Available online at www.derpharmachemica.com

Scholars Research Library

Der Pharma Chemica, 2015, 7(9):80-89
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X
CODEN (USA): PCHHAX

Studying the efficiency of Regenerated Spent Bleaching Earth (RSBE) in removing cyanide from coke industry wastewater in Kerman

Mohammad Hassan Ehrampoush[1], Ali Almasi[2] and Behnam Salmani[3*]

[1]Department of Environmental Health Engineering, School of Public Health, Shahid Sadoughi University of Medical Sciences and Health Services, Yazd, Iran
[2]Department of Environmental Health Engineering, School of Public Health, Kermanshah University of Medical Sciences, Kermanshah, Iran
[3]Department of Environmental Health Engineering, School of Public Health, International Campus of Shahid Sadoughi University of Medical Sciences and Health Services, Yazd, Iran

---

ABSTRACT

Cyanide is a toxic pollutant found in different industrial wastewater, and wastewater of these industries is discharged to the environment without any treatment. The main aim of this research was to remove cyanide from aqueous solutions using bleaching earth adsorbent recycled from vegetable oil industries. In this study, Regenerated Spent Bleaching Earth (RSBE) obtained from vegetable oil industries was used to remove cyanide from aqueous solutions. Effects of pH, cyanide initial concentration, contact time and adsorbent dose were investigated in a batch reactor. The optimum conditions obtained in this study on Kerman coke industry wastewater were also examined. Finally, kinetics and isotherms of cyanide adsorption were analyzed. Results showed that the regenerated bleaching earth with a concentration of 1 N NaOH had a higher adsorption capacity than other regenerated agents. The maximum cyanide adsorption was achieved at a pH of 7 and a contact time of 140 minutes. As cyanide initial concentration increased, adsorption rate increased but removal efficiency decreased. Moreover, as adsorbent dose increased, removal efficiency increased but adsorbent capacity decreased. The effect of bleaching earth on coke industry wastewater in optimal conditions revealed that cyanide removal rate was 86%. The data of this research had the greatest conformity with Langmuir-2 isotherm. The maximum adsorption capacity of cyanide on RSBE was 13 mg/g. In addition, Elovich was the most appropriate model to determine the reaction kinetics. The results of this study showed that treatment costs of cyanide-containing wastewater could be reduced by regenerating this industrial waste.

Keywords: adsorption, regeneration, cyanide, coke industry wastewater

---

INTRODUCTION

Removal of hazardous components from industrial effluents is one of the basic needs of the present era. Wastewater of coke industries contains large amounts of different pollutants which are usually discharged to the environment without any treatment [1]. Coke and its by-products are produced by the pyrolysis process on coal. During coke processing, large amounts of toxic compounds enter into the effluent which contains cyanide, phenol, ammonium nitrogen, chlorides, lower levels of heavy metals and much lower amounts of phosphorus [2]. Among the pollutants of coke industry effluent, cyanide is one of the most toxic pollutants to humans, other animals and the environment;

it is found in levels higher than the limit level (500 to 1000 times). Maximum contaminant limit for discharging cyanide to the nature is considered 0.2 mg/L by WHO and USEPA [3]. Cyanide is a carbon-nitrogen radical available in the form of different organic and inorganic compounds. All cyanide types are toxic; however, hydrogen cyanide is the most lethal one. Short-term exposure to cyanide can increase breathing rate, tremors and other neurological effects, and prolonged exposure causes weight loss, affects the thyroid, damages nerves and finally causes death. Moreover, exposure to solutions containing cyanide can cause skin irritation and painful lesions [4,5]. The most common methods mainly used to treat coke industry wastewater include making use of biological treatment methods such as anoxic-oxic (AO), anaerobic-anoxic-oxic (A_1-A_2-O) and SBR. Since effluents of these industries contain large amounts of toxic organic matters, they may cause problems in the biological treatment systems. As a result, they must be pre-treated prior to making use of wastewater biological treatment processes. Many processes like coagulation and advanced oxidation processes have been used to treat wastewater of coke industries. However, these methods are undesirable economically or complex technically, so they are difficult to use [6-9]. The adsorption process is one of the most effective wastewater treatment methods used in many industries to reduce the amount of dangerous organic and inorganic pollutants. Adsorption means the accumulation of materials on the surface of a solid, and it can be used as a physicochemical process. Adsorbents are some materials with large surface area and high porosity; they can separate contaminants from the liquid phase. The most important adsorbent which has been used to separate and remove cyanide from aqueous solutions and wastewater is the activated carbon. Making use of the activated carbon as an adsorbent to remove contaminants from water and wastewater has several drawbacks, including regeneration of the activated carbon and high initial cost of production of the activated carbon. Therefore, making use of low-cost materials and waste of other industries to remove various contaminants from wastewater is increasing [10-13]. Refining is an important step in the production of vegetable oil. Spent bleaching earth is used in vegetable oil industries to remove undesirable contaminants; its main task is to improve the appearance, taste and stability of the final product. Spent bleaching earth mainly consists of bentonites and montmorillonites which are products of the deformation of volcanic ash [14-16]. Oil refining process by spent bleaching earth has four stages, namely bleaching, neutralization, degumming and deodorization. Bleaching produces large quantities of waste (bleaching earth). In many countries, burning this waste is prohibited because it is very smelly and flammable and causes the discharge of toxic and organic materials to the environment. This waste is usually landfilled near the companies without any usage. In Algeria, for example, more than 8,000 tons of bleaching earth is annually produced in vegetable oil industries. To reduce the risk of bleaching earth contamination, several studies have been conducted on reuse of bleaching earth for different applications [17,18]. The aim of this study was to obtain a low-cost adsorbent from an industrial waste, to use it to remove cyanide from aqueous solutions and to conduct a case study on Kerman coke industry wastewater in the optimum conditions.

MATERIALS AND METHODS

Chemicals and solvents

All chemicals used in this experiment were purchased from the German Merck Company. The experiment temperature was 25°C at all steps. Stock solution containing 100 mg/L of cyanide was prepared by solving 0.25 g of KCN in 1 L of millipore water. Cyanide samples with different concentrations required at each stage of the experiment were made of this solution.

Regeneration of RSBE

Bleaching earth is produced as waste in Golnar vegetable oil industries in Kerman. To regenerate the bleaching earth, hydrochloric acid and NaOH 0.01, 0.1 and 1 N are used. In all soil regeneration stages, the ratio of earth to water was (1 to 20). To solve the earth appropriately in the regenerating solution, a mixer with 100 rpm was used. After earth regeneration, earth was washed with distilled water until pH was adjusted to 7.

Batch adsorption studies

Batch experiments were done in 500 mL beakers; 200 mL of sample was inside these beakers. To determine the concentration of cyanide samples, the titration method presented in the 4500-D section of the book “Standard Method for Examination of Water and Wastewater” was used [19].

Effect of contact time

To investigate the effect of contact time on the adsorption level, 200 m/L of cyanide solution with initial concentration of 20 mg/L was prepared. Its pH was adjusted to 7 by adding hydrochloric acid and 0.1 N NaOH solution. 10 g/L of RSBE was added to the solution; then, they were mixed using a 100 rpm mixer. Samples were

taken every 30 minutes. It continued until the adsorption rate reached zero or adsorption and desorption rate became equal. Samples were then separated from then liquid. After they were passed through the filter, concentration of the cyanide ion remained in solution was determined.

Effect of pH

To investigate the effect of pH on the adsorption rate, 200 m/L of cyanide solution with initial concentration of 20 mg/L was prepared. Its pH was adjusted to 2-12 by adding hydrochloric acid and 0.1 N NaOH solution. Then, 10 g/L of RSBE was added to the solution; they were mixed using a 100 rpm mixer. After 180 minutes of the reaction time, the concentration of cyanide ion remained in solution was determined.

Effect of cyanide initial concentration

To study the effect of initial concentration of cyanide, solution containing different cyanide concentrations (10, 30, 60, 90 mg/L) were prepared, and 10 g/L of adsorbent was added to each. Then, samples were taken every 15 minutes (up to contact time of 240 minutes, i.e. 15 different contact times). After that, samples were separated from the liquid. After they were passed through the filter, concentration of the cyanide ion remained in solutions was determined.

Effect of adsorbent dose

To evaluate the effect of adsorbent dose, 10, 15 and 20 g/L of RSBE was used. One-liter solutions containing different cyanide concentrations (5, 10, 15, 20, 30, 40, 50) were provided. The above-mentioned amounts of RSBE were added to them, and they were mixed at 100 rpm for 180 minutes. After that, samples were separated from the liquid. After they were passed through the filter, concentration of the cyanide ion remained in solutions was determined.

Effect of RSBE in Kerman Coke industry wastewater

In this step, a sample was prepared from coke industry effluent and its characteristics were determined. At this stage, the optimum parameters obtained in the previous step were used to measure the amount of cyanide removed from coke industry effluents.

RESULTS AND DISCUSSION

Regeneration of bleaching earth

Structural properties of the bleaching earth such as surface area and volume of pores play an important role in its efficiency to adsorb pollutants, and these properties can be expanded and developed by various activating techniques such as acidic regeneration, basic regeneration, etc. [20]. Results of regenerating the bleaching earth using the mentioned acids and bases were shown in figure 1. Results showed that the bleaching earth regenerated by bases had higher adsorption capacity to adsorb the cyanide ion than that regenerated by the acids. Moreover, basic regeneration with a concentration of 1 N NaOH had higher adsorption capacity than other concentrations of base; in this study, basic regenerated bleaching earth with a concentration of 1 N NaOH was used. Properties of basic regenerated earth are shown in table 1. Other similar studies which had used regenerated bleaching earth to remove various pollutants from water and wastewater revealed that basic regeneration had the highest effect on activating and regenerating recycled bleaching earth; their results were in line with the results of the present study [17,21].

Table 1. Properties of basic regenerated earth

Parameter	Value (mg/L)
Special Weight	0.65
SiO_2	52
Al_2O_3	11.9
CaO	290
MgO	0.9
Fe_2O_3	2.6
Na_2O	10.3
K_2O	1.4
LOI (lost of ignition)	18.6

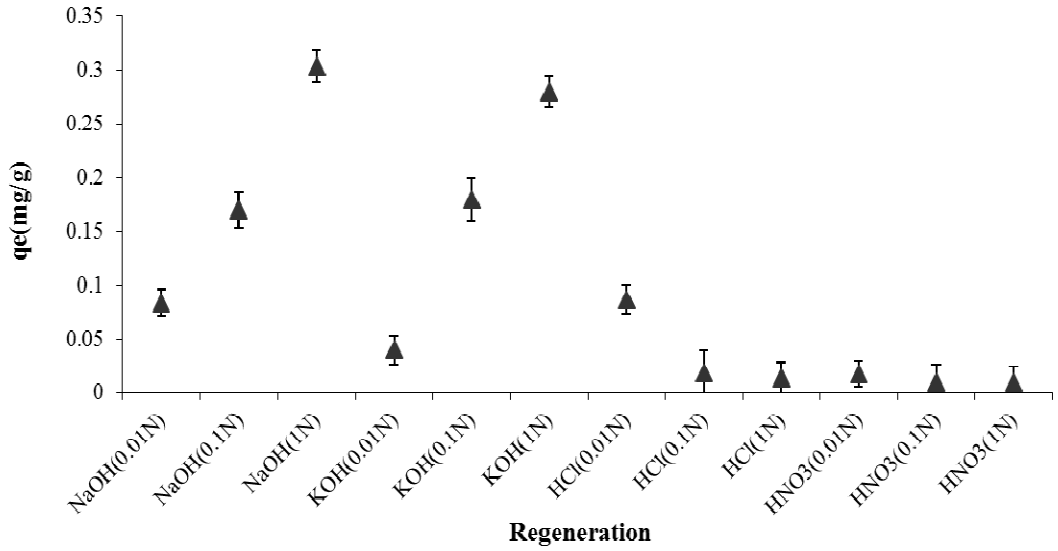

Figure 1. Regeneration of bleaching earth with different acid and base concentration

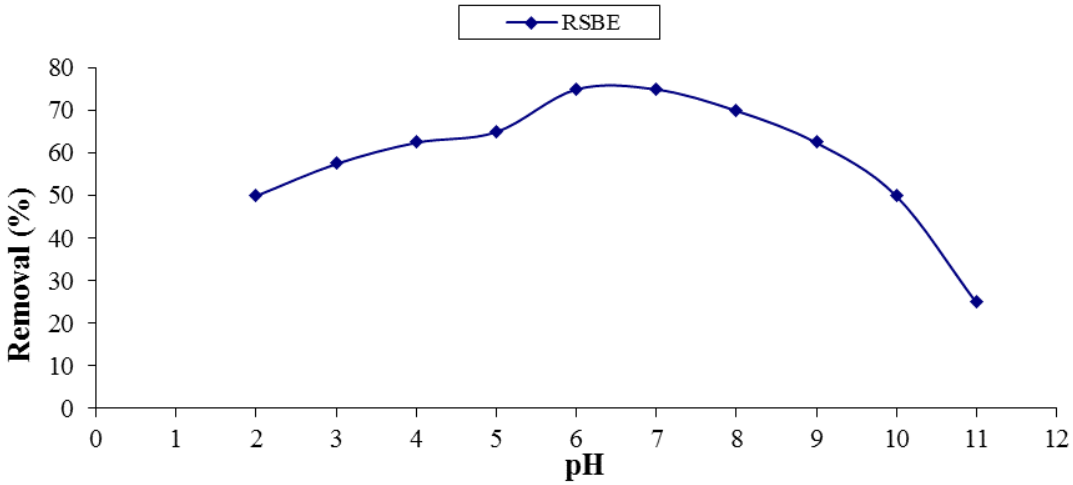

Figure 2. Cyanide adsorption in different pHs

Effect of pH

Cyanide is one of ions which can be separated by controlling pH in aqueous solutions. Solution pH can affect the adsorbent surface charge, ion creation of organic and inorganic contaminants as well as features of adsorbent surface such as porosity. Therefore, pH parameter plays an important role in optimizing the adsorption of cyanide and other pollutants from basic aqueous solutions [22]. Results obtained from examining pH were shown in figure 2. As shown in this figure, efficiency decreased in neutral and acidic pHs (the highest removal efficiency of cyanide was achieved in neutral pH, i.e. pH of 6 and 7). As pH increased from 2 to 7, adsorption level increased too; the highest adsorption level was obtained in pH of 6 and 7. As pH increased more, adsorption rate decreased and the graph had a descending trend. Therefore, pH of 7 was considered the optimum pH. The effect of pH on the adsorption process is emphasized less than that of other parameters. However, it plays a significant role in the stability of cyanide ion [23]. At very low or acidic pHs, cyanide is found in the form of HCN which is a weak acid which is very soluble. A tendency to form HCN at low pH inhibits the adsorption of cyanide on the adsorbent surface. At acidic pH, adsorbent surface charge is increasingly positive, and cyanide ions tend to separate from the adsorbent surface due to competition of hydrogen ions to form a bond with the adsorption sites [23, 24]. At alkaline pHs, adsorption level decreases; it may be due to the formation of cyanide soluble compounds that remain dissolved in the solvent and aren't adsorbed by the adsorbent. In addition, cyanide adsorption decreases at high pH because hydroxide ions act as

a competitor to adsorb cyanide anions [25]. In a study by Malakoutian et al and also in a study by Naeem et al, the optimal pH was 7. Their results were in line with the results of the present study [17, 26]. In a study conducted by Nsaif Abbas et al, the optimum pH was 8; their results were consistent with the results of this study [24].

Effect of contact time and cyanide initial concentration

Results of this study were shown in figure 3. As shown in this figure, as contact time increased from zero to 140 minutes, removal efficiency increased. Experiments continued up to the contact time of 200 minutes; after contact time of 140 minutes, increased contact time had no effect on cyanide removal efficiency. Therefore, contact time of 140 minutes was chosen as the optimal contact time. The contact time between a pollutant and an adsorbent plays an important role in treating wastewater using adsorption processes. Since adsorption processes are equilibrium reactions, the contact time is essential in reaction progress [13, 27]. Results obtained from adsorption of various pollutants by an adsorbent clarify the fact that adsorption of pollutants on adsorbent surface is fast at initial steps but it slows down and then reaches equilibrium. The reason is that in the early adsorption steps, the adsorbed part can have an easy access to adsorption places of the adsorbent and thus needs lower contact time. When this access becomes difficult, contact time must increase so as to obtain the maximum adsorption [5, 28]. In a study conducted by Agarwal et al, the contact time to adsorb cyanide using granular activated carbon was 24 hours which was much more than the contact time obtained in the present study [29]. Similarly, Naeem et al reported that the contact time to remove cyanide by the activated alumina adsorbent was 24 hours [26]. In a study by Dash et al, contact time of 48 hours was found to remove the cyanide by the activated carbon [22]. Moussavi et al used the activated carbon produced from the pistachio shell to remove cyanide from wastewater and reported that the optimum contact time was 60 minutes; this time was less than the time obtained in the present study [13].

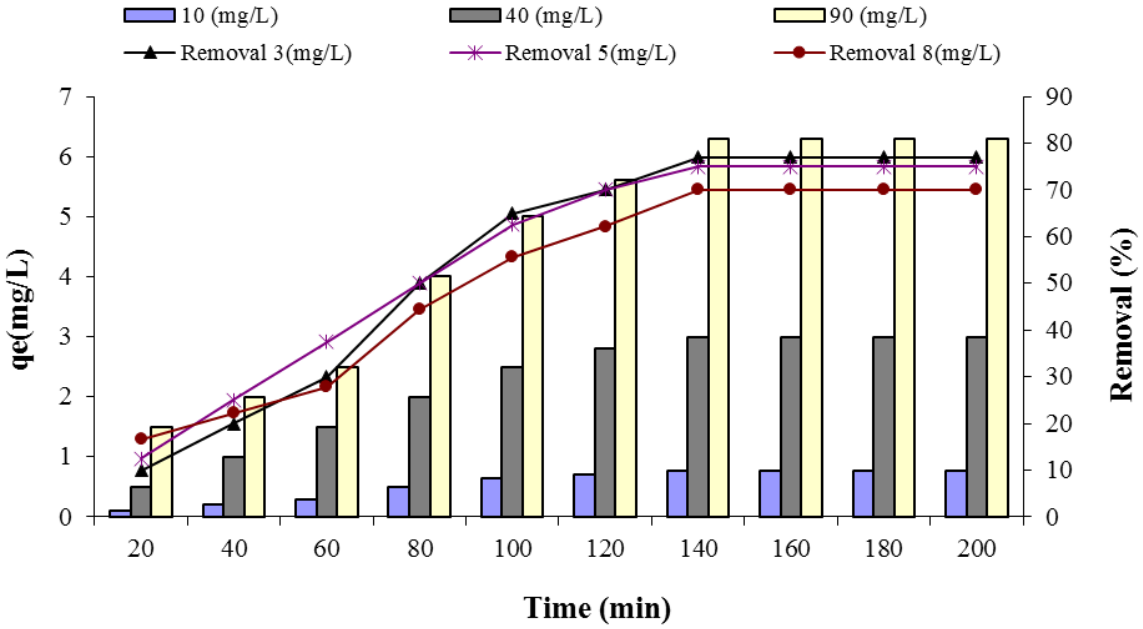

Figure 3. Cyanide adsorption in different initial concentration of cyanide and contact time

As initial concentration of cyanide increased, adsorption level increased but removal efficiency decreased. The highest and lowest removal levels were obtained at initial cyanide concentrations of 10 and 90 mg/L respectively. The reason is that as the initial concentration of cyanide increased, the number of cyanide molecules increased in the reaction medium; on the other hand, cyanide was adsorbed slowly at higher concentrations and removal efficiency decreased due to the saturation of active sites of the adsorption surface [27, 30]. As initial concentration of cyanide increased, adsorption capacity increased too. It can be due to the concentration gradient. Another reason for increased adsorption capacity of the regenerated bleaching earth is increased chance of contact between the adsorbent and the adsorbed material, i.e. cyanide [5, 30]. Results of this study were consistent with the results of other studies conducted on adsorbing cyanide using different adsorbents [31, 32].

Effect of adsorbent dose

Results of this part of the study were shown in figure 4. As shown in this figure, as adsorbent dose increased, removal efficiency increased but adsorption capacity decreased. Since adsorption is primarily a surface phenomenon, levels available for adsorption and therefore the adsorbent mass can dramatically affect the performance of the adsorption process [13]. Results showed that as adsorbent dose increased, removal efficiency increased but adsorption capacity decreased. Increased adsorbent dose through increased contact area between the pollutant and creation of more adsorption active sites to replace cyanide ions increased the process efficiency in adsorbing pollutants. Decreased adsorption capacity by increasing adsorbent dose can be due to overlap of adsorbent of regenerated bleaching earth and thus decreased effective surface area available for cyanide adsorption [33, 32].

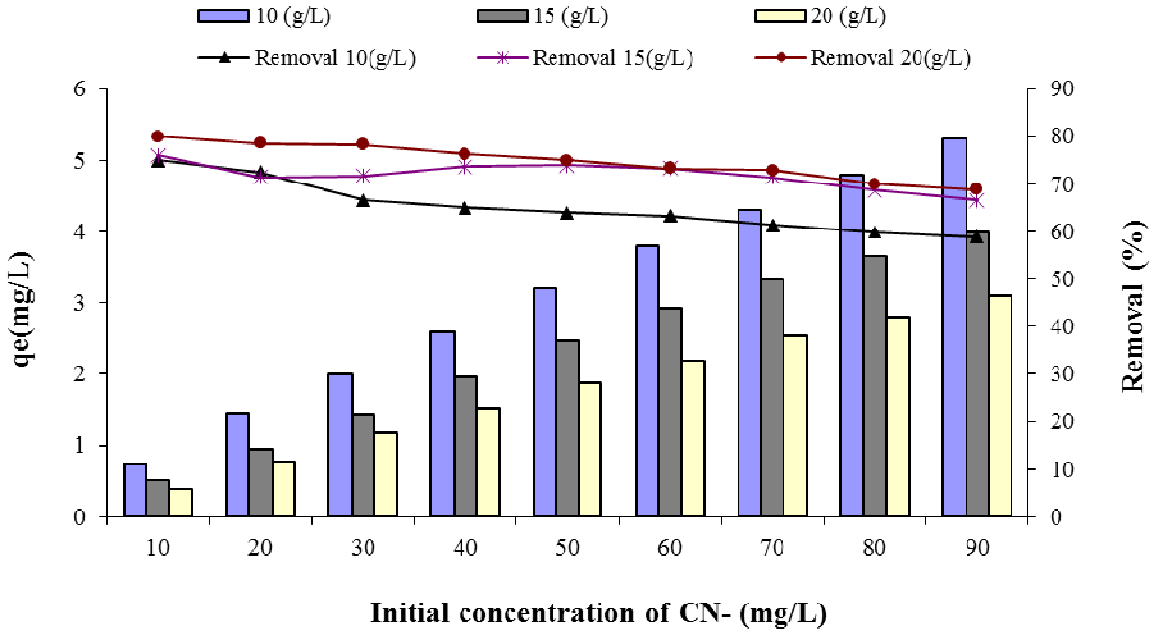

Figure 3. Cyanide adsorption in different adsorbent dose value

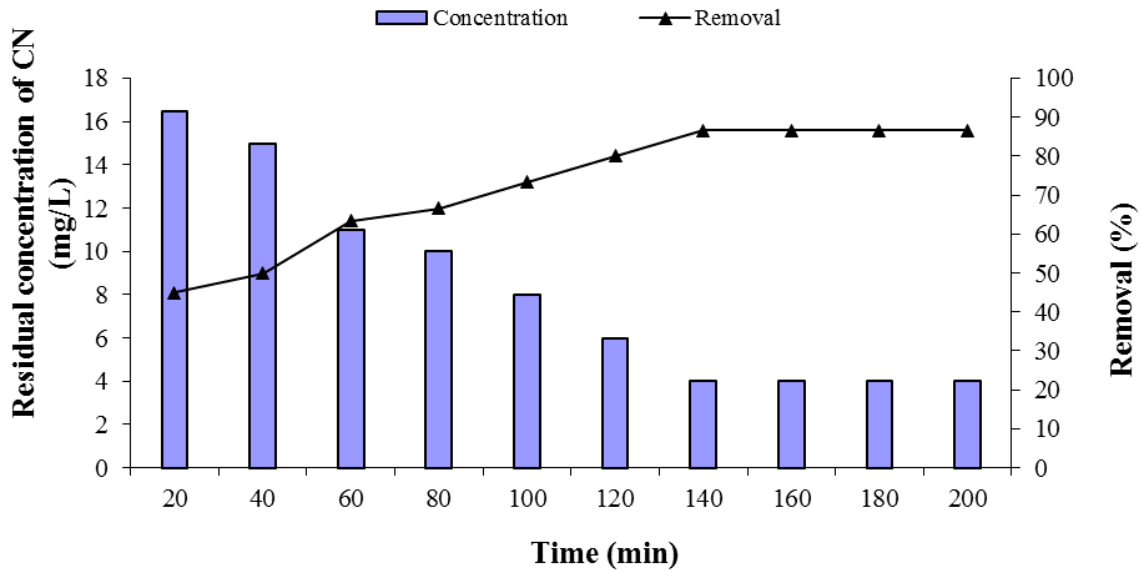

Figure 5. Results of the effect of adsorbent on coke industry wastewater

Effect of RSBE in Kerman Coke industry wastewater

Results of this part of the study were shown in figure 5. Based on these results, after the contact time of 140 minutes, 86% of cyanide was removed.

Isotherm studies

Adsorption is a very well-known equilibrium separation process. Adsorption isotherm parameters provide information about the adsorption capacity of the adsorbent. Constant and certain amounts in isotherms represent the surface and dependency of the adsorbent and can be used to compare adsorption capacity of the adsorbent for various pollutants. Adsorption isotherms are some charts between adsorption level and final concentration of the adsorbed material remained in the solution. In this study, typical isotherms were used to analyze water and wastewater experiments. Linear equations and relations of isotherms examined in this study were summarized in table 2.

Table 2. Equations and linear forms of isotherms [13, 17]

Isotherms	Equation	Linear form
Freundlich	$q_e = K_f C_e^{\frac{1}{n}}$	$\log q_e = \log K_f + \left(\frac{1}{n}\right)\log C_e$
Langmuir-1		$\frac{C_e}{q_e} = \left(\frac{1}{K_L Q_m}\right) + \left(\frac{1}{Q_m}\right) C_e$
Langmuir-2	$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}$	$\frac{1}{q_e} = \frac{1}{Q_m} + \left(\frac{1}{K_L Q_m}\right)\frac{1}{C_e}$
Langmuir-3		$q_e = Q_m - \left(\frac{1}{K_L}\right)\frac{q_e}{C_e}$
Langmuir-4		$\frac{q_e}{C_e} = K_L Q_m - K_L q_e$
Temkin	$q_e = \frac{RT}{b} Ln(A_T C_e)$	$q_e = B_T \ln A_T + B_T \ln Ce$
Dubinin-Radushkevich	$q_e = \exp\left(-K_{D-R}\varepsilon^2\right)$ $\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right)$	$\ln q_e = \ln Q_m - K_{D-R}\varepsilon^2$
Generalized	-	$\log\left(\frac{Q_m}{q_e} - 1\right) = \log K_G - N_b \log C_e$
BET	$q_e = \frac{K_B C_e Q_m}{(C_s - C_e)\left[1 + (K_B - 1)\left(\frac{C_e}{C_s}\right)\right]}$	$\frac{C_e}{(C_s - C_e)q_e} = \left(\frac{1}{K_B Q_M}\right) + \left(\frac{K_B - 1}{K_B Q_m}\right)\frac{C_e}{C_s}$

According to the results obtained in this study, adsorption of cyanide by RSBE followed Langmuir adsorption model (type 2). According to table 2, for the RSBE, Langmuir constant values including Q_m and K_L were obtained by drawing C_e/q_{eq} plot against C_e; correlation coefficients (R^2) were also obtained in the same way. The correlation coefficient (R^2) for adsorbent doses of 10, 15 and 20 g/L was 0.99, 0.99 and 0.99 respectively. The Q_m values for adsorbent doses of 10, 15 and 20 g/L were 7.27, 10.58 and 6.34 mg/g respectively; results were shown in table 3.

Table 3. Isotherm parameters obtained from the various linear forms of the isotherm model In their study, Gupta et al used granular activated carbon to remove cyanide. Among different models of Langmuir isotherm, types 1 and 2 had the highest conformity to adsorb cyanide. Correlation coefficients for type 1 and type 2 were 0.98 and 0.99 respectively. Q_m values were 10.6 and 9.8 mg/g respectively. They were almost in line with the results of this study [28].

Mousavi et al used activated carbon made from pistachio shell to adsorb cyanide. Among different models, Langmuir isotherm had the highest conformity to adsorb cyanide. Correlation coefficient was 0.99; Q_m value was 156.2 mg/g [13]. Comparison of the adsorption capacity of different materials was shown in table 4. Comparing these results revealed that the regenerated bleaching earth could be used as a relatively effective and low-cost adsorbent to adsorb cyanide.

Isotherm type	Isotherm parameter	Adsorbent dose (g/L)		
		10	15	20
Freundlich	n	1.39	1.15	1.3
	K_F	0.4	0.63	0.6
	R^2	0.99	0.98	0.99
Langmuir-1	Q_m	10	13	6.4
	K_L	0.028	0.016	0.034
	R^2	0.93	0.69	0.99
Langmuir-2	Q_m	7.27	10.58	6.43
	K_L	0.046	0.021	0.034
	R^2	0.99	0.99	0.99
Langmuir-3	Q_m	8.40	8.72	6.37
	K_L	0.037	0.016	0.034
	R^2	0.85	0.50	0.98
Langmuir-4	Q_m	9.18	14.6	6.45
	K_L	0.032	0.014	0.033
	R^2	0.85	0.50	0.98
Temkin	A_T	2.24	2.42	1.82
	B_T	1.69	1.50	1.05
	R^2	0.93	0.94	0.96
Dubinin-Radushkevich	Q_m	3.54	2.7	2.13
	K_{D-R}	2×10^{-6}	3×10^{-7}	2×10^{-6}
	R^2	0.75	0.73	0.79
BET	Q_m	12.17	14.32	8.08
	K_B	11.75	7.35	13.31
	R^2	0.95	0.75	0.99

Table 4. Comparison of the adsorption capacity of different materials with present study

Study	Year	Adsorbent	Adsorption Capacity (mg/g)
Gupta et. al [28]	**2012**	Granular activated carbon	10.6
Moussavi et. al [13]	**2010**	pistachio shell	156.2
Asgari et. al [7]	**2012**	Bone Charcoal	140
Mbadcam et. al [6]	**2010**	ɤ-Alumina	6.44
Kumar et. al [3]	**2002**	Plain AC	7
Barakat et. al [1]	**2005**	TiO_2	13
Present study	-	RSBE	10.58

Kinetic studies

Studying the adsorption kinetics to predict the adsorption rate that is important for designing and modeling the process is useful. First- and second-order kinetics, Elovich and inter-particle distribution model were examined in this study. Table 5 showed linear equations and forms of each of the mentioned kinetics.

Table 5. Equation and linear form of kinetics [13, 17]

Kinetic	Equation	Linear form
Pseudo first order	$\frac{dq_t}{dt} = k_1(q_e - q_t)$	$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t$
Pseudo second order	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$	$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right)t$
Elovich	$\frac{dq_t}{dt} = \alpha\exp(-\beta q_t)$	$q_e = \left(\frac{1}{\beta}\right)\ln(\alpha\beta) + \left(\frac{1}{\beta}\right)\ln t$
Intraparticle diffusion	-	$q_t = K_{dif}\, t^{0.5} + C$

In this study, Elovich kinetics was considered the most appropriate model to determine the reaction rate. The linear correlation coefficient of this model to adsorb cyanide with concentrations of 10, 40 and 90 mg/L on the RSBE (20 g/L) was 0.94, 0.97 and 0.93 respectively. In studies conducted on the adsorption of cyanide by different adsorbents, adsorption kinetics followed the second-order model [29, 13]. Table 6 summarized the results of kinetics examined in this study.

Table 6. The parameters obtained from various kinetics models

Kinetic	Kinetic parameter	Cyanide concentration (mg/L)		
		10	40	90
Pseudo first order	k_1	0.002	0.007	0.010
	q_e cal	3.17	1.92	5.20
	R^2	0.02	0.25	0.76
Pseudo second order	k_2	0.0005	0.0004	0.0003
	q_e cal	3.68	8.81	13.7
	h×1000	0.48	0.79	0.76
	R^2	0.26	0.73	0.75
Elovich	α	6.34	19.03	37.96
	β	2.9	0.8	0.40
	R^2	0.94	0.97	0.93
Intraparticle diffusion	K_{dif}	0.08	0.29	0.6
	C	0.25	0.64	1.37
	R^2	0.93	0.94	0.94

REFERENCES

[1] M.A Barakat, *J. Colloid Interface Sci*, **2005**, 291, 345-352.
[2] N Adhoum, L Monser, *Chem Eng Process*, **2002**, 41, 17-21.
[3] N Adhoum, L Monser, *Chem Eng Process*, **2002**, 41, 17-21.
[4] G Busca, S Berardinelli, C Resini, L Arrighi, *J Hazard Mater*, **2008**, 160, 265-288.
[5] R. R Dash, A Gaur, Ch Balomajumder, *J Hazard Mater*, **2009**, 163, 1-11.
[6] J Ketcha Mbadcam, G. F Tchatat wouaha , V Hambate Gomdje, *E-Journal of Chemistry*, **2010**, 7(3), 721-726.
[7] Gh Asgari, A. M Seid Mohammadi, A Poormohammadi, M Ahmadian, *Fresenius Environmental Bulletin*, **2014**, 23(3), 720-727.
[8] P Lai, H. Z Zhao, C Wang, J. R Ni, *J Hazard Mater*, **2007**, 147, 232–239.
[9] P Ning, H. J Bart, Y. J Jiang, A de Haan, C Tien, *Sep Purif Technol*, **2005**, 41, 133-139.
[10] M Ahmadian, N Yosefi, A Toolabi, N Khanjani, S Rahimi, A Fatehizadeh, *Asian Journal of Chemistry*, **2012**, 24(7), 3094-3098.
[11] S. P Moussavi, M. H Ehrampoush, A. H Mahvi, S Rahimi, M Ahmadian, *Asian Journal of Chemistry*, **2014**, 26(3), 821-826.
[12] M. T Samadi, H Zolghadrnasab, K Godini, A Poormohammadi, M Ahmadian, S Shanesaz, *Der Pharma Chemica*, **2015**, 7(5), 267-274.
[13] Gh Moussavi, R Khosravi, *J Hazard Mater*, **2010**, (183) 724-730.
[14] F Hussin, M Kheireddine Aroua, W. M. A Wan Daud, *Chem Eng J*, **2011**, 170, 90-106.
[15] M. Mana, M.S. Ouali, L.C. de Menorval, J.J. Zajac, C. Charnay, *Chem Eng J*, **2011**, 174, 275-280.
[16] Ch Meziti, A Boukerroui, *Procedia Engineering*, **2012**, 33, 303-312.
[17] M Malakootian, A Fatehizadeh, N Yousefi, M Ahmadian, M Moosazadeh, *Desalination*, **2011**, 244-249.
[18] M Mana, M. S Ouali, L. C de Menorval, *Journal of Colloid and Interface Science*, **2007,** 307, 9-16.
[19] APHA, Standard Method for Examination of Water and Wastewater, 21st ed American public health association publication, Washington DC, **2005**.
[20] M Mana, M. S Ouali, L. C de Menorval, J. J Zajac, C Charnay, *Chem Eng J*, **2011,** 174, 275-280.
[21] F. R Valenzuela-Diaz, P Souza-Santos, *Quim Nova*, **2001**, 24, 345-353.
[22] R. R Dash, C Balomajumder, A Kumar, *Chem Eng J*, **2009**, 146 (1), 408-413.
[23] R. K Vedula, C Balomajumder, *Res J Chem Sci*, **2011**, 1, 30-39.
[24] M. N Abbas, F. S Abbas, S. A Ibrahim, *Journal of Asian Scientific Research*, **2014**, 4(5), 239-247.
[25] L Giraldo, J. C Moreno-Piraján, *Natural Science*, **2010,** 2, 1066-1072.
[26] S Naeem, U Zafar, *Pak J Anal Environ Chem*, **2009**, 10(1&2), 83-87.
[27] M Larsen, S Trapp, A Pirandello, *Chemosphere*, **2004,** 54, 325-333.
[28] N Gupta, Ch Balomajumder, V. K Agarwal, *Chem Eng J*, **2012**, 191, 548-556.

[29] B Agarwal, Ch Balomajumder, P. K Thakur, *Chem Eng J*, **2013**, 228, 655-664.
[30] E. Y Yazici, H Deveci, I Alp, *J Hazard Mater*, **2009**, 166, 1362-1366.
[31] H Deveci, E. Y Yazici, I Alp, T Uslu, *Int J Miner Process*, **2006**, 79(3), 198-208.
[32] A Behnamfrad, M. M Salarirad, *J Hazard Mater*, **2009**, 170, 127-133.
[33] B Bozzini, L D'Urzo, C Mele, V Romanello, *J Phys Chem C*, **2008,** 112(16),6352-6358.