therefore an attempt has been made (i) to determine the optimum process parameters viz., pH, temperature, and contact time for efficient removal of phenol and cyanide from multicomponent solution using isolated strain of *Serratia sp.* and Iron impregnated-Granular Activated Carbon (Fe-GAC); (ii) to determine the extent of competition and applicability of multicomponent equilibrium models; and (iii) to study the kinetics of the process.

2. Materials and Methods

2.1 Materials and Methods

All the chemicals used in this study were of analytical grade and obtained from Himedia Laboratories Pvt. Ltd. Mumbai India. Stock solution containing 100 mg/L cyanide was prepared by dissolving 0.25 g of KCN in 1 L of millipore water (Q-H_2O, Millipore Corp. with resistivity of 18.2 MX-cm) whose pH was pre-adjusted to 10 using 1N NaOH. Stock solution containing 1000 mg/L of phenol was prepared by dissolving 1 g of pure phenol crystal in 1 L of millipore water. Iron impregnated GAC (Fe-GAC) was prepared as described elsewhere (Agarwal et al., 2013).

2.2 Batch experiments

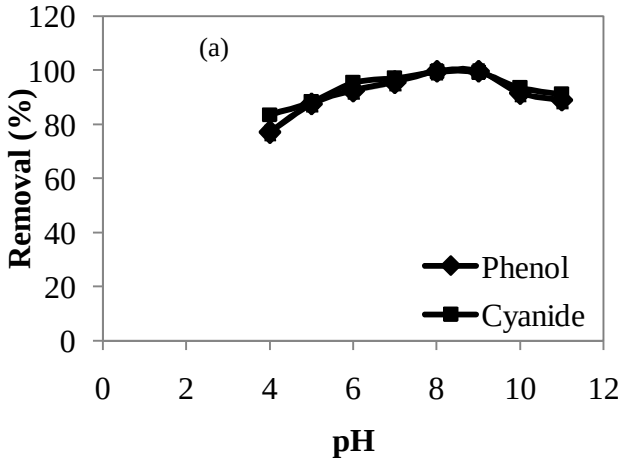
Batch experiments for optimization of process parameters were carried out in 250 mL round bottom flasks with working volume of 100 mL at 125 rpm in an incubator cum orbital shaker (Metrex, MO-250, India). Multi-component system was obtained by taking concentration of phenol and cyanide in the ratio of 10:1 as they are discharged

from coke wastewaters generally in this ratio. Initial adsorbate concentrations were selected as 200 mg/L for phenol and 20 mg/L for cyanide. The optimum pH and temperature were selected from a range of pH 4–11 and temperature 20–40 ^{0}C. All the experiments were carried out for 60 h allowing sufficient time for achieving equilibrium. After every 2 h pH of the mixture was tested and readjusted to predefined value with 1 N NaOH or HCl in case of any change during operation. For study of adsorption isotherms initial concentrations of phenol and cyanide were varied from 100 to 1000 mg/L and 10–100 mg/ L respectively. For study of adsorption kinetics an appropriate volume of sample was withdrawn at an interval of every 6 h till the equilibrium conditions was achieved, filtered with standard Whatman filter paper Cat No. 1001 125 and the filtrate was analyzed for cyanide and phenol by colorimetric picric acid and 4-aminoantipyrene methods, respectively (APHA, 2001).

3. Results and Discussions

3.1 Optimization of process parameters

Figure 1 (a), (b) and (c) represents the effect of pH, temperature and contact time respectively. As could be seen from Figure 1 (a), percentage removal of both phenol and cyanide increases with increase in pH, reaches a maximum at pH 8-9 and decreases with further increase in pH. This phenomenon could be explained on the basis of pKa of phenol (9.96) and cyanide (9.39). As the pH of the medium approaches towards the pKa, percentage removal of phenol and cyanide increases indicating adsorption of phenol and cyanide in their ionic form. Figure 1(b) depicts the effect of changing temperature on percentage removal of phenol and cyanide. As is evident on increasing temperature from 20 ^{0}C to 30 ^{0}C a slight increase in percentage removal of both phenol and cyanide is observed indicating maximum efficiency of bacteria at 30 ^{0}C. However on further increasing the temperature sharp decrease in percentage removal is observed.



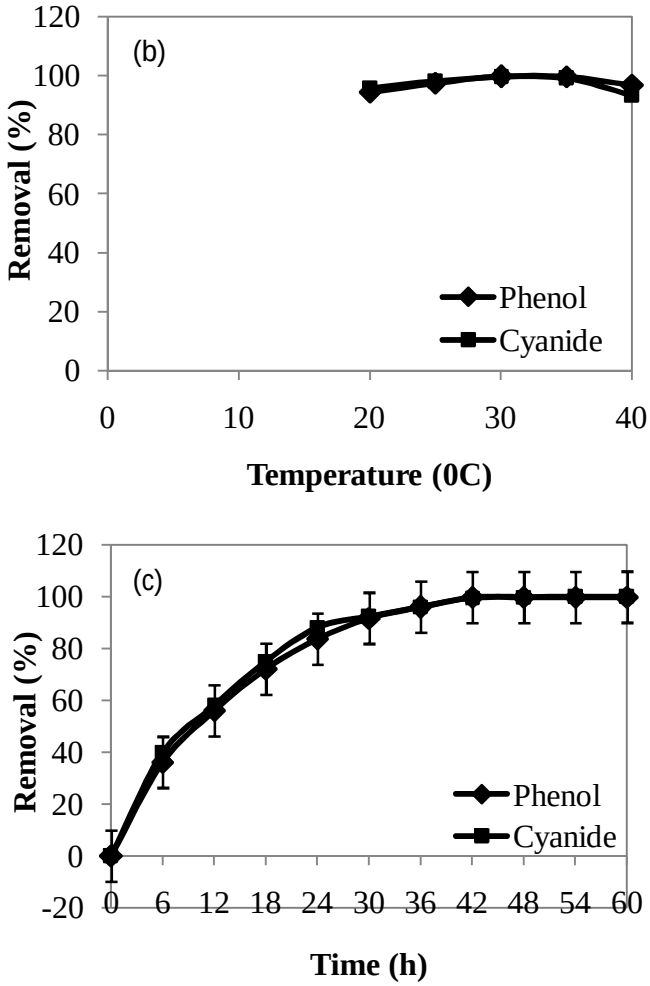


Figure 1: Effect of (a) pH, (b) Temperature and (c) contact time on percentage removal of phenol and cyanide by SAB process.

Figure 1 (c) represents the effect of contact time on the percentage removal of phenol and cyanide. It could be observed that in the initial stage of agitation (0-18 h) percentage removal increases linearly, owing to rapid adsorption of phenol and cyanide. In second stage (18-36 h) biodegradation predominates over adsorption leading to almost 95 % removal. Equilibrium is achieved in 42 h attaining 99.69 % removal of phenol and 99.53 % removal of cyanide.

3.2 Equilibrium Modeling

Equilibrium isotherms generally applicable to single solute systems viz. Langmuir, Freundlich, Redlich–Peterson, Toth, Temkin, etc. are not applicable to binary systems owing to competition for the same binding sites as well as solute–surface interactions

(Mohan and Chander, 2001; Wu et al., 2002). Therefore, equilibrium modeling of SAB of phenol and cyanide was carried out using four multi-component isotherms namely, non-modified Langmuir, Modified Langmuir, Extended Langmuir and Extended Freundlich isotherms using Microsoft Excel Solver function and the results are summarised in Table 1. From the table it is clear that adsorption of phenol and cyanide follows extended Freundlich isotherm with maximum adsorption capacity of 943.795 and 4.431065 mg/g for phenol and cyanide respectively.

Table 1: Parameters of phenol and cyanide adsorption onto GAC as estimated by multicomponent modeling.

Isotherm model	**Parameter**	**Phenol**	**Cyanide**
Non-Modified Langmuir	MPSD	46.03	87.42
Modified Langmuir	n_j	1.96	2.62
	MPSD	40.87	70.87
Extended Langmuir	$Q_{o,i}$	943.79	4.43
	b_i	0.05	10.31
	MPSD	36.14	35.18
Extended Freundlich	MPSD	16.52	16.73

3.3 KineticModeling

Non linear curve fitting of pseudo-first and -second order was carried out on contact time data and it was found that both the orders predict adsorption behavior satisfactorily indicating adsorption of phenol and cyanide to be via physical interactions as well as chemisorptions. Intraparticle modeling indicated presence of both surface and intraparticle diffusion reinforcing the fact that intraparticle diffuison is not the rate limiting step in the adsorption of phenol and cyanide.

4. Conclusion

In the present study, capability of SAB system for efficient removal of phenol and cyanide from synthetic coke wastewater was evaluated. It was observed that the system was capable of almost complete removal of 200 mg/L phenol and 20 mg/L cyanide. A pH of 8, temperature of 30 ^{0}C and contact time of 42 h was sufficient to achieve equilibrium. Multi-component isotherms in an initial concentration range of 100–1000 mg/L of phenol and 10-100 mg/L of cyanide were applied and extended Freundlich isotherm was found to be the best fit.

5. Acknowledgement

The authors are thankful to Ministry of Human Resource Development, Government of India and Institute's Instrumentation Center, IIT Roorkee for extending their financial and technical support for present research work.

References

[1] R R Dash, C Balomajumder and A Kumar (2009), Treatment of cyanide bearing water/ wastewater by plain and biological activated carbon, *Ind. Eng. Chem. Res.* **48,** *7*, pp. 3619–3627.

[2] G Busca, S Berardinelli, C Resini and L Arrighi (2008), Technologies for removal of phenol from fluid streams: a short review on recent developments, *J. Hazard. Mater.* **160**, *2–3*, pp. 265–288.

[3] B Agarwal, P K Thakur and C Balomajumder (2013), Use of Iron-Impregnated Granular Activated Carbon for Co-Adsorptive Removal of Phenol and Cyanide: Insight into Equilibrium and Kinetics, *Chem. Eng. Comm.*, **200**, pp. 1278–1292.

[4] APHA (2001) *Standard Methods for the Examination of Water and Wastewater*, 20th ed, American Public Health Association, Washington, DC.

[5] D Mohan and S Chander (2001), Single component and multi-component adsorption of metal ions by activated carbons, *Colloids Surf. A*, **177**, *2–3*, pp. 183–196.

[6] C.H. Wu, C Y Kuo, C F Lin and S L Lo (2002), Modeling competitive adsorption of molybdate, sulfate, selenate, and selenite using a Freundlich-type multicomponent isotherm, *Chemosphere*, **47**, *3*, pp. 283–292.