

The Investigation of Kinetic and Isotherm of Cyanide Adsorption onto Bone Charcoal

Ghorban Asgari¹, Bahman ramavandi², Abdol Motaleb Seid Mohammadi¹, Jamal Mehr ali pour¹

¹Dept. Environmental Health Engineering, Hamadan University of Medical Sciences
Hamadan, Iran.

²Dept. Environmental Health Engineering, Bushehr University of Medical Sciences, Bushehr, Iran.

Abstract. In this study, bone charcoal (BC) is used as an adsorbent for the removal of cyanide from aqueous solutions. The effects of cyanide concentration, pH, contact time and the adsorbent dose were performed with batch procedure. The equilibrium data were fitted to Langmuir, Freundlich, Temkin and Dubinin–Radushkevich, isotherm models. Apart from R^2 , normalized deviation and sum of squared errors (SSE) were used for validation of isotherm and kinetics data. The experimental adsorption isotherm fitted very well with Langmuir equation model and the amount of adsorption (q_e) was 140 mg/g. The kinetic studies revealed that the adsorption of cyanide complied with the pseudo-second-order kinetic. Analysis of data with Dubinin Radushkevich isotherm showed that the energy of cyanide adsorption process onto BC was 15.5 kJ/mol, which implies the adsorption of cyanide onto BC is chemisorption in nature.

Keywords: Bone charcoal, Adsorption, Cyanide, Industrial wastewater

1. Introduction

Cyanide as carbon–nitrogen radical are very toxic compound and highly harmful to humans and aquatic organisms[1,2]. In the CERCLA list, the cyanide presented as priority of hazardous substances. Cyanide are commonly found in the effluent wastewaters that generated from gold refining and base metals milling operations and other industries such as coke-processing plants metal plating, petrochemical, finishing industries, photography industry, thermal cracking of organic, coal carbonization , chemical manufacturing and iron and steel industries [2,3]. The effluents generated from these processes often contain free and metal-complexes cyanides at different levels. As a class of free cyanide, a concentration of 0.02mg/L has been reported highly toxic and to be lethal for certain species of sea animals. Hence, the cyanide concentration must be reduced in wastewater to below 0.02 mg/L prior to discharge into the environment to meet environmental standard requirements [2,3].

Several technologies (Physical, chemical, and biological) have been investigated for the removal of cyanides from wastewater. Many studies on biological processes have been demonstrated the capacity of microorganisms to degrade free cyanide in wastewater and these studies reported biological processes are environmental friendliness and the preferred technique for degradation of cyanide[3,4]. However, Cyanide in high concentrations leads to a low biodegradation rate and it is toxic to microorganisms and restricts the potential of biological processes for efficiently removing cyanide and its compounds. In addition, this technology is not well established, requires combination of metallurgy, biology and process engineering, tends to be very site specific with specific evaluation and study require for each type. The chemical oxidation techniques have several disadvantages such as adds potentially objectionable cations/anions to water, excess toxic hypo-chlorite, formation chlorinated compounds due to reacted chlorine with organics materials, poor

⁺ Corresponding author. Tel.: + 989123609313; fax: +988118255.
E-mail address: Asgari@umsha.ac.ir

process control results in toxic intermediates, reacts preferentially with thiocyanate, many of the less expensive hypochlorite sources require special handling with this type of treatment. Adsorption processes in the removal of cyanide from wastewaters has received great attention. Activated carbon as adsorbent is the most widely used in adsorption of cyanide [3,4,5]. However, this adsorbent has several disadvantages, that making it impractical for full-scale applications, such as low capacity for cyanide removal, production and regeneration of the activated carbon is very expensive and 10–15% loss during conventional regeneration [1]. It is therefore necessary to develop new low-cost adsorbents with higher adsorption capacities to make the adsorption process attractive and feasible. Presently, bone char (BC) is widely used as an adsorbent to remove pollutants from water [1,6,7,8] because it is available at low cost and can be manufactured in sufficient amounts [7]. Consequently, in this study, BC was used as an adsorbent in adsorption processes to remove cyanide from aqueous solutions. To our knowledge, cyanide adsorption by BC has been never reported. Therefore, the performance of BC that it can find available in high quantities, easily available tested as an adsorbent to adsorb cyanide from wastewater. Thus, this research is aimed to study the capacity of BC to remove cyanide under varying conditions. The influences of solution pH, adsorbent dose, cyanide concentration, and contact time were evaluated. The kinetics and isotherm of the cyanide adsorption process were also analyzed.

2. Material and Methods

Bone char (BC) was prepared and characterized according to the procedure described previously [7]. The pH of point of zero charge (pH_{pzc}) for BC was determined as Ghanizadeh and Asgari study [7]. Other characteristics of BC are described in our previous study [8]. In the summary, BC is not uniformly porous and the size of pores are less than 20 nm, micropore sorbent with Brunauer-Emmett-Teller (BET) specific surface area $100 \text{ m}^2/\text{g}$ and Barrett-Joyner-Halenda (BJH) specific surface area $116 \text{ m}^2/\text{g}$ as determined by N_2 gas adsorption-desorption. Cyanide solution was prepared by diluting aliquots of 1 g/L stock cyanide solution into distilled water. The stock solution was made by dissolving NaCN in distilled water.

For convenient evaluation of the effective parameters, the adsorption of cyanide within BC was performed with batch procedure. These tests were carried out in a 250 ml high-density polyethylene bottles. The bottles were stirred with a shaker (GFL 3017) at 150 rpm at room temperature. The pH of solutions was measured using a pH meter (Wagteck Mi 151). The pH of solutions was adjusted at the beginning of experiments and controlled afterwards and no significant pH variation was observed during each experiment. All of adsorption experiments were carried out at $25 \pm 0.5 \text{ }^\circ\text{C}$ and the average of three replicates experiments was reported. At the end of adsorption tests, the concentration of cyanide ions in solution was measured by the titrimetric method as described in section 4500-CN D. of the standard methods. The amount of adsorbed cyanide ions at equilibrium, adsorption capacity (q_e), was calculated from Eq (1).

$$q_e = \frac{V}{M} \times (C_0 - C_e) \quad (1)$$

where C_e and C_0 are the equilibrium and initial concentrations of cyanide ions (mg/l), respectively; q_e is equilibrium cyanide ions concentration on adsorbent (mg/g), V is the volume of dye solution (L), W is the mass of BC sample used (g) [9].

Apart from the correlation coefficient (R^2), the applicability of the isotherm equations is quantitatively judged by comparing a normalized deviation $\Delta g(\%)$, which can be described as:

$$\Delta g(\%) = 100 \times \sqrt{\frac{\sum_{i=1}^N [(q_{e,\text{exp}} - q_{e,\text{cal}}) / q_{e,\text{exp}}]^2}{(n - 1)}} \quad (2)$$

where $q_{e,\text{exp}}$ is observed from the batch experiment, $q_{e,\text{cal}}$ is the estimated from the isotherm for corresponding $q_{e,\text{exp}}$, and N is the number of measurements in experimental isotherm. The smaller of $\Delta g(\%)$ value indicates the better isotherm fitting [10]. Apart from the correlation coefficient (R^2) in the kinetics studies, the validity of kinetic models for the sorption data evaluated by calculating the sum of squared errors (SSE) which can be expressed as:

$$SSE = \sum \frac{(q_t^{\text{exp}} - q_t^{\text{cal}})^2}{q_t^{\text{exp}2}} \quad (3)$$

where q_t^{exp} (mg/g) is experimental sorption capacity of cyanide on BC at time t and q_t^{cal} (mg/g) was obtained from the kinetic models. The lower values of SSE indicate the better fit of the model [10]. All chemicals used were analytical grade and purchased from Merck.

3. Results and Discussion

3.1. Effect of Solution pH

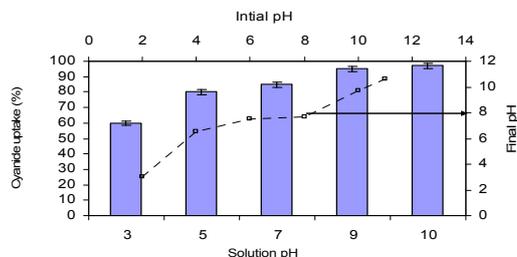


Fig. 1: Adsorption efficiency of cyanide Vs pH and pHzpc of BC

Since the pH of the aqueous solution plays a key role in the adsorption process, the effect of solution pH on the removal of cyanide by BC was examined in a range of 3-10. The means of three replicate experiments are shown in Fig. 1. As shown in Fig. 1, it is clear that the adsorption of cyanide is highly influenced by the solution pH. As shown in Fig. 1, the highest removal of 99% obtained at pH 10. Peak cyanide adsorption at pH 10 can be explained by considering the fact that the pH of the solution influences both the surface charge of the BC particles and dominant species of cyanide in the solution. The pK_a of HCN is 9.0 [1] and the pH_{zpc} of the BC surface is 8.3 (Fig.1), implying that HCN is completely dissociated to CN^- at a solution pH of 10, whereas the BC particle surfaces are negatively charged for a pH over 8.3. Because CN^- is a nucleophilic ion, when in contact with the negatively charged adsorbent, it binds with the anionic functional groups present on the surface of adsorbent and thus improves adsorption [1]. Therefore, chemical ion exchange is determined to be the prevailing mechanism for the adsorption of cyanide ions onto BC. Moreover, some removal may occur through surface precipitations and chemical reactions with surface sites, complexation of CN^- with functional groups, and chemisorption adsorption. Our findings are in agreement with results reported previously about cyanide adsorption [1,2].

3.2. Effect of SMP Dosage

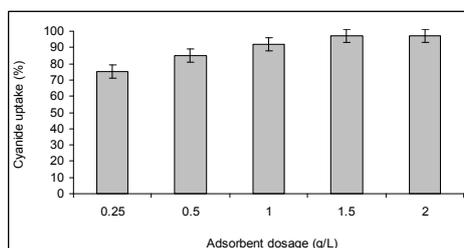


Fig. 2: Effect of BC dosage on cyanide adsorption

The effect of BC dosage on cyanide adsorption was studied in the range of 0.25-2 g/L. The results regarding cyanide removal at various BC doses are presented in Fig. 2. According to Fig 2, increasing the BC dosage from 0.25-2 g/L also increases percentage cyanide removal from 72% to 97%. The enhancement of cyanide adsorption as a function of BC dose to 1.5 g/L is due to the greater availability of active binding sites and to the presence of a greater surface area for adsorption. In addition, it can be seen that the rate of cyanide adsorbed to BC did not significantly increase with the increasing dosage of BC to 2 g/L. One plausible reason could be due to overlap of active sites at higher adsorbent masses resulting in reduced

effective surface area required for sorption [10]. Thus, 1.5 g/L of BC was fixed as the optimum dosage, and the rest of the studies were performed at this optimum adsorbent dose.

3.3. Effect of Contact Time and Cyanide Concentration

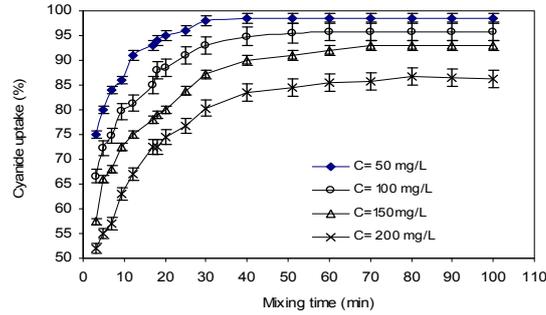


Fig. 3: Adsorption of cyanide in different concentration

Fig. 3, represent the results of the effects of contact time and cyanide concentration on the adsorption. As illustrated in Fig 3, it can be concluded that the equilibrium was reached at 40 min. It is clear that increasing the contact time beyond the 40 min had not significant impact on adsorption performance. In addition, this Fig. implies that adsorption led to saturation that displays the possible monolayer sorption of cyanide onto BC. As shown in Fig. 3, increasing initial cyanide concentration from 50 up to 200 mg/L led to decrease of uptake efficiency from 99% to 80% that implies that removal efficiency is dependent on preliminary cyanide concentration. The kinetic adsorption data are probably the most important factor in the design of an adsorption system, to determine the adsorbate uptake rate and the time needed to attain equilibrium for industrial applications [1,8]. To analyze the kinetics of adsorption onto BC, two simplified kinetics models including the pseudo first-order Lagergren and pseudo-second order were used. Linear forms of these models are given in Eqs. (3) and (4).

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.203} t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

The parameters in these models (first and second order) can be determined experimentally from plotting $\log(q_e - q_t)$ vs. t , (t/q_t) vs. t , respectively [10]. The fitted linear regression plots showed that the experimental data are well fitted to the pseudo-second-order kinetic model with higher value correlation coefficient ($R^2 > 0.999$), compared to the pseudo-first-order model (data not shown). The fitted kinetic models were further evaluated by determining the SSE. The comparisons of SSE confirm that cyanide adsorption onto BC fits well with pseudo-second order kinetic model. In addition, the fitness of experimental data to the pseudo-second order model, the basic assumption in the model, implies that chemisorption plays a major role and likely controls the adsorption process [10].

3.4. Equilibrium Adsorption Isotherms

In order to describe the cyanide uptake capacity and its adsorption behavior onto BC, isotherm data obtained were fitted by four isotherm including Langmuir, Freundlich, Dubinin-Radushkevich and Temkin [1, 10]. The linear form of the selected models can be represented by the following equations [8, 10]:

Freundlich :
$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (6)$$

Langmuir :
$$\frac{C_e}{q_e} = \frac{1}{bQ_{\max}} + \frac{C_e}{Q_{\max}}$$

Temkin:
$$q_e = B_T \ln A_T + B_T \ln C_e \quad (7)$$

Dubinin-Radushkevich (D-R):
$$\ln q_e = \ln Q_{\max} - K_{DR} \epsilon^2 \quad (8)$$

The coefficient (R^2) and $\Delta g(\%)$ were used to select the best-fit isotherm model (data not shown). The data show that the experimental results are best described by the Langmuir isotherm equation. Therefore, the experimental results suggest that a monolayer of cyanide ions is adsorbed on homogeneous adsorption sites on the surface of BC.

The experimental data were further interpreted by D–R isotherm. Analysis of data with D–R isotherm showed that the energy of Cr (VI) adsorption process onto BC was 15.5 kJ/mol. Based on literature for adsorption type and energy of adsorption, this range of energy is between the typical range of bonding energy for chemisorption (8-16 KJ/mol) and demonstrates that in the adsorption of cyanide onto BC chemisorption plays a significant role, which is in agreement with the information obtained from kinetic evaluation [8]. The essential feature of the Langmuir isotherm can be described with a dimensionless separation factor or equilibrium constant R_L , which is used for the explanation of the adsorption condition, expressed as [9, 10]: $R_L = 1/(1 + bC_0)$. The value of R_L represents the adsorption situations to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($R_L < 1$), or irreversible ($R_L = 0$) [8]. Based on the Langmuir constant, the value of this parameter ($R_L = 0.167$) for cyanide adsorption with BC falls between 0- 1, which confirms that cyanide adsorption with this adsorbent is favorable under the conditions of this research. In addition, the n value, a constant of the Freundlich model (2.2), is greater than 1, which indicates that BC is an appropriate adsorbent and beneficial for the adsorption of cyanide from water.

4. Conclusions

In the present work, Bone charcoal, as a low-cost and efficient adsorbent, was evaluated for the removal of cyanide from aqueous solution. The adsorption process is pH dependent and the optimum pH was 10. The kinetic studies showed that adsorption data were fitted well to the pseudo-second order model with high interrelation coefficient under selected condition and smaller the squared sum of errors (SSE). Furthermore, the isotherm equilibrium studies confirmed that the Langmuir form is the best-fitted model for the adsorption process of cyanide by BC. The maximum adsorption capacity of fluoride was 140 mg/g, and the optimal dosage of BC was 1.5 g/L. A result from analysis of data with Dubinin–Radushkevich isotherm showed that adsorption of cyanide onto BC is chemisorption in nature. Accordingly, the BC was shown to be an efficient adsorbent for the removal of cyanide and a promising option for wastewater cyanide treatment. However, further studies will be required to scale up and optimize process variables

5. Acknowledgements

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6. References

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