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Study for the treatment of Cyanide bearing Wastewater using Bioadsorbent *Prunus Amygdalus* (Almond shell): Effect of pH, adsorbent dose, Contact Time, Temperature, and initial Cyanide concentration

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Abstract

In the present study, the bio-removal of cyanide ions from aqueous solution by Prunus amygdalus (Almond Shell) granule has been investigated as a function of equilibrium pH, bio adsorbent dose, contact time, temperature and initial cyanide concentration. Batch study revealed that the bio-adsorption of cyanide on Prunus amygdalus (Almond Shell) granule was strongly pH dependent, and maximum cyanide removal was found to occur at equilibrium pH of 7. Optimum adsorbent dose, contact time, and temperature were found 20g/L, 90 minutes, and 30^{0}C respectively. Initial cyanide concentration was also investigated as a function of cyanide removal efficiency of bioadsorbent.

Keywords: Cyanide, wastewater bioadsorbent, *prunus amygdalus.*

Introduction

Cyanide is one of the toxic chemical found in wastewater discharges of the electroplating, metal finishing, steel tempering, mining (extraction of metals such as gold and silver), automobile parts manufacturing, photography, pharmaceuticals and coal processing units[1-3]. Cyanide is included in the CERCLA priority list of hazardous substances[4] and it occupies 28th position in the list of most hazardous chemicals[5]. Different forms of cyanide have awful health effects on people as well as other living organisms[6]. Therefore the permissible limit of cyanide in the surface water according to Indian standard has set a minimal national standard (MINAS) limit for cyanide in effluent as 0.2 mg/L[7]. USEPA (US Environmental Protection Agency) standard for drinking and aquatic-biota waters regarding total cyanide are 200 and 50 ppb respectively[8,9]. Therefore, environmental regulations require reducing the cyanide concentration in wastewater to below 0.2 mg/L prior to discharge into the environment. All forms of cyanide can be toxic at high levels, but the more toxin form of cyanide is hydrogen cyanide. Therefore, cyanide and metal cyanide complexes in industrial waste water must be treated or reduced to lowest levels before being discharged. Several treatment processes such as physical, chemical and biological oxidation have been exploited for the reduction of cyanide levels in waste solutions/ slurries in compliance with environmental regulations [10]. Biological process is generally the preferred technique for treating wastewater owing to its cost-effectiveness and environmental easiness, there is little work on the use of bioprocesses for treatment of cyanide-laden wastewater[11-13]. Another conventional method for cyanide removal is Chemical process[14]. It is uninvited technique because it requires the various chemical and regents and secondary pollutants are created furthermore it also needs some additional treatment prior to its disposal. Chemical processes of cyanide removal are not appropriate for environmental and economic perspectives[15]. 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. Adsorption systems are not affected by the toxicity of the target compound(s) and do not require hazardous chemicals. Moreover, adsorption facilitates concentrating and then recovering the adsorbed compounds if desired[16]. 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 water and wastewater due to their abundant availability and low cost[16]. However, industrial wastewater mainly from electroplating and mining industries normally contains higher cyanide concentration such as 5-250 mg/ l [3] and there is very few literature on the removal of cyanide from water containing cyanide at higher concentration. For making adsorption process more feasible and cost effective, there is urgent need of low cost adsorbents with higher adsorption capacities. Further, almond shell has hardly been investigated for cyanide removal from water. Therefore, in this work the potential of *Prunus amygdalus* (Almond Shell) granule, an agro- based biomass for the removal of cyanide from water has been explored. Experimental studies on cyanide removal have been done in batch reactor configuration. The effects of solution pH, bio-adsorbent dose, contact time, temperature and initial cyanide concentrations on the removal of cyanide have been studied.

Material and Methods

The raw material used was almond shell *(Prunus Amygdalus)*, which were 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 [17]. 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).

Characterization of bio adsorbent: The BET (Brunauer-Emmett-Teller) method was extensively used for measuring the surface area and pore volume. It is essential for understanding the potential of an adsorbent in the adsorption process. Ultimate analysis and physical properties of the untreated almond shell are shown in table 1.

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.

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.

Analytical measurements: Analysis of cyanide was done by using picric acid methods [18] 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 520 nm. The dissolved alkali metal picrate was converted by cyanide to the colored salt of *iso*-purpuric acid and its concentration was measured.

Table-1
Physical properties and ultimate analysis of the untreated almond shell

Elemental analysis of almond shell				**Physical properties of almond shell**					
C	**H**	**N**	**S**	**M (%)**	**Ash (%)**	**VM (%)**	**FC (%)**	**BET surface area (m^2/g)**	**Total pore volume (m^2/g)**
50.5	6.6	0.21	0.006	4.9	1.10	79.5	14.5	49.5694	0.0250

VM: Volatile matter, FC: Fixed carbon

Table-2
Ranges of operating parameters for pH, adsorbent dose, contact time, temperature and Initial cyanide concentration

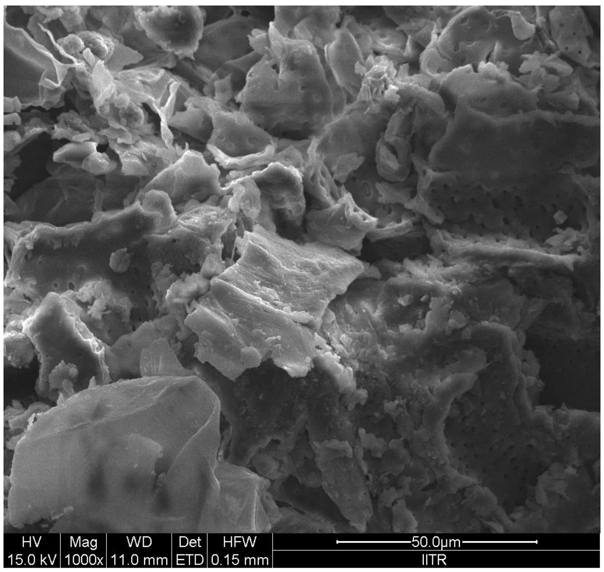
Objective of experiment	Operating parameters
To study the effect of pH on cyanide removal	AD: 20 g/L; ICC: 100 mg/l; Temp.: 30^0C; Contact time: 90 min; pH: 2-12
To study the effect of adsorbent dose on cyanide removal	ICC: 100 mg/l; Temp.: 30^0C; time: 90 min; solution pH 7; AD: 5, 10, 15, 20, 25, 30, 40 g/L.
To study the effect of contact time on cyanide removal	AD: 20 g/L, ICC: 100 mg/l; Temp.: 30^0C; solution pH 7; time: 15, 30, 45, 60, 75, 90, 105, 120 min;
To study the effect of temperature on cyanide removal	AD: 20 g/L; ICC: 100 mg/l; Time.: 90 min; solution pH:7; Temp: 20, 25, 30, 35, 40, 45^0C
To study the effect of Initial cyanide concentration on cyanide removal	AD: 20 g/L; Time.: 90 min; solution pH:7; Temp: 30^0C; ICC: 100-800 mg/l;

AD: Adsorbent dose, IFC: Initial cyanide concentration.

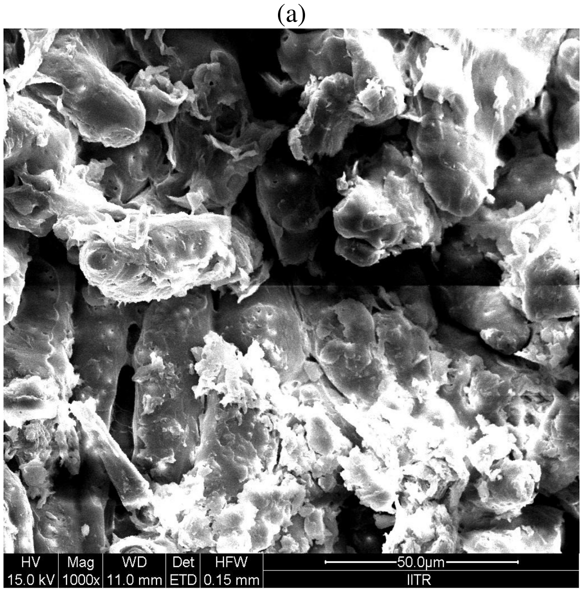
Results and Discussion

The most extensively used technique for estimating surface area is the BET method[19]. BET surface area and total pore volume on the adsorbent were 49.5694 m^2/g and 0.0250 m^2/g, respectively. It depicts the almond has an extensive allocation of surface area and excellent pore volume. These properties make it a good adsorbent.

From Field Emission SEM (FE SEM) micrographs of untreated almond shell adsorbents before and after adsorption as shown in Figure 1(a-b) it is evident that active sites of adsorbents are covered due to the adsorption of cyanide on it.



(a)



(b)

Figure-1
Scanning Electron Micrograph of untreated almond shell (a) Untreated almond shell before adsorption, (b) Untreated almond shell after adsorption

Removal of cyanide species by untreated *Prunus amygdalus* (Almond Shell) granule has been studied in the present investigation and the effects of various process parameters such as pH, adsorbent dose, contact time, temperature and initial cyanide concentration are discussed as follows:

Effect of pH: An effect of solution pH on the removal of cyanide for adsorbent is shown in figure 2. From figure 2 it seems that pH played an important role for the removal of cyanide from aqueous solutions by adsorption. It alters the surface charge of the adsorbent. The effect of pH on the adsorption could be attributed to several mechanisms such as electrostatic interaction, complexation, ion exchange and surface charge on carbon[20,21]. The effect of initial pH on the adsorption equilibrium of cyanide has been shown in figure 2. At pH < 4, percent removal of cyanide increases with the increase in solution pH. Significant improved in percentage removal of cyanide are observed within the pH range of 5-6. The highest cyanide removal of 91.5% obtained at pH 7 and then decreases considerably with the increase in solution pH up to 12. Based on the above observations it could be concluded that the surface charges on adsorbent and behavior of cyanide in water influence the % removal of cyanide.

Effect of adsorbent dose: An effect of adsorbent dose on the removal of cyanide for adsorbent is shown in figure 3. From figure 3 it is evident that adsorption is mainly a surface phenomenon, the amount of surface vacant for adsorption and therefore the mass of adsorbent can extensively influence adsorption efficiency. Therefore, the effect of almond shell dosage on cyanide removal was investigated under the conditions given in table 2. As illustrated in figure 3, the increase in percentage removal of cyanide in the initial stage is due to the increase in adsorbent concentration. The removal of cyanide at a dose of 5 g/L was 35.6%; removal improved to 91.5% when the almond shell dosage was increased to 20 g/L and remained almost unchanged thereafter.

The above observations can be explained by the fact that with the increase in adsorbent dose the number of active sites in unit volume of solution increases, which leads to an increase in the percentage removal of cyanide[22]. Bhumica et al. reported the removal of 20 mg/L cyanide given outcome 82% with the adsorbent dose of 40 g/L coal fly ash after 48 h contact time; and similarly H. Deveci et al. reported the removal of 100 mg/L cyanide given outcome 14.3, 35.4 and 92.3%, respectively with the adsorbent dose of 4.5 g/L plain, copper- and silver-impregnated GAC, after about 48 and 24 h contact time. The most conventional industrial adsorbent considering the low adsorption capacity of GAC (plain and modified) as well as its high production cost, coal fly ash has very little adsorption capacity on removal of cyanide ion at high concentration. The almond shell is certainly much more competent and cost effective and is therefore a proficient adsorbent for treating cyanide-laden wastewaters.

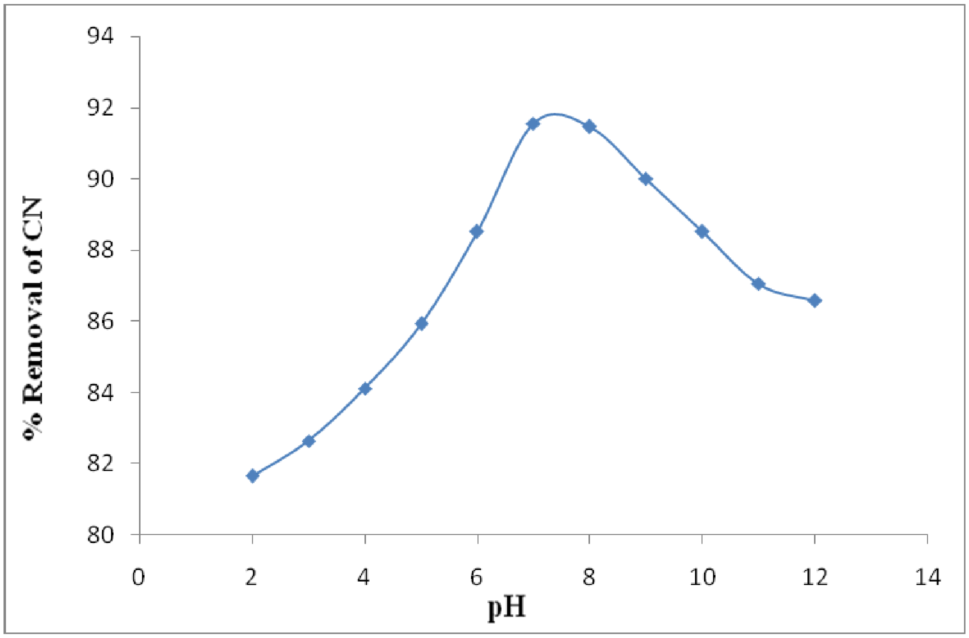


Figure-2
Effect of pH on the removal of cyanide by almond shell
(Process conditions: temp: 30 ^{0}C, concentration of adsorbents: 20g/L, Contact time: 90 min; initial concentration of cyanide: 100 mg/l, rpm: 125)

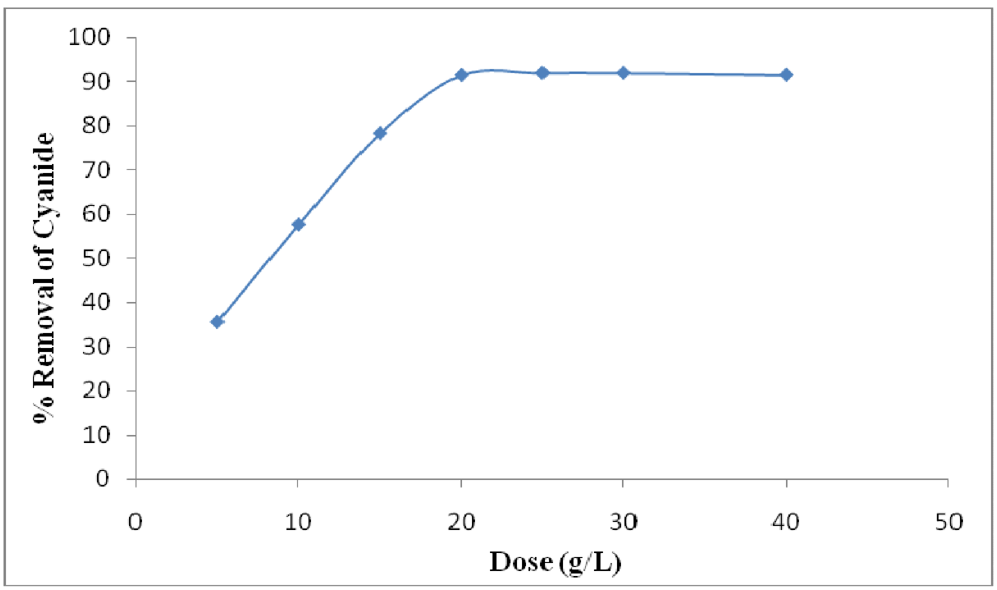


Figure-3
Effect of adsorbent dose on cyanide removal from water by almond shell,
(Process conditions: pH: 7; temp: 30 ^{0}C; Contact time: 90 min; initial concentration of cyanide: 100 mg/l; rpm: 125.)

Effect of contact time: The effect of contact time on adsorption was investigated under the conditions given in table 2. Figure 4 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.

Effect of temperature: Cyanide removal at different temperature range, it was seen that equilibrium adsorption slightly increased and optimum temperature was established at 30^{0}C. Figure 5 depicts the temperature dependency of cyanide removal. Adsorption processes are exothermic in nature; the extent and the rate of adsorption in most cases decrease with the increase in temperature[23]. At higher temperatures there is possibility of desorption of cyanide[24,25].

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[26].

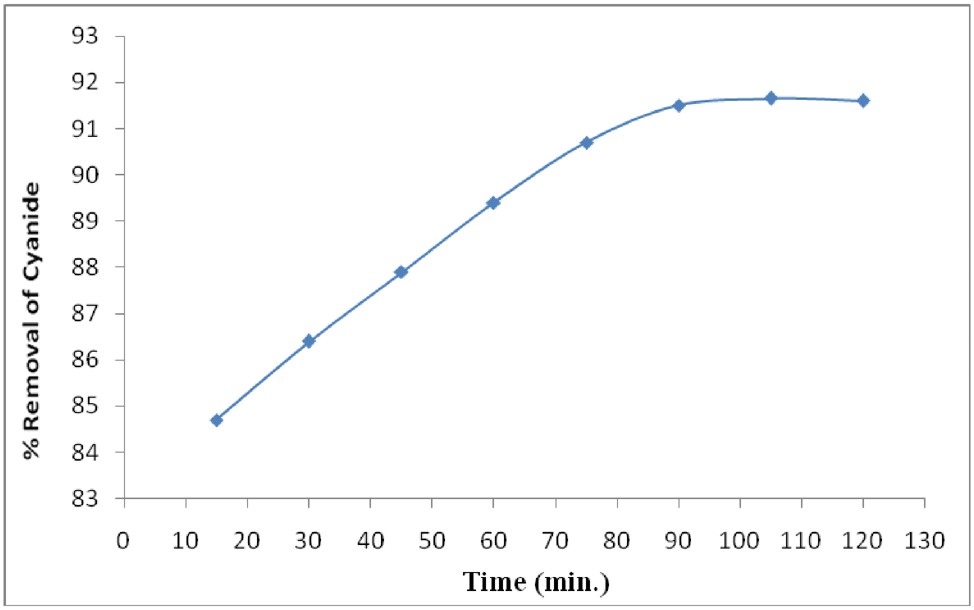


Figure-4
Effect of contact time (15-120 min.) on cyanide removal by almond shell
(Process conditions: pH: 7; temp: 30 ^{0}C; Adsorbent dose: 20 g/L; initial concentration of cyanide: 100 mg/l; rpm: 125)

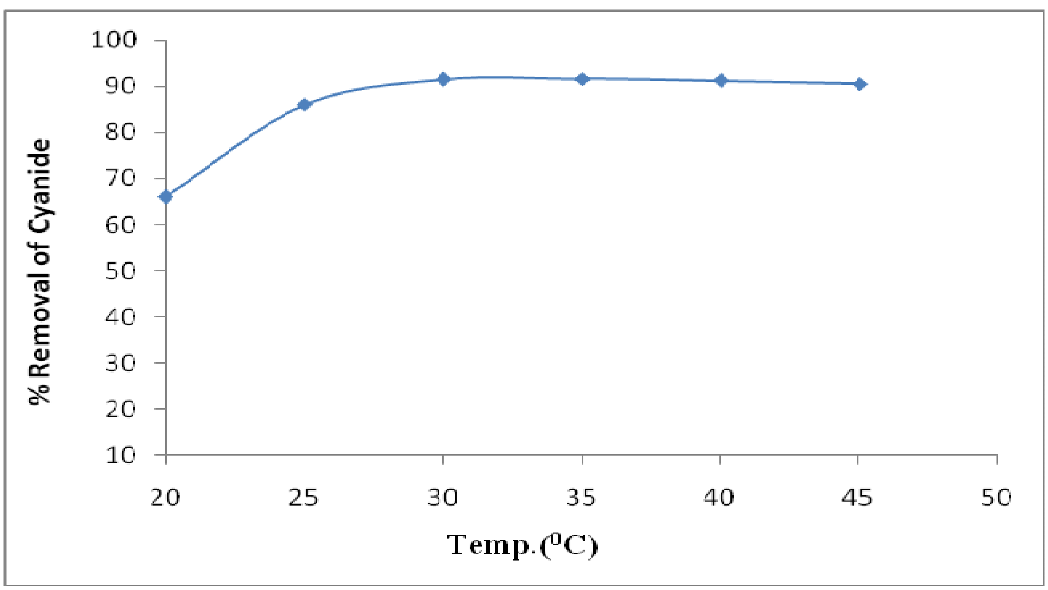


Figure-5
Effect of temperature on cyanide removal by almond shell,
(Process conditions: pH: 7; adsorbent dose: 20g/L; Contact time: 90 min; initial concentration of cyanide: 100 mg/l; rpm: 125.)

Comparison of present method with some latest literature on cyanide bio adsorption: The performance of the present bio-adsorbent is compared with some recently reported bio-adsorbents on cyanide removal from waste water as shown in table 3. From table 3 it seems that the adsorbents have been used under various conditions, therefore it is difficult to assess their performance preciously.

However, the present adsorbent has been used at the highest concentration of cyanide with respect to other adsorbents and is competitive to other reported adsorbents.

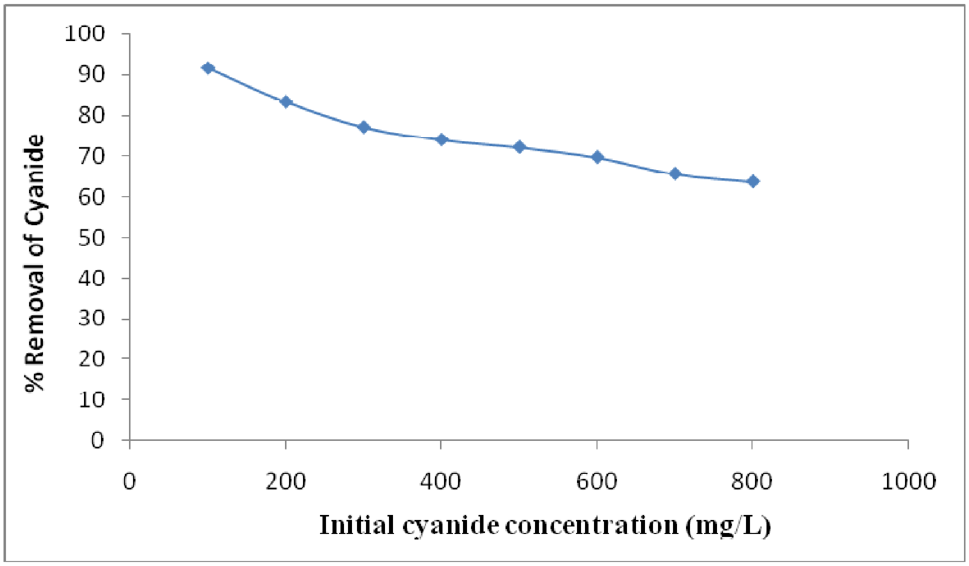


Figure-6
Effect of initial cyanide concentration
(Process conditions: pH: 7; temp: 30 ^{0}C; Contact time: 90 min; adsorbent dose 20 g/L; rpm: 125.)

Table-3
Comparison of present method with some latest literature on cyanide bio-adsorption

Adsorbent	Cyanide compound	pH	Temp. (^{0}C)	Contact time (min)	Dose (g/L)	Initial CN concentration (mg/L)	Cyanide removal (%)	Reference
Activated carbon	NaCN	10	25	4320	1.5	102-532	-	27
GAC	NaCN, ZnCN FeCN	6	25-35	60 36 60	5-50 20 5-50	50 100 200	85.6 80.1 70.2	28
Rice husk ash (RHA)	NaCN	7-8	40	-	0.5	80	33.9	29
Raw/ heat activated Sepiolite	$[Cu(CN)_3]^{2-}$	-	20-22	-	.05	100	40-90	30
Plain and Metal-impregnated GAC	NaCN	10.5-11	-	22	0.2-4.5	100	1.5-14.3 (plain) 5.7-92.3 (AC-Ag) 4.4-35.4 (AC-Cu)	31
Sulfonated coal	ZnCN	4.0	-	5	1.0	13	BDL*	32
Cu-II impregnated carbon	KCN	10.5	-	-	-	500	99.56	33
Coal fly ash	KCN	9	30	48	40	20	82	34
Almond shell	NaCN	7	30	90	20	100	91.5	Present study

*BDL: Below detection Limit.

Conclusion

From the above discussions the following conclusions are made. i. The optimum pH for the removal of cyanide by almond shell adsorbent is ~ 7. ii. The optimum adsorbent dose is 20 g/l for the removal of cyanide from water. iii. The optimum temperature for cyanide removal is ~ 30 ^{0} C. iv. The removal efficiency of almond shell is 91.5% at 100 mg/L and 63.6% at 800 mg/L cyanide concentration. v. The present adsorbent is proven to be potentially high affinity with cyanide ions and low-cost adsorbent for the removal of cyanide from aqueous solution as high concentration of cyanide ions in a relatively short contact time.

References

1. Monser L. and Adhoum N., Modified activated carbon for the removal of copper, zinc, chromium and cyanide from wastewater, *Sep. Purif. Technol*., **(26)** 137-146 (**2002**)
2. Aksu Z., Calik A., Dursun A.Y., Demircan Z., Biosorption of iron(III)–cyanide complex ions on *Rhizopus arrhizus*: application of adsorption isotherms, *Process Biochem.,* **(34)** 483–491 (**1999**)
3. Patil Y.B. and Paknikar K.M., Development of a process for biodetoxification of metal cyanides from wastewater, *Pro. Biochem,* **(35)** 1139-1151 **(2000)**
4. ATSDR, CERCLA priority list of hazardous substances, Available at: http://www.atsdr.cdc.gov/cercla/07list.html (accessed 11.01.2010) **(2007)**
5. ATSDR and USEPA, Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), priority list of hazardous substances, Available at: http://www.atsdr.cdc.gov/cercla/07list.html (accessed 12.02.2011) (**2007)**
6. Dursun A.Y., Alik A.C., Aksu Z., Degradation of ferrous(II) cyanide complex ions by Pseudomonas fluorescens, *Process Biochem,* **(34),** 901–908 **(1999)**
7. Indian standard Institution, Guide for treatment of effluents of electroplating industry, IS: 7453-(**1974)**
8. Young C.A. and Jordan T.S., Cyanide remediation: current and past technologies Proceedings of the 10th Annual Conference on *Hazardous Waste Research*: 104-129 (**2004)**
9. USEPA, *Drinking water criteria document for cyanide*, **,** EPA/600/X-84-192-1**(1985)**
10. Young, C.A., Jordan, T.S., *Cyanide remediation: current and past technologies*. Proceedings of the 10th Annual Conference on Hazardous Waste Research, Great Plains/Rocky Mountain Hazardous Substance Research Center, Kansas State University, Kansas, 104-129 **(1995)**
11. Kaewkannetra P., Imai T., Garcia-Garcia F.J., Chiu T.Y., Cyanide removal from cassava mill wastewater using Azotobacter vinelandii TISTR 1094 with mixed microorganisms in activated sludge treatment system, *J. Hazard. Mater.,* **(172)** 224–228 **(2009)**
12. Sirianuntapiboon S., Chairattanawan K., Rarunroeng M. , Biological removal of cyanide compounds from electroplating wastewater (EPWW) by sequencing batch reactor (SBR) system, *J. Hazard. Mater.* **(154)** 526–534 **(2008)**
13. White D.M., Pilon T.A., Woolard C., Biological treatment of cyanide containing wastewater, *Water Res*. **(34)** 2105–2109(**2000**).
14. EPA, Technical report: Treatment of cyanide heap leaches and tailings, U.S. Environmental Protection Agency, Office of Solid Waste, Washington, DC, (EPA530R94037, PB94201837) **(1994)**
15. Chen C.Y., Kao C.M., Chen S.C., Application of Klebsiella oxytoca immobilized cells on the treatment of cyanide wastewater*, Chemosphere* **(71)** 133–139 **(2008)**
16. Moussavi G., Khosravi R., Removal of cyanide from wastewater by adsorption onto pistachio hull wastes: Parametric experiments, kinetics and equilibrium analysis, *J. Hazard. Mater.* **(183)** 724-730 **(2010)**
17. Mehrasbi Mohammad Reza, Farahmandkia Zohreh, Taghibeigloo Bahareh, Taromi Azra, Adsorption of Lead and Cadmium from Aqueous Solution by Using Almond Shells, *Water Air Soil Pollut,* **(199)** 343–351**(2009)**
18. Iamarino P.F., The direct spectrophotometric determination of cyanide with picric acid reagent. JRGRL INCO Ltd. (based on V.J. Zatka method) JRGRL, November 1980 which was a modification of the method of D.J. Barkley and J.C. Ingles, Report 221, CANMET, (February 1970) **(1989)**
19. Brunauer, S., Emmett, P. H., and Teller E., Adsorption of gases in multimolecular layers, *J. Am. Chem*., **60(2)**, 309–319 **(1938)**
20. Guo R., Chakrabarti C.L., Subramanian K.S., X. Ma, Lu Y., Cheng J., Pickering W.F., Sorption of low levels of cyanide by granular activated carbon, *Water Environ. Res.* **(65)** 640–644**(1993)**
21. McKay G., Bino M.J, Adsorption of pollutants onto activated carbon in fixed beds, *J. Chem. Techol. Biotechnol*. **(37)** 81–83 **(1987)**
22. Mondal, P., Majumder, C. B., and Mohanty, B., Effects of adsorbent dose, its particle size and initial arsenic concentration on the removal of arsenic, iron and manganese from simulated groundwater by Fe^{3+} impregnated activated carbon, *J. Hazard. Mater.*, **150(3)** 695–702 (**2008)**
23. Gupta Neha, Majumder C. B. and Agarwal V. K., Adsorptive treatment of cyanide-bearing wastewater: A prospect for sugar industry waste, *Chem. Eng. Comm*., 200:993–1007 (**2013)**

24. Jorapur, R., and Rajvanshi, A. K., Sugarcane leaf-bagasse gasifiers for industrial heating applications, *Biomass Bioenergy*, **13(3)** 141–146 **(1997)**

25. Swamy, M. M., Studies on the treatment of phenolic wastewaters using adsorption and immobilized whole cells, PhD diss., University of Roorkee, India **(1998)**

26. Katyal, S., Thambimuthu, K., and Valix, M., Carbonation of bagasse in a fixed bed reactor: Influence of process variables on char yield and characteristics, *Renew. Energy*, **28(5)** 713–725 **(2003)**

27. Behnamfard Ali, Mehdi Salarirad Mohammad, Equilibrium and kinetic studies on free cyanide adsorption from aqueous solution by activated carbon, *J. Hazard. Mater*., **(170)** 127–133 **(2009)**

28. Dash R.R., Gaur A., Majumder C.B., Removal of cyanide from water and wastewater using granular activated carbon, *Chem. Eng. J*. **(146)** 408–413**(2009)**

29. Naeem S. Zafar U. and Amann T., Adsorption Studies of Cyanide (CN)- on Rice Husk Ash (RHA), *Bangladesh J. Sci. Ind. Res,* **46(1),**101-104, **(2011)**

30. Yel Esra, Onen Vildan, Tezel Ggulay, Ali ozkan Ilker, Artificial neural network model for $[Cu(Cn)_3]^{2-}$ adsorption by raw and activated sepiolite, *Recent Advances in Energy, Environment and Geology*, 62-69 .

31. Deveci H., Yazıcı E.Y., Alp I., Uslu T., Removal of cyanide from aqueous solutions by plain and metal-impregnated granular activated carbons, *Int. J. Miner. Process,* **(79)** 198–208 **(2006)**

32. Bose Purnendu, Bose Aparna M., Kumar Sunil, Critical evaluation of treatment strategies involving adsorption and chelation for wastewater containing copper, zinc and cyanide, *Advan. Environ. Res.,* **(7)** 179-195 **(2002)**

33. Baghel A., Singh B., Pandey P., Dhaked R.K., Gupta A.K., Ganeshan, K., Sekhar K., Adsorptive removal of water poisons from contaminated water by adsorbents, *J. Hazard. Mater.,* **(137)** 396–400 **(2006)**

34. Agarwal Bhumica and Balomajumder Chandrajit, Use of coal fly ash for simultaneous co-adsorptive removal of phenol and cyanide from simulated coke wastewater, *Sustain. Environ. Res.,* **23(6)**, 359-368 **(2013)**