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Removal of cyanide from water and wastewater using granular activated carbon

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ABSTRACT

Cyanide is used extensively in the electroplating and mining industries due to its strong affinity to metal cations. Commercial granular activated carbon (GAC) was used as adsorbent for the adsorptive study of sodium, zinc and iron, cyanide complexes in the present study. The effect of process parameters such as pH, temperature, adsorbent size and dose, contact time on the performance of adsorption was investigated. Optimum pH was found to be 9, 7 and 5 for sodium, zinc and iron cyanides respectively. In the higher temperature range more percentage removal was observed for iron cyanides, whereas, sodium and zinc cyanides were removed optimally at 25–35 °C. Although particle size did not show any major influence on the percentage removal, but optimum size was taken as 2–4 mm. The percentage removal of cyanide compounds increased with the increase in adsorbent (GAC) concentration. However, specific uptake did not increase at GAC concentration above 20–25 g/L. Hence 20 g/L was considered as the optimum dose of adsorbent. Higher removal efficiency was achieved for metal cyanides as compared to sodium cyanide at optimal conditions.

1. Introduction

Cyanide is highly toxic to humans and aquatic organisms [1]. It is a potent inhibitor of respiration due to its extreme toxicity towards cytochrome oxidase and by tightly binding to terminal oxidase [2]. At short-term exposure [3], cyanide causes rapid breathing, tremors, and other neurological effects and long-term exposure to cyanide cause weight loss, thyroid effects, nerve damage and death. Skin contact with liquids containing cyanide may produce irritation and sores. The presence of cyanide in effluents can attain considerable concentrations and occurs both naturally (biogenes by plants and microorganisms) and from human activities (wastes from metal plating, ore leaching, production of synthetic fibers, plastics, pharmaceuticals, coal gasification, metal extraction and cyanogenic crop plants), which forms the major source of contamination of natural water by this compound [4]. Cyanide's strong affinity to metal ions makes it favourable agent in electroplating/metal plating, extraction of gold, silver in mining industries hence produced in a large volume from these industries [5]. Cyanide compounds present in environmental matrices and waste streams as simple and complex cyanides, cyanates and nitriles [6–8] can be broadly classified as (1) total cyanide, (2) weak acid dissociable (WAD) cyanide and (3) free cyanide [6–8]. The most toxic form of cyanide is free cyanide, which includes the cyanide anion itself and hydrogen cyanide (HCN), either in a gaseous or aqueous state. The salts of sodium, potassium and calcium cyanide are quite toxic, as they are highly soluble in water, and thus readily dissolve to form free cyanide. Operations typically receive cyanide as solid or dissolved NaCN, KCN or $Ca(CN)_2$. Weak or moderately stable complexes such as those of cadmium, copper, nickel and zinc (e.g. $Cu(CN)_3{}^-$, $Ni(CN)_4{}^{2-}$ and $Zn(CN)_4{}^{2-}$) are classified as WAD as they are easily dissolved under acidic conditions [5]. In the presence of metal ions, such as nickel, copper, zinc and iron cyanide forms complex compounds of varying toxicity and stability [1,8,9]. Although metal–cyanide complexes by themselves are much less toxic than free cyanide, their dissociation releases free cyanide as well as the metal cation, which can also be toxic [8]. However, both ferro- and ferri-cyanides decompose to release free cyanide when exposed to direct ultraviolet light in aqueous solutions [3,8]. The cyanide ion also combines with sulphur to form thiocyanates (SCN^-). Although thiocyanate is a WAD and dissociates under weak acidic conditions,

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Nomenclature

C_i	initial cyanide concentration (mg CN^-/L)
D_c	dose/mass of GAC in aqueous solution (g/L)
P_c	particle size of GAC (mm)
S_a	agitation speed (rpm)
t_c	contact time (h)

it is often considered in its own category. The stability of cyanide salts and complexes is pH dependent, and therefore, their potential environmental impacts. The oxidation of cyanide, either by natural processes or from the treatment of effluents containing cyanide, can produce cyanate (OCN^-). Cyanate is less toxic than HCN, and readily hydrolyzes to ammonia and carbon dioxide [7–9].

To protect the environment and water bodies, wastewater containing cyanide must be treated before discharging into the environment [9,10]. The acceptable level of cyanide at the effluent outlet lies between 4 and 40 μM [4]. U.S. Health Service, Central Pollution Control Board India and many other countries cites 0.2 mg/L as permissible limit for cyanide in effluent [1,8]. Hence, the removal of cyanide from industrial wastewater is required before it is discharged into the municipal sewer. Currently, wastewater containing cyanide is treated by chemical oxidation methods (alkaline chlorination, ozonization and wet-air oxidation) [11,12]. However, these methods are expensive and hazardous chemicals are used as the reagents (chlorine and sodium hypochlorite) [12] and this treatment produces toxic residues which implies the presence of an additional level of detoxification [4,10]. The other treatment methods used such as Caro's acid, copper-catalyzed hydrogen peroxide, electrolytic oxidation, ion exchange, acidification, AVR (acidification, volatilization and re-neutralization) process, lime–sulphur, reverse osmosis, thermal hydrolysis and INCO process (by SO_2/air) [5–8] are highly expensive and cannot completely degrade all cyanide complexes in many cases [10].

1.1. Background of cyanide adsorption

Processes involving sorption on activated carbon have received greater attention. Granular/powered carbon is the most widely used adsorbent, as it has a good capacity for the adsorption of inorganic/organic molecules. A typical activated carbon particle, whether in a powdered or granular form, has a porous structure consisting of a network of inter-connected macropores and mesopores that provide a good capacity for the adsorption due to its high surface area [13]. Activated carbon is known to be effective for the oxidation of cyanide. It acts both as an adsorbent and as a catalyst for the oxidation of cyanide. Adsorption is a widely used technology for the removal and recovery of cyanide [14]. The method requires the sparging of the solution with air or oxygen. Cyanide is oxidized to cyanate in the presence of activated carbon [15].

The mining operations mostly use adsorbents for recovery and removal of cyanide from effluents [16,17]. Huff et al. examined the feasibility of removing cyanide from refinery wastewater with powdered activated carbon [17]. Bernardin conducted a series of tests using granular activated carbon and various metals. The metals studied formed cyanide complexes that had a greater adsorbance than either the metals or the cyanide alone [18]. Adams found that activated carbon enhance the removal of cyanide, mainly as HCN from aqueous solutions at pH values of 7 and lower [15]. Adams and Fleming [19] and Adams [20] examined mechanism of adsorption of aurocyanide onto activated carbon and its subsequent elution with special reference to the effects of acid and alkali treatment on the system. Jones et al. showed that the carbon-in-pulp process for gold processing depends on the adsorption of dissolved $Au(CN)_2^-$ from solution onto activated carbon [21]. Guo et al. investigated the sorption of cyanide at levels up to 1 mg/L in solution by granular activated carbon (GAC) in order to define the conditions required to reduce residual levels to below the maximum acceptable concentration value specified in the Guidelines for Canadian Drinking Water Quality [16]. The sorption process proceeded slowly with uptake continuing over a 30-h mixing period [16]. Williams and Petersen used coconut shell carbon, impregnated with different metals, and then used for the recovery of free cyanide [22]. Adhoum and Monser concluded that Ag-impregnated carbon has a higher efficiency of CN^- removal in comparison with plain or Ni-impregnated carbon [23]. Although activated carbons have a greater quality of removal of cyanides from industrial wastewaters, it has never been used as a main treatment method.

There are many reports on the adsorptive removal of NaCN, KCN and gold cyanide complexes in mining sites, but not many reports mentioned about the adsorption of metal cyanides on plain activated carbon. So the behaviour of the process parameters for adsorption of metal cyanide compounds is not clear. In this study an attempt has been made to analyze the efficiency of activated carbons for the removal of zinc and iron metal cyanide complexes and sodium cyanide from effluents in batch reactors in laboratory conditions.

2. Materials and methods

All the chemicals were of analytical grade and solutions were prepared by Milli-Q water (Q-H_2O, Millipore Corporation with resistivity of 18.2 MΩ cm). The stock sodium cyanide (NaCN), zinc cyanide (ZnCN) and iron cyanide (FeCN) solutions of 1.0 g CN^-/L was prepared in 1.0 L of Milli-Q water. Sodium cyanide and iron cyanide solutions were prepared by adding required quantity of NaCN and $K_4[Fe(CN)_6]\cdot 3H_2O$ respectively, but zinc cyanide was prepared by adding equal volume of zinc sulphate salts and potassium cyanide solution. The commercial GAC of apparent density and particle size of 0.4 g/cm^3 and 2–5 mm was used in the batch experiments after purification with Milli-Q water and dried at 110 °C for 24 h. The GAC particles were sieved to various fractions of 1.2–2, 2–3.5, 3.5–4 and 4–5 mm by standard sieves and effect of particles size on adsorption was examined. GAC doses (D_c) of 5–50 g/L were used for the adsorption of cyanide complexes and optimum dose was decided. Effect of pH and temperature on adsorption were studies for pH 4–11 and temperature 20–45 °C at initial cyanide concentration (C_i) 100 mg CN^-/L and GAC 20 g/L. Adsorption studies were conducted in 250 mL Erlenmeyer flasks containing varying concentration of cyanide in the range of 50–400 mg CN^-/L with an increase of 50 mg CN^-/L with optimum adsorbent doses of 20 g/L. All adsorption studies were conducted in a rotary incubator shaker at agitation speed (S_a) of 150 rpm for an agitation period (t_a) of 90–120 h. The effect of process parameters such as pH, temperature, particle size, adsorbent dose and agitation time on adsorption of the three cyanide species (NaCN, ZnCN and FeCN) were investigated separately and compared. Total cyanide was determined by pyridine–barbituric acid colourimetric method at 578 nm after distillation as described in Standard Methods [24,25] with a precision up to 0.001 mg/L. pH was measured using pH meter as specified by standard methods [25] by WTW® Germany (makes pH 720). All spectrometric measurements were carried out using DR-4000 UV–VIS spectrophotometer (Hach®, USA).

3. Results and discussion

The experiments were conducted to investigate the effect of various process parameters on the adsorptive removal of cyanide from

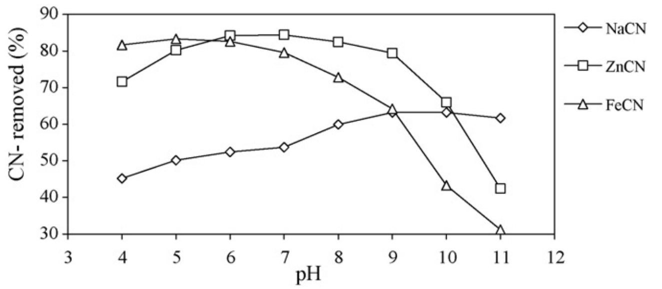

Fig. 1. Effect of pH on adsorption of CN^- on GAC (C_i = 100 mg CN^-/L, P_c = 2–4 mm, D_c = 20 mg/L, t_c = 72 h).

synthetic solutions of NaCN, ZnCN and FeCN on GAC surface. The results and observations from the present investigation have been discussed below.

3.1. *Effect of pH*

pH of the solution affects the surface charge of the adsorbents as well as the degree of ionisation and speciation of different pollutants [26]. The influence of pH on the extent of adsorption of cyanide for the three cyanide species is shown in Fig. 1. The increase in adsorption of cyanide was above pH 8 in NaCN solution. Maximum adsorption had occurred in between pH 9 and 10. This may be due to the hydrolysis of CN^- at pH < 8. There was decrease in adsorption above pH 10. In case of ZnCN solutions the adsorption was optimum in the pH range of 6–7. At higher or lower pH values there was decrease in adsorption. ZnCN are the WAD cyanide complexes as they are easily dissolved under mildly acidic conditions (pH 4–6) [27]. Hence in lower pH ranges (pH < 6) there was the possibility of dissociation of ZnCN, which reduced the adsorption efficiency. The FeCN complexes showed adsorption was greater at lower pH values and decreased as pH increased. Above pH 10 adsorption of ferrocyanide was negligible.

Equilibrium adsorption between GAC and free cyanide indicated that the extent of adsorption was not dependent on pH, up to less than 10 where free cyanide is predominately in the neutral HCN form [27]. But pH plays an important role for the adsorption of metal cyanides on GAC [27]. Davidson [28] related the effect of pH on the adsorption of metal cyanide complexes to the strong adsorption of both hydroxide and hydronium ions, whereas Adams et al. [29] and Adams [30] favoured a mechanism in which OH^- reacts with the functional groups on the surface of the carbon. Van der Merwe [31] reported that log–log plots of the equilibrium metal loading versus the pH for four sets of published data resulted in straight lines in all cases [32].

Huang and Wu [33] found that at initial cyanide concentrations of more than 4 mg/L, the uptake versus pH plot showed a region of minimum retention at pH 3–4 and a region of maximum retention at pH 7–9. However, at 1 mM concentration, the uptake was independent of pH at values less than 6, but showed an upward undulation at pH 7–11. Guo et al. using dilute cyanide solutions (0.04 mM) found that the effect of pH was even less pronounced although there was a slight rise in the pH 8–9 region [16]. At pK_a value of cyanide (9.39), pH had a marked effect on the stability of cyanide [20]. Even in the absence of activated carbon, much higher rates of cyanide loss were observed at pH values below the pK_a value [16]. At lower pH values cyanide ion exists as HCN which was a weak acid and is highly soluble in water [16,20]. The affinity with water could reduce its tendency to interact with the active sites of GAC. In this higher pH region, hydrolysis of CN^- would be minimal [20]. Also, in this pH region deprotonation on the GAC surface provides functional groups that can undergo an ion exchange type of interaction with the cyanide ion [16]. Huang and Ostovic [34] proposed that hydration of the activated carbon may result in the formation of reactive surface functional groups. The relative proportion of the surface functional groups may vary with the method of preparation of the activated carbon, thereby causing a difference in the value of the surface acidity constants (equilibrium constants) [16]. The cyanide ion is a nucleophile, and in contact with the surface of activated carbon, could replace the OH^- present in various surface functional groups. Both the processes would be equivalent to CN^- uptake by ion exchange. In acidic medium (pH < 3), complexes such as hexacyano-iron(II) or (III) probably are adsorbed as the protonated anion [16]. Chank [35] studied the adsorption of ferrocyanide on activated carbon as a function of pH and found greater adsorption at low pH and below pH 3 there was possibility of volatilization of ferrocyanide [27]. From the present study it was observed that the optimum pH of adsorption for NaCN, ZnCN and FeCN are 9, 7 and 5 respectively.

3.2. *Effect of temperature*

The influence of temperature on CN^- adsorption onto activated carbon was examined at optimum conditions for the three cyanide compounds. Fig. 2 represents the effect of temperature on the adsorption of cyanide by granular activated carbon and it was observed that although the difference was not great, the adsorption and equilibrium adsorption increased slightly as the temperature was increased up to 35–40 °C for FeCN. Increase in adsorption behaviour for higher temperatures for FeCN may be due to the dissociation of iron cyanide complexes. But for ZnCN and NaCN compounds the adsorption is optimum in the temperature ranges of 25–35 °C. At higher temperature there is possibility of desorption of cyanide from activated carbon.

Adsorption processes are exothermic in nature and the extent and rate of adsorption in most cases decrease with the increase in temperature. The decrease in adsorption for sodium cyanide (NaCN) and zinc cyanide (ZnCN) with the increase in temperature may be explained on the basis of rapid increase in the rate of desorption of the adsorbed species from the surface of the adsorbent. However, an alternative approach for explaining the decrease in adsorption with the rise in temperature may be drawn from Le-Chatelier's principle. A small amount of a solute adsorbed with the rise in solution temperature may also be explained from the fact that solubility of almost all compounds in water decreases with the increase in solution temperature, thereby decreasing the adsorption capacity [36].

Adsorption of iron cyanide (FeCN) indicated that adsorption increases with the rise in temperature. Diffusion of adsorbate species from the bulk phase into pores of adsorbent, observed in

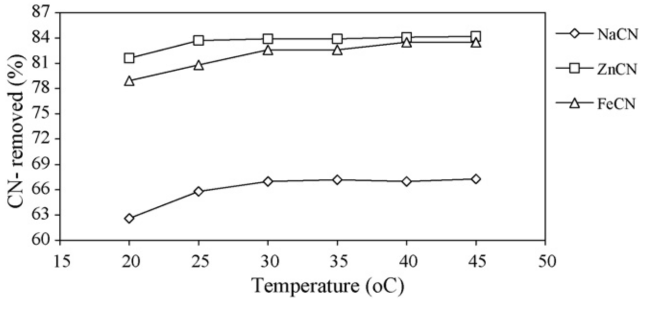

Fig. 2. Effect of temperature on adsorption of CN^- on GAC (C_i = 100 mg CN^-/L, P_c = 2–4 mm, D_c = 20 mg/L, t_c = 72 h).

case of FeCN adsorption processes was of endothermic nature. Here the rise in temperature favoured the adsorbate transport within the pores of the adsorbent. The increase in adsorption with temperature is mainly due to an increase in number of adsorption sites caused by breaking of some of the internal bonds near the edge of the active surface sites of the adsorbent [36,37]. Milenković et al. reported the velocity progress of CN^- sorption onto activated carbon impregnated by copper acetate monohydrate with increase in temperature showed dominance of chemisorption process and absence of cyanide physical sorption onto activated carbon, which happened to be reduced with increase in temperature [38]. Adams found that loss of cyanide was enhanced in the presence of activated carbon at lower temperatures and in the initial stages of reaction. Hydrolytic decomposition reaction was more important than oxidation to cyanate at high temperatures in presence of activated carbon [20].

3.3. *Effect of particle size*

Table 1 shows the effect of particle size on adsorption of CN^-. For all the particle sizes of GAC more than 80% removal of ZnCN and FeCN and more than 65% for NaCN was achieved. There was increase in percentage removal of cyanide with the decrease in particle size. But the increase in percentage removal of all cyanide species with the decrease in particle size (from 4–5 mm to 1.2–2 mm) of the adsorbent was very small (less than 2.0%). Among the particle sizes considered in the experiment the percentage removal was maximum for the particle size of 1.2–2 mm.

For commercial activated carbons, the fine fractions may have undergone greater surface oxidation during the activation process yielding a great density of functional group sites, which in turn may have accelerated cyanide sorption [16]. For GAC and most granular adsorbents the internal pore surface area is much bigger than the outer surface area. Hence, a reduction of the particle size (by grinding) does not lead to a higher total number of active sites available. However, the higher relative number of sites at the outer adsorbent surface results in more favourable kinetics. Therefore, the reduction of particle size does not improve the percentage removal much in these adsorbents [39]. However, the lesser the particle size more is the grinding cost. The influence of surface area was less significant, as specific surface area was found to be similar for various sieved fractions [16]. During sieving of the GAC particles it was found that 2–3.5 and 3.5–4 mm particles together are more than 80% of the total. Hence, the optimum particle size was considered as 2–4 mm. Guo et al. [16] reported that initial rate of percentage cyanide removal is better for less than 0.5 mm size GAC particles as compared to more than 1.4 mm size particles. The higher rate with the smaller particle was attributed to greater access to the internal pores (that is, shorter path length) and to the large surface area per unit weight of GAC. Adams [20] reported the increase in cyanide removal for crushed GAC particles. It was unlikely that this was due to the increase in external surface area, although catalytic reactions such as the oxidation of cyanide by activated carbon took place predominantly at the carbon/solution interface, since the additional external surface area generated by crushing was small in comparison to that is available in micropores. The enhanced reaction with cyanide is most likely due to formation of very reactive broken bond sites along the plane of fracture [15]. It is important to note that the adsorption of cyanide compounds on the surface of GAC was not much influenced by its particle size. This indicates that the CN^- adsorption occurs predominately by chemical adsorption rather than physical adsorption (outer sphere complex) but physical adsorption may occur in considerable amount.

Table 1
Effect of particle size on adsorption of CN^- on GAC

GAC particle size (mm)	% CN^- removed		
	NaCN	ZnCN	FeCN
4–5	66.3	83.9	81.8
3.5–4	67	84	82.1
2–3.5	67	84.2	82.6
1.2–2	67.6	84.7	82.9

$C_i = 100$ mg CN^-/L, $D_c = 20$ mg/L and $t_c = 72$ h.

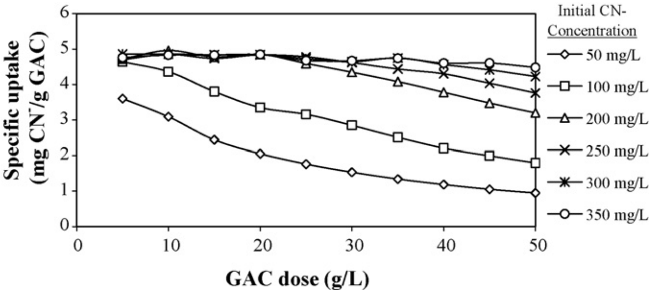

Fig. 3. Specific uptake of NaCN on GAC ($P_c = 2–4$ mm, $t_c = 72$ h).

3.4. *Effect of adsorbent concentration*

From the experimental results it was found at various cyanide concentrations, the percentage removal of the cyanide species (NaCN, ZnCN and FeCN) increased with the increase in adsorbent dose. Figs. 3–5 present the specific uptake of cyanide for various concentrations of GAC and cyanide compounds. From the figures it was evident that, the specific uptake was decreased beyond GAC dose of 15–20 g/L for low initial concentrations of cyanide. However, for higher initial cyanide concentrations, there was reduction in the rate of decrease in specific uptake. From the figures, it was observed

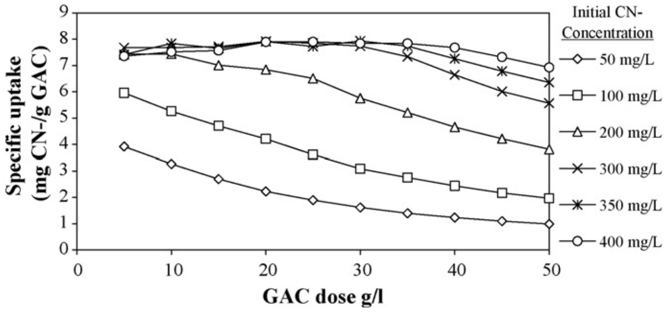

Fig. 4. Specific uptake of ZnCN on GAC ($P_c = 2–4$ mm, $t_c = 72$ h).

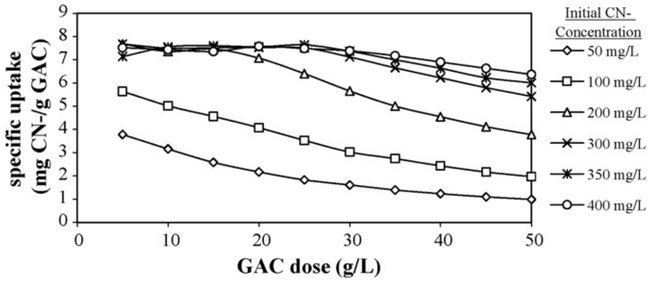

Fig. 5. Specific uptake of FeCN on GAC ($P_c = 2–4$ mm, $t_c = 72$ h).

that at higher concentrations the specific uptake remained constant even at higher adsorbent concentrations. The maximum specific uptakes for the adsorption of NaCN, ZnCN and FeCN by GAC, under the experimental conditions were 4.85, 7.91 and 7.65 mg/g, respectively. With the increase in adsorbent dose the number of active sites in unit volume of solution increased, which lead to the increase in the percentage removal of cyanide. However, increase in adsorbent dose beyond 20–25 g/L, there was not significant increase in percentage removal with the increase in adsorbent concentration. It may be due to the two stages of cyanide adsorption (i.e., fast formation of mono layer followed by slow plateau stage) [39]. From the figures it was observed that the increase in percentage removal and specific uptake of cyanide for various cyanide species was not much higher after minimum GAC dose of 20 g/L. Hence, the optimum dose of GAC for removal of cyanide species can be taken as 20 g/L GAC.

It is observed from Figs. 3–5 that the specific uptake of ZnCN was more as compared to FeCN and specific uptake of FeCN solution was more as compared to NaCN. The uptake of ZnCN solution was maximum as ZnCN is a WAD cyanide compound can be easily dissociable as compared to the stable FeCN compound. It is a well-known fact that at a particular environment the percentage removal of an adsorption process depends upon the ratio of the number of adsorbate moiety to the available active sites of adsorbent. In the present experimental conditions (near neutral pH), GAC contains both positive as well as negative sites on its surface, with negative charges predominating over positive charges [39]. The presence of positive charge of the metal ions get attracted towards the negatively charged GAC surfaces sites [23] neutralizing some negative charges of GAC surface after their adsorption on the negative sites of GAC and create some additional positive sites on the GAC surface. The higher percentage removal of cyanide from ZnCN and FeCN solutions as compared to the NaCN solutions may be due to the fact of presence of positive metal ions, which neutralize the negative active sites on GAC surface reducing the repulsive force. The positive sites created on the GAC surface make the cyanide ion adsorbed on the surface of the GAC. Here chemisorption predominated over physical adsorption for adsorption of metal cyanides on GAC.

3.5. Effect of contact time

The contact time between the pollutant and the adsorbent is of significant importance in the wastewater treatment by adsorption. A rapid uptake of the pollutants and establishment of equilibrium in a short period signifies the efficacy of that adsorbent for its use in wastewater treatment. Figs. 6–8 present the plot of percentage CN^- removed against contact time (contact time) for GAC at adsorbent concentration of 20 g/L at various initial CN^- concentration of cyanide (NaCN, ZnCN and FeCN) at optimum pH and temperature conditions. It was observed from Figs. 7 and 8 that the rate of cyanide removal was rapid in first 24 h for metal cyanide compounds, but the process was slow for NaCN (Fig. 6). For the metal cyanide compounds the equilibrium condition was reached at about 18–24 h, but for NaCN compounds the equilibrium condition was achieved only after 42 h.

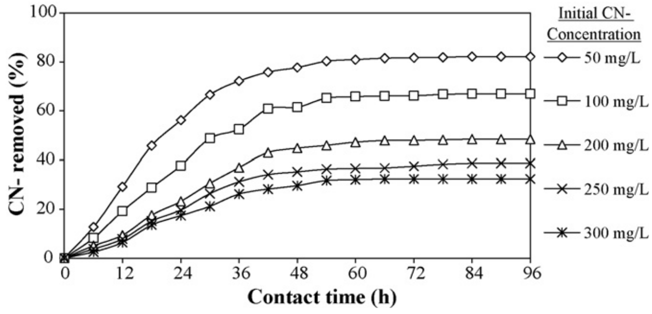

Fig. 6. Effect of contact time on adsorption of NaCN on GAC (P_c = 2–4 mm, D_c = 20 g/L).

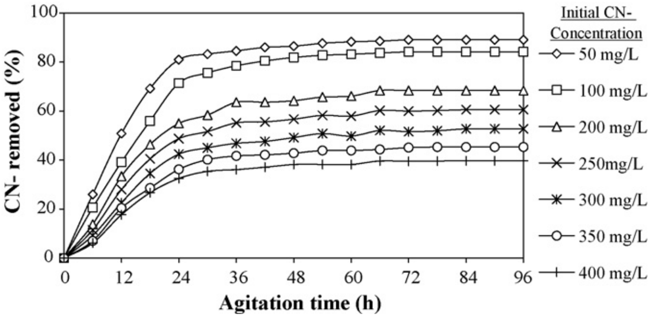

Fig. 7. Effect of contact time on adsorption of ZnCN on GAC (P_c = 2–4 mm, D_c = 20 g/L).

The slow step in the NaCN solution was considered to be the diffusion of CN^- from the bulk solution to the active surface sites. This process would be influenced by the concentration gradient between those two points and the thickness of the diffusion layer which was a function of agitation process [16]. In physical adsorption most of the adsorbates species are adsorbed within a short interval of contact time [36]. However, strong chemical binding of adsorbates with adsorbent requires a longer contact time for the attainment of equilibrium. Available adsorption results reveal that the uptake of adsorbate species were fast at the initial stage of contact time, and thereafter, it becomes slower near the equilibrium. In between these two stages of the uptake, the rate of adsorption was found to be nearly constant. This was obvious from the fact that a large number of vacant surface sites were available for adsorption during the initial stage and after a lapse of time, the remaining vacant surface sites were difficult to be occupied due to repulsive forces between the solute molecules of the solid and bulk phase [36]. The resistance to mass transfer between bulk phase and adsorbent is overcome by the energy provided by agitation to bring the cyanide species from bulk of the solutions to the active sites of the adsorbent. However, at the initial stage, percentage removal of cyanide species increased very fast with the increase in contact period due to the combination of all the above effects. From all these plots it was found that the adsorptive removal of the simple and metal cyanides ceases after 48 and 36 h respectively with adsorbent concentration of 20 g/L.

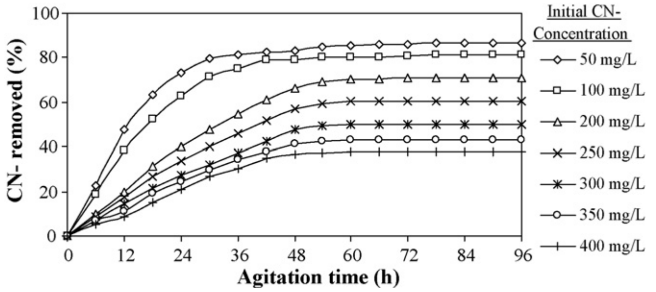

Fig. 8. Effect of contact time on adsorption of FeCN on GAC (P_c = 2–4 mm, D_c = 20 g/L).

4. Concluding remarks

From the above discussions and results the following conclusions are made:

(1) NaCN was highly adsorbed in alkaline conditions, where iron cyanides adsorbed optimally at acidic conditions. However, the removal of zinc cyanides was maximum in the neutral pH range.
(2) Percentage removal of sodium and zinc cyanide species decreases with the increase in temperature, but there was a little increase in percentage removal with the increase in temperature for iron cyanide complexes.
(3) Although the percentage removal increased with the increase in adsorbent dose, but above 20–25 g/L, there was decrease in specific uptake of cyanide on GAC.
(4) The GAC gives more percentage removal for metal cyanide complexes (ZnCN and FeCN) as compared to the simple cyanide (NaCN).
(5) There was negligible removal of NaCN concentration over 300 mg CN^-/L, however there was significant removal of metal cyanides at 350 mg CN^-/L.
(6) Hence, GAC may be used to treat the low concentrated cyanide contaminated water.

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References

[1] A.Y. Dursun, A. Çalik, Z. Aksu, Degradation of ferrous(II) cyanide complex ions by *Pseudomonas fluorescens*, Process Biochem. 34 (1999) 901–908.
[2] N. Porter, J.W. Drozd, J.D. Linton, The effects of cyanide on the growth and respiration of *Enterobacter aerogenes* in continuous culture, J. Gen. Microbiol. 129 (1983) 7–16.
[3] Department of Interior U.S., Cyanide Fact Sheet. Bureau of Reclamation, Technical Service Center: Water Treatment Engineering and Research Group, 2001, p. 1.
[4] M.G. Campos, P. Pereira, J.C. Roseiro, Packed-bed reactor for the integrated biodegradation of cyanide and formamide by immobilised *Fusarium oxysporum* CCMI 876 and *Methylobacterium* sp. RXM CCMI 908, Enzyme Microb. Technol. 38 (2006) 848–854.
[5] C.A. Young, T.S. Jordan, Cyanide remediation: current and past technologies, in: Proceedings of the 10th Annual Conference on Hazardous Waste Research, 1995, pp. 104–129.
[6] A. Zheng, D.A. Dzombak, R.G. Luthy, B. Sawer, W. Lazouska, P. Tata, M.F. Delaney, L. Zilitinkevitch, J.R. Sebriski, R.S. Swartling, S.M. Drop, J.M. Flaherty, Evaluation and testing of analytical methods for cyanide species in municipal and industrial contaminated water, Environ. Sci. Technol. 37 (2003) 107–115.
[7] S. Ebbs, Biological degradation of cyanide compounds, Curr. Opin. Biotechnol. 15 (2004) 1–6.
[8] J.D. Desai, C. Ramakrishna, Microbial degradation of cyanides and its commercial application, J. Sci. Ind. Res. 57 (1998) 441–453.
[9] Y.B. Patil, K.M. Paknikar, Development of a process for biodetoxification of metal cyanides from wastewater, Process Biochem. 35 (2000) 1139–1151.
[10] C.M. Kao, J.K. Liu, H.R. Lou, C.S. Lin, S.C. Chen, Biotransformation of cyanide to methane and ammonia by *Klebsiella oxytoca*, Chemosphere 50 (2003) 1055–1061.
[11] S.A.K. Palmer, M.A. Breton, T.J. Nunno, D.M. Sullivan, N.F. Suprenant, Metal/Cyanide Containing Wastes: Treatment Technologies, Noyes Data, Park Ridge, NJ, 1988.
[12] A. Watanabe, K. Yano, K. Ikebukuro, I. Karube, Cyanide hydrolysis in a cyanide-degrading bacterium, *Pseudomonas stutzeri* AK61 by cyanidase, Microbiology 144 (1998) 1677–1682.
[13] K. Hanaki, T. Saito, T. Matsuo, Anaerobic treatment utilizing the function of activated carbon, Water Sci. Technol. 35 (1997) 193–201.
[14] G. McKay, M.J. Bino, Adsorption of pollutants onto activated carbon in fixed beds, J. Chem. Technol. Biotechnol. 37 (1987) 81–83.
[15] M.D. Adams, Removal of cyanide from solution using activated carbon, Miner. Eng. 7 (2003) 1165–1177.
[16] R. Guo, C.L. Chakrabarti, K.S. Subramanian, X. Ma, Y. Lu, J. Cheng, W.F. Pickering, Sorption of low levels of cyanide by granular activated carbon, Water Environ. Res. 65 (1993) 640–644.
[17] J.E. Huff, E.G. Fochtman, J.M. Bigger, Cyanide removal from refinery wastewater using powdered activated carbon, in: P.N. Cheremisinoff, F. Ellenbusch (Eds.), Carbon Adsorption Handbook, Ann Arbor Science, Ann Arbor, MI, 1978.
[18] F.E. Bernardin, Cyanide detoxification using adsorption and catalytic oxidation on granular activated carbon, J. Water Pollut. Control Fed. 45 (1973) 221–234.
[19] M.D. Adams, C.A. Fleming, Mechanism of adsorption of aurocyanide onto activated carbon, Metall. Trans. B: Process Metall. 20 (1989) 315–325.
[20] M.D. Adams, The mechanism of adsorption of aurocyanide onto activated carbon. Part 1. Relation between the effects of oxygen and ionic strength, Hydrometallurgy 25 (1990) 171–184.
[21] W.G. Jones, C. Klauber, H.G. Linge, Fundamental aspects of gold cyanide adsorption on activated carbon, CSIRO Division of Mineral Products, Australia, Gold Forum Technol. Pract. World Gold 89 (1989) 278–281.
[22] N.C. Williams, F.W. Petersen, The optimisation of an impregnated carbon system to selectively recover cyanide from dilute solutions, Miner. Eng. 10 (1997) 483–490.
[23] N. Adhoum, L. Monser, Removal of cyanide from aqueous solution using impregnated activated carbon, Chem. Eng. Process. 41 (2002) 17–21.
[24] R.R. Dash, C. Balomajumdar, A. Kumar, Treatment of metal cyanide bearing wastewater by simultaneous adsorption and biodegradation (SAB), J. Hazard. Mater. 152 (2008) 387–396.
[25] APHA, Standards Methods for the Examination of Water and Wastewater, American Public Health Association, Washington, DC, 2001.
[26] H.A. Elliott, C.P. Huang, Adsorption characteristics of some Cu(II) complexes on alumino silicates, Water Res. 15 (1981) 849–854.
[27] D.A. Dzombak, R.S. Ghosh, G.M. Wong-Chong, Cyanide in Water and Soil Chemistry, Risk and Management, Taylor and Francis Group, CRC Press, NW, 2006.
[28] R.J. Davidson, V. Veronese, Further studies on the elution of gold from activated carbon using water as the eluant, J. S. Afr. Inst. Min. Metall. 79 (1979) 437–469.
[29] M.D. Adams, G.J. McDougall, R.D. Hancock, Models for the adsorption of aurocyanide onto activated carbon. Part III. Comparison between the extraction of aurocyanide by activated carbon, polymeric adsorbents and 1-pentanol, Hydrometallurgy 19 (1987) 95–115.
[30] M.D. Adams, The chemical behavior of cyanide in the extraction of gold. Part 1. Kinetics of cyanide loss in the presence and absence of activated carbon, J. S. Afr. Inst. Min. Metall. 90 (1990) 37–44.
[31] P.F. Van der Merwe, Fundamentals of the elution of gold cyanide from activated carbon, Ph.D. Thesis, University of Stellenbosch, South Africa, 1991, p. 453.
[32] J.S.J. Van Deventer, P.F. Van Der Merwe, Factors affecting the elution of gold cyanide from activated carbon, Miner. Eng. 7 (1994) 71–86.
[33] C.P. Huang, M.H. Wu, The removal of chromium (VI) from dilute aqueous solution by activated carbon, Water Res. 11 (1977) 673–679.
[34] C.P. Huang, F.B. Ostovic, Removal of cadmium (II) by activated carbon adsorption, J. Environ. Eng. Div. ASCE. 104 (1978) 863–878.
[35] J.K. Chank, pH-dependent adsoption of hexacyanoferrate (II) onto selected sorbents, M.S. Thesis, Clarkson University, Potsdam, NY, 1997.
[36] M. Mahadeva Swamy, Studies on the treatment of phenolic wastewaters using adsorption and immobilized whole cells, Ph.D. Thesis, University of Roorkee, India, 1998.
[37] I.D. Mall, S.N. Upadhyay, Y.C. Sharma, A review on economical treatment of wastewaters and effluents by adsorption, Int. J. Environ. Studies 51 (1996) 77–124.
[38] D.D. Milenković, Lj.V. Rajaković, S. Stoiljković, The sorption of cyanides from the water onto activated carbon, Working Living Environ. Protect. 2 (2004) 251–258.
[39] P. Mondal, C.B. Majumder, B. Mohanty, Effects of adsorbent dose, its particle size and initial arsenic concentration on the removal of arsenic, iron and manganese from simulated ground water by Fe3+ impregnated activated carbon, J. Hazard. Mater. 150 (2008) 695–702.