Research Article

Co-Adsorptive removal of Phenol and Cyanide using a novel, low cost Adsorbent: An Optimization Study

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Abstract

The present study deals with the use of residual coal, an alternative, low cost adsorbent for the co-adsorptive removal of phenol and cyanide from synthetic waste water. The effect of pH, initial concentration, adsorbent dose and contact time on percentage removal was studied. Optimization was performed for maximizing the simultaneous phenol and cyanide adsorption capacity. A maximum of 50.09% phenol at an initial concentration of 200 mg/L and 78.89% cyanide at an initial concentration of 20 mg/L was removed at an optimum pH of 9 and adsorbent dose of 40 g/L. Time required to achieve equilibrium in case of phenol was 26 h and of cyanide was 32 h.

Keywords: Phenol, Cyanide, Residual Coal, Co-Adsorption.

1. Introduction

Ever increasing urbanization and industrialization has led to the discharge of a number of pollutants into water streams thereby leading to deterioration of their quality and raising concerns of the environmentalists worldwide. Industrial discharge from coke processing industry contains large quantities of toxicants like phenol, cyanides, thiocyanides, thiosulphates, ammoniacal nitrogen, chlorides etc. Among these, phenol and cyanide have been listed as priority pollutants by the Central Pollution Control Board (CPCB), India and Environmental Protection Agency (EPA), USA. Exposure to even low concentrations of phenol and/or cyanide can cause coma, heart pains, breathing disorders, thyroid gland enlargement, headaches, skin and eye injuries, vomiting, gastrointestinal disorders, central nervous system depression, lung, kidney, liver and heart damage ultimately leading to death (ATSDR, 2006, ATSDR, 2008). The USEPA has set the threshold concentration of phenol in effluent discharge as 0.5 mg/L and cyanide as 0.2 mg/L.

To achieve the MCL (Maximum Contaminant Level) values during waste water treatment a number of chemical, physical and biological methods are available. Among available waste water treatment technologies, adsorption, particularly using granular activated carbon (GAC), has gained much popularity owing to its efficiency and ease. However high cost of GAC and difficulty in its regeneration has led to exploration of non-conventional adsorbents. In last few decades, materials which are produced as agricultural and/or industrial byproducts and require further action/ treatment have attracted attention of

researchers owing to their easy availability and cost effectiveness. Some of these adsorbents include saw dust (D. N. Jadhav and A. K. Vanjara, 2004), vegetable and fruit peels (L. Mandi *et al*, 2009), peat, fly ash, bentonite (T. Virarghavan and F.M. Alfaro, 1998) etc. Another problem, other than choosing a suitable adsorbent, is studying the effect of multicomponents present in waste water on adsorptive capacity of adsorbent. A number of isotherms namely Langmuir, Freundlich, Redlich-Peterson, Toth, Temkin etc. are studied to model the process of adsorption of single component adsorption. However these models are not applicable to binary systems in most of the cases owing to the complexities arising due to different solute-surface interactions (D. Mohan and S. Chander, 2001, C. H. Wu *et al*, 2002, B. Agarwal *et al*, 2013).

The present study deals with the evaluation of adsorption capacity of residual coal as a non-conventional, low cost adsorbent, and optimization of process parameters for maximum removal of phenol and cyanide from synthetic waste water.

2. Materials and Methods

2.1 Chemicals and Adsorbent

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 gm of KCN in 1 L of Millipore water (Q-H$_2$O, 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. Residual Coal, obtained

from a Steel industry from Sidcul industrial area, Haridwar, India, was washed with millipore water and soaked in 0.5 M H_2SO_4 for 24 h in 2:1 ratio of liquid to solid. The adsorbent was then washed several times with millipore water and dried in hot air oven at 110 ^0C for 2 h to completely remove moisture, cooled to room temperature and stored in polybags until further use. Fourier Transform Infrared Spectroscopy (FTIR, Nicolet 6700, USA) was employed to determine the type of functional groups present on adsorbent's surface before and after adsorption since the extent of adsorption depends greatly on surface characteristics of adsorbent. Unloaded and loaded samples were also visualized through scanning electron microscopy (Quanta 200F, FEI, Netherlands) to take into account the changes in surface morphology due to the adsorption of phenol and cyanide.

2.2 Batch Experiments

Batch experiments for optimization of process parameters studies were carried out in 250 ml round flasks with working volume of 100 ml at 125 rpm in an incubator cum orbital shaker (Metrex, MO-250, India). To avoid photo-oxidation of phenol the incubator was properly covered with black cardboard throughout the experiment. All the experiments were carried out in triplicates and average results were used. Considering the ratio of phenol and cyanide discharged from coke waste waters (generally 10:1), initial adsorbate concentrations were selected as 200 mg/L for phenol and 20 mg/L for cyanide. Since at industrial level narrow temperature ranges are preferred for pollution abatement temperature of 30 ^0C was selected for further studies (A. Seidel *et al*, 1985). The optimum pH and adsorbent dose were selected from a range of 4-12 and 5-60 g/L respectively on the basis of maximum percentage removal of phenol and cyanide. All the experiments were carried out for 48 h allowing sufficient time for achieving equilibrium. After every 2 h pH of the mixture was tested and readjusted to predefined value with 1N NaOH or HCl in case of any change during operation. Effect of initial concentrations of phenol and cyanide on their removal was studied in the concentration range of 100-1000 and 10-100 mg/L respectively. For contact time studies an appropriate volume of sample was withdrawn at an interval of every 2 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 Characterization of Residual Coal

Fig. 1 represents the FTIR spectrum of unloaded and loaded residual coal. The peak at 1628.56 cm^{-1} indicates the presence of deformations due to primary amines as well as C-C stretching vibrations due to phenyl conjugation.

A shift in peak from 1628.56 to 1635.57 cm^{-1} indicates adsorption of cyanide in form of amides and of phenol in

the form of conjugated phenol. A shift in peak from 1462.43 to 1475.97 cm^{-1} indicates the adsorption of phenol and cyanide due to symmetric -CH$_3$ vibrations. Fig. 2a demonstrate smooth surface of acid treated residual coal which is considerably hardened upon adsorption of phenol and cyanide (Fig. 2b).
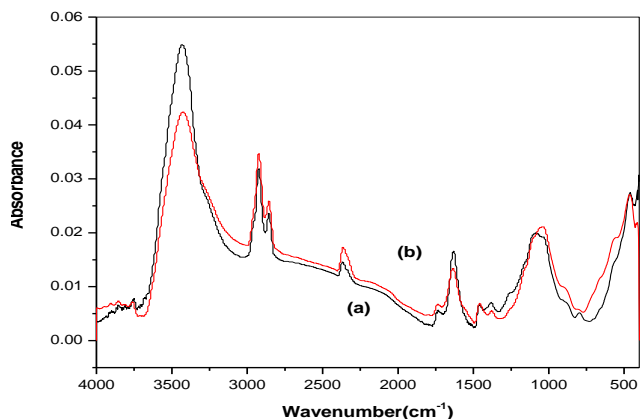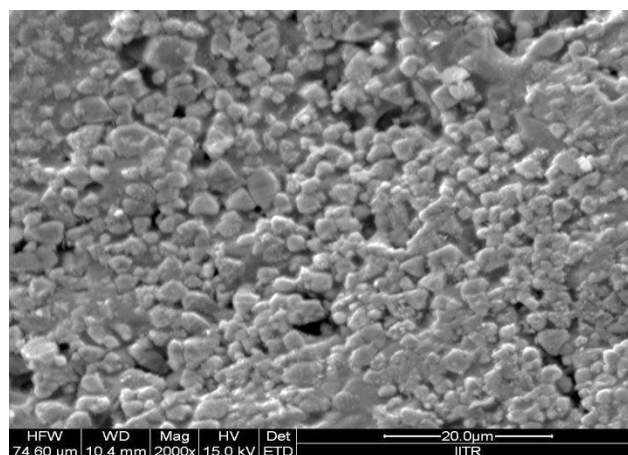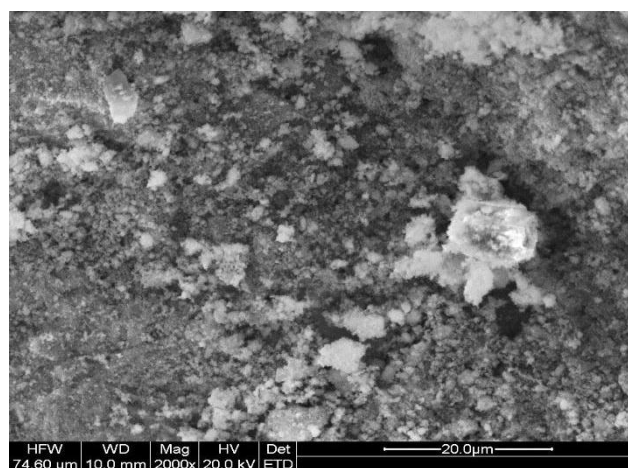

Figure 1: FTIR spectra of (a) unloaded residual coal and (b) loaded residual coal

(a)

(b)

Figure 2: SEM Micrograph of (a) Acid treated unloaded residual coal and (b) Loaded residual coal

3.2 Optimization of process parameters

Phenol and cyanide are both easily dissociable species in aqueous solutions at controlled pH. As the extent of ionization and speciation of organic and/or inorganic pollutants vary with changing pH therefore pH plays an important role in optimizing adsorptive removal of these compounds (M. Ahmaruzzaman and D. K. Sharma, 2005). Fig. 3a represents the effect of pH on adsorption of phenol and cyanide onto residual coal. Maximum removal of phenol occurs at pH 9 and decreases on both increasing and decreasing the pH. This phenomenon could be explained on the basis of pKa of phenol (9.96). As the pH of solution approaches the pKa dissociation of phenol increases leading to increase in adsorption. A similar trend was observed by Kilic et al. (M. Kilic *et al*, 2011) who found pH 7 to be most appropriate for phenol adsorption. In case of cyanide, in lower pH range (4-8) there is a sharp decrease in percentage removal of cyanide which could be attributed to hydrolysis of weak acid dissociable cyanides to HCN. Since HCN is highly hydrophilic its tendency to be adsorbed at low pH is markedly decreased. However at higher pH most of the cyanide exists in undissociated form. At pH above 9 the percentage removal of cyanide remains almost constant. The results are in compliance with several researches carried out recently on adsorption of cyanide by various adsorbents where optimum pH for maximum cyanide removal lies between 8-11 (S. Saxena *et al* 2001, R. R. Dash *et al* 2009, G. Moussavi and R. Khosravi, 2010). From the above results (Fig. 3a) pH 9 was selected for further optimization studies.
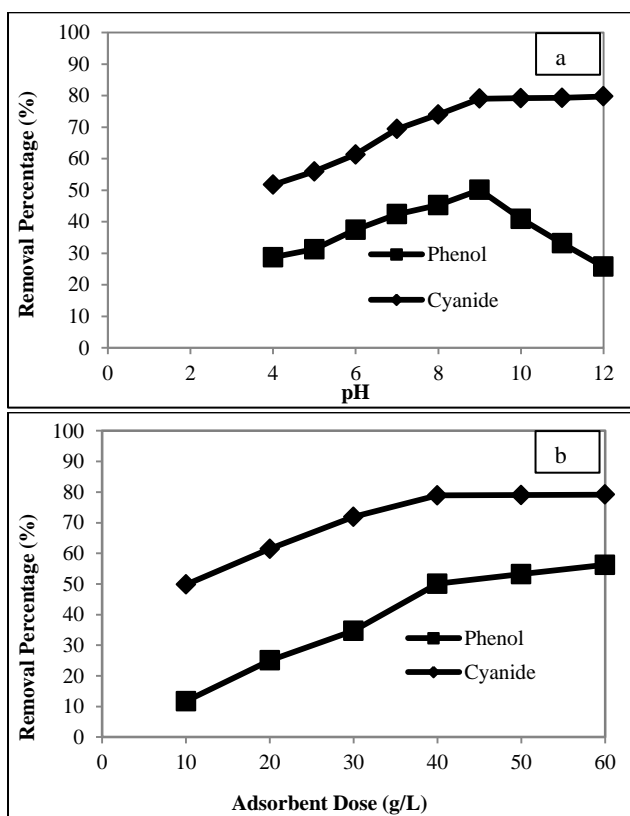
Fig. 3b demonstrates the effect of adsorbent dose on percentage removal of phenol and cyanide. As the adsorbent dose was increased percentage removal of adsorbate increased owing to increase in surface area as well as number of possible active sites. However above a certain value percentage removal reaches an asymptotic value. As is evident from Fig. 3b percentage removal of phenol and cyanide increases on increasing dose of residual coal from 10 g/L to 40 g/L but becomes almost constant above this dose. Therefore 40 g/L of residual coal was selected as optimum adsorbent dose for further studies.

Fig. 4(a) and (b) represents the effect of increasing phenol and cyanide initial concentration on their percentage removal respectively. It could be observed that percentage removal increased on increasing initial concentration from 100 to 200 and 10 to 20 mg/L which could be attributed to greater mass driving force at higher concentration which helps in overcoming mass transfer limitations (A. T. M. Din *et al*, 2009). However percentage removal decreases on further increasing initial concentration which could be explained by the limitation of available free sites for adsorption of adsorbate with increased concentration in bulk solution for a fixed mass of adsorbent, as well as by the increase in intraparticle diffusion (G. Moussavi and R. Khosravi, 2010).
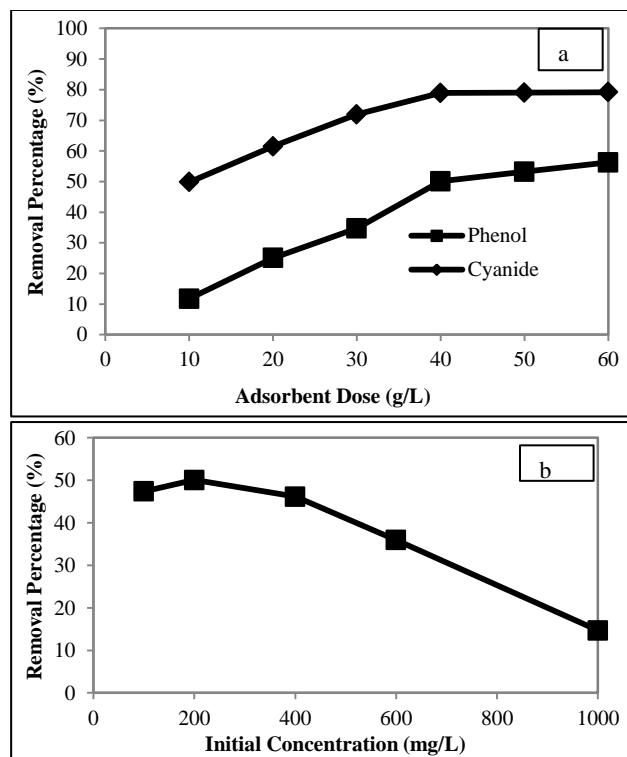

Figure 4: Effect of initial concentration on adsorption of (a) phenol and (b) cyanide.

Figure 3: Effect of (a) pH and (b) adsorbent dose on adsorption of phenol and cyanide

To evaluate the time of equilibrium, when the concentration of adsorbate in solution and on adsorbent does not change with time, contact time studies were carried out. During the initial stage of the process, percentage removal of both phenol and cyanide was extremely fast indicating physical adsorption involving

weak Van Der Waal forces only. Thereafter adsorption of both phenol and cyanide proceeded at almost a constant rate (4-24 h). This phase is indicative of strong bond formation between the adsorbent and adsorbate which requires increased time as well as energy to overcome repulsive forces (A. T. M. Din *et al*, 2009).
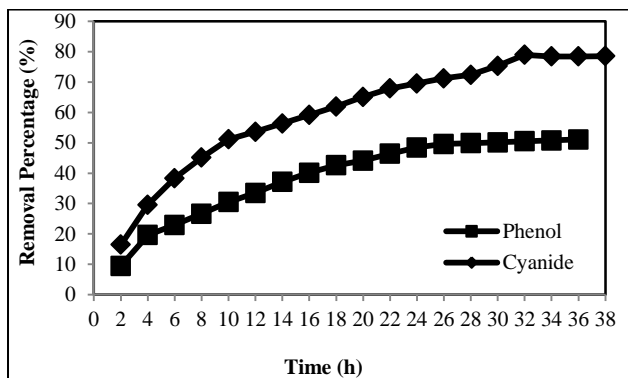

Figure 5: Effect of contact time on adsorption of phenol and cyanide

From Fig. 5 it could be observed that after 26 h no or very little increase in percentage removal of phenol took place. Therefore it was assumed that adsorption of phenol onto residual coal in binary mixture achieved equilibrium within 26 h. Similarly, study of cyanide adsorption revealed that adsorption of cyanide onto residual coal in the presence of phenol achieved asymptotic state within 32 h.

4. Conclusions

Residual coal, an industrial, low cost by-product was used for the co-adsorptive removal of toxic components from synthetic waste water. Experimental data revealed that residual coal could adsorb around 50.09% phenol and 78.89% cyanide at a pH of 9 and adsorbent dose of 40 g/L and could be used as an alternative to activated carbon at bench scale.

Acknowledgements

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