



## Equilibrium and kinetic studies on free cyanide adsorption from aqueous solution by activated carbon

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### ABSTRACT

Adsorption equilibrium and kinetics of free cyanide onto activated carbon were investigated in the batch tests, and the effects of contact time (1–72 h) and initial cyanide concentrations in the range of 102–532 mg/L were studied. Linear regression was used to determine the best fit of equilibrium and kinetics expressions. The two-parameter models including Freundlich, Dubinin–Radushkevich, Temkin and four different linearized forms of Langmuir and three-parameter models including Redlich–Peterson and Koble–Corrigan were employed for fitting the equilibrium data and it was found that, three-parameter models fitted the data better than the two-parameter models and among the three-parameter models the equilibrium data are best represented by Koble–Corrigan model. A number of kinetic models including fractional power, zero order, first order, pseudo-first order, Elovich, second order, intraparticle diffusion and four different linearized forms of pseudo-second order models were tested to fit the kinetic data. The latter was found to be consistent with the data. Intraparticle diffusion plots show that the adsorption process of free cyanide is a two steps process. In the first step, the adsorption of cyanide is fast while in the second step, cyanide adsorption slows down.

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### 1. Introduction

Wastewaters generated from gold and base metals milling operations [1,2] and other industries such as petrochemical and coke-processing plants [3] contain free and metal-complexed cyanides at different amounts and are highly harmful to humans and aquatic organisms [1,4].

To protect the environment and water resources, cyanide containing wastewaters from various industries must be treated before discharging into the environment. Hence many countries and environmental protection agencies have ordained implemented standards for discharge of cyanide bearing wastewaters. The current U.S. Environmental Protection Agency water quality criterion for cyanide is 5.2 µg/L for freshwater aquatic life, and 1.0 µg/L for marine aquatic life and wildlife [1].

Alkaline-chlorination-oxidation [5], electrowinning [6], hydrolysis-distillation [7,8], flotation [9], iron cyanide precipitation [10], resin [11], “acidification–volatilization–reneutralisation” [12], reverse osmosis [13], hydrogen peroxide [14], electrodialysis [7] and caro’s acid [15] are various cyanide removal technologies. Each of the above technologies has their own advantages and constraints.

Removal of cyanide from waste waters by sorption onto activated carbon has received great attention [16]. Activated carbon performs both as an adsorbent and as a catalyst for the oxidation of cyanide. The adsorptive properties of activated carbons result from their high surface area and high degree of surface reactivity. The large surface area relative to the particle actual size of carbon makes it easy to remove large amounts of harmful constituents from gases and liquid solutions in a relatively small enclosed space [16–19]. Furthermore, activated carbon has no disadvantages of other treatment methods such as complexity and difficulty of controlling process, consuming expensive and hazardous reagents and producing toxic residues [16].

Finding an appropriate isotherm for representing the equilibrium state of an adsorption system is the most important step to design and optimize an adsorption process as well as the adsorbate and adsorbent. Also, the study of adsorption kinetics is highly relevant to the design of an adsorption system because it provides beneficial information in the reaction pathway, rate of adsorption and adsorption mechanism of adsorbate onto adsorbent [20–22].

There have been many studies on the adsorptive properties of activated carbon for removal of free cyanide from aqueous solutions. The process parameters for adsorption of free and metal cyanide compounds by granular activated carbon have been recently reported [16]. Guo et al. found that the equilibrium data for adsorption of free cyanide by activated carbon from dilute solution (1 mg/L) are best represented by Freundlich isotherm model [49].

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## Nomenclature

$K_F$	Freundlich constant (mg/g) (L/g) <sup>1/n</sup>
$1/n$	Freundlich exponent
$K_L$	Langmuir isotherm constant (L/mg)
$K_T$	Temkin isotherm constant (L/mg)
$D$	Dubinin–Radushkevich isotherm constant (mol <sup>2</sup> kJ <sup>-2</sup> )
$A_{RP}$	Redlich–Peterson isotherm constant (L/g)
$B_{RP}$	Redlich–Peterson isotherm constant (L/mg) <sup>g</sup>
$g$	Redlich–Peterson constant
$A_{KC}$	Koble–Corrigan isotherm constant (mg/g) (L/mg) <sup>P</sup>
$B_{KC}$	Koble–Corrigan isotherm constant (L/mg) <sup>P</sup>
$P$	Koble–Corrigan constant
$k$	fractional power kinetic model constant (mg g <sup>-1</sup> h <sup>-ν</sup> )
$k_0$	zero order kinetic model constant (mg g <sup>-1</sup> h <sup>-1</sup> )
$k_1$	first order kinetic model constant (1/h)
$k_{1p}$	pseudo-first order kinetic model constant (1/h)
$k_2$	second order kinetic model constant (g mg <sup>-1</sup> h <sup>-1</sup> )
$k_{2p}$	pseudo-second order kinetic model constant (g mg <sup>-1</sup> h <sup>-1</sup> )
$k_p$	intraparticle diffusion kinetic model constant (g mg <sup>-1</sup> h <sup>-0.5</sup> )
$R^2$	correlation coefficient
MPSD	Marquardt's percent standard deviation
HYBRID	hybrid fractional error function
ARE	average relative error
NSD	normalized standard deviation
$p$	number of parameters in isotherm
$N$	number of experimental measurements
$C_e$	equilibrium concentration (mg/L)
$C_0$	initial concentration (mg/L)
$C_t$	concentration at time $t$ (mg/L)
$q_e$	amount of cyanide adsorbed at equilibrium (mg/g)
$q_m$	monolayer sorption capacity (mg/g)
$t$	time (h)
$T$	temperature (K)
$R$	ideal gas constant (JK <sup>-1</sup> mol <sup>-1</sup> )
$V$	volume of the solution (L)
$W$	mass of dry carbon used (g)

### Greek letters

$\alpha$	Elovich kinetic model constant (mg g <sup>-1</sup> h <sup>-1</sup> )
$\beta$	Elovich kinetic model constant (g/mg)
$\nu$	fractional power kinetic model constant

Deveci et al. examined the kinetics of cyanide removal from the solutions containing high concentrations of cyanide (10–200 mg/L) by activated carbon using the pseudo-first order and second order kinetic models and found that the experimental data were consistent with the pseudo-second order kinetic model [4]. Also, they tested the Langmuir and Freundlich models to describe the resultant adsorption isotherms and they found that the equilibrium data to be consistent with both models ( $R^2 = 0.976$  and  $0.970$ , respectively) [4].

In the present study, the adsorption equilibrium and kinetic of free cyanide onto activated carbon by different adsorption isotherm and kinetic models were investigated. To examine the relationship between sorbed and aqueous cyanide concentrations at equilibrium, different two- and three-parameter sorption isotherm models were employed for fitting the equilibrium data. Fractional power, zero order, first order, pseudo-first order, Elovich, second order, intraparticle diffusion and four different linearized forms of

pseudo-second order equations have been used for modeling the kinetics of cyanide sorption.

## 2. Materials and methods

### 2.1. Reagents

In this study analytical grade sodium cyanide (NaCN), silver nitrate (AgNO<sub>3</sub>), potassium iodide (KI), sodium hydroxide (NaOH) and industrial grade coconut shell activated carbon, produced through a steam activation process by Haycarb company, Sri Lanka, were employed. Before use the activated carbon a size fraction of  $-2.36 +2$  mm of it was obtained and dried in air and divided into 1.5 g portions. Following acid treatment of carbon with 1% hydrochloric acid solution, the sample was thoroughly rinsed with distilled water and then added to the cyanide aqueous solution of predetermined initial concentration.

### 2.2. Batch equilibrium experiments and analytical method

Adsorption tests were carried out using a 2.5 L capacity glass bottles at ambient temperature ( $25 \pm 2^\circ\text{C}$ ). Stock solution of cyanide at the concentration of 2000 mg/L was prepared by dissolving 2.0 g of sodium cyanide in 1 L of distilled water preadjusted to pH 10. Experimental solutions at desired concentrations were obtained by dilution of the stock solution with distilled water preadjusted to pH 10. The cyanide concentration of each solution was analyzed by titrating against standard silver nitrate solution (0.001 M) in the presence of potassium iodide (10 g/L in distilled water) as indicator. Analyses were repeated in triplicate and averaged. The initial cyanide concentrations of experimental solutions were determined 102, 202, 306, 396 and 532 mg/L. 500 mL of experimental solutions were placed in bottles and then 1.5 g prepared activated carbon was added to each bottle. The bottles were rolled at a constant rotation of 100 rpm for 72 h to reach the equilibrium.

Sampling was performed by removing 5 mL aliquots at predetermined time intervals. The samples were then analyzed for cyanide as above mentioned method. The amount of adsorption at equilibrium,  $q_e$  (mg/g), was calculated by

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

where  $C_0$  and  $C_e$  (mg/L) are initial ( $t=0$ ) and equilibrium cyanide concentrations, respectively.  $V$  is the volume of the solution (L) and  $W$  is the mass of dry carbon used (g).

### 2.3. Batch kinetic experiments

Batch kinetic experiments were conducted under similar conditions mentioned above for equilibrium experiments. The experiments were performed at ambient temperature using 1.5 g of prepared activated carbon with 500 mL of aqueous cyanide solutions in 2.5 L glass bottles of which initial cyanide concentration (102, 202, 306, 396 and 532 mg/L) and pH (10) has already been known. The contents were rolled at 100 rpm by bottle roll apparatus. Samples were drawn at regular time intervals and the concentration of cyanide was similarly measured. The amount of cyanide adsorbed by carbon at time  $t$ ,  $q_t$  (mg/g), was calculated by

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (2)$$

where  $C_t$  (mg/L) is cyanide concentration at time  $t$ .

#### 2.4. Validity of adsorption isotherm

Apart from the correlation coefficient ( $R^2$ ), the Marquardt's percent standard deviation (MPSD) and the hybrid error function (HYBRID) were also used to measure the goodness-of-fit. MPSD and HYBRID can be defined as

$$\text{MPSD} = 100 \sqrt{\frac{1}{N-p} \sum_{i=1}^N \left( \frac{q_{e_i}^{\text{exp}} - q_{e_i}^{\text{cal}}}{q_{e_i}^{\text{exp}}} \right)^2} \quad (3)$$

$$\text{HYBRID} = \frac{100}{N-p} \sum_{i=1}^N \left[ \frac{(q_{e_i}^{\text{exp}} - q_{e_i}^{\text{cal}})^2}{q_{e_i}^{\text{exp}}} \right] \quad (4)$$

where  $q_{e_i}^{\text{exp}}$  is the observation from the batch experiment  $i$ ,  $q_{e_i}^{\text{cal}}$  is the estimate from the isotherm for corresponding  $q_{e_i}^{\text{exp}}$ ,  $N$  is the number of observations in the experimental isotherm and  $p$  is the number of parameters in the regression model. The smaller MPSD and HYBRID values indicate more accurate estimation of  $q_e$  value [23].

MPSD and HYBRID functions were used in addition to  $R^2$  because the number of parameters in the regression model (i.e.,  $p$  parameter) is effective in them.

#### 2.5. Validity of kinetic model

The applicability of the kinetic model to describe the adsorption process, apart from the correlation coefficient ( $R^2$ ), was further validated by the normalized standard deviation (NSD), and average relative error (ARE) which are defined as

$$\text{NSD} = 100 \sqrt{\frac{1}{N-1} \sum_{i=1}^N \left[ \frac{q_t^{\text{exp}} - q_t^{\text{cal}}}{q_t^{\text{exp}}} \right]^2} \quad (5)$$

$$\text{ARE} = \frac{100}{N} \sum_{i=1}^N \left| \frac{q_e^{\text{exp}} - q_e^{\text{cal}}}{q_e^{\text{exp}}} \right| \quad (6)$$

where  $q_t^{\text{exp}}$  and  $q_t^{\text{cal}}$  (mg/g) are experimental and calculated amount of cyanide adsorbed on activated carbon at time  $t$  and  $N$  is the number of measurements made. The smaller NSD and ARE values indicate more accurate estimation of  $q_t$  values [23,24].

### 3. Results and discussion

#### 3.1. Equilibrium isotherms

An equilibrium isotherm expresses the relation between the amounts of adsorbate removed from solution at equilibrium by unit of mass of adsorbent at constant temperature. In this study, equilibrium data were fitted by four "two-parameter isotherms" including Freundlich, Langmuir, Dubinin–Radushkevich and Temkin and two "three-parameter isotherms" including Redlich–Peterson and Koble–Corrigan.

Langmuir isotherm model can be linearized into at least four different types including as shown in Table 1. The relative parameters of four different linearized forms of Langmuir isotherm were obtained from the plots between  $[C_e/q_e \text{ vs. } C_e]$ ,  $[1/q_e \text{ vs. } 1/C_e]$ ,  $[q_e \text{ vs. } q_e/C_e]$ ,  $[q_e/C_e \text{ vs. } q_e]$ . Also, the relative parameters of Freundlich, Dubinin–Radushkevich, Temkin, Redlich–Peterson and Koble–Corrigan isotherms were obtained from the plots between  $[\ln(q_e) \text{ vs. } \ln(C_e)]$ ,  $[\ln(q_e) \text{ vs. } \varepsilon^2]$ ,  $[q_e \text{ vs. } \ln(C_e)]$ ,  $[\ln((AC_e/q_e) - 1) \text{ vs. } \ln(C_e)]$  and  $[(1/C_e^p) \text{ vs. } (1/q_e)]$ , respectively. The linear regression method of least squares is used for drawing the trend lines. In the case of Redlich–Peterson and Koble–Corrigan isotherms, the constants  $A_{RP}$  and  $P$  were obtained by maximizing the  $R^2$  value using a

trial and error method which was optimized by 20 iterations using the solver add-in function, in Microsoft Excel. Linear expression of these isotherm equations and the way to obtain the isotherm parameters are given in Table 1.

The Langmuir adsorption model describes monolayer adsorption of adsorbate onto a homogeneous adsorbent surface [25–28]. Moreover, there is negligible interaction between the adsorbed molecules and adsorption sites having uniform energies [29]. The empirical Freundlich model is based upon the assumption of multilayer formation of adsorbate on the heterogeneous solid surface of the adsorbent and assumes that the stronger binding sites are occupied first and that the binding strength decreases with the increasing degree of site occupation [30,31]. Values  $K_F$  and  $1/n$  are Freundlich constants related to adsorption capacity and intensity of adsorption, respectively. The lower fractional value of  $1/n$  [ $0 < (1/n) < 1$ ] indicates that weak adsorptive forces are effective on the surface of activated carbon [32]. The Temkin model considered the effects of some indirect adsorbate/adsorbate interactions on adsorption isotherms [21,24]. As a result of adsorbate/adsorbate interactions, the heat of adsorption of all the molecules in the layer would decrease linearly with coverage [24]. The Dubinin–Radushkevich equation assumes that the amount adsorbed corresponding to any adsorbate concentration is a Gaussian function of the Polanyi potential [33]. The three-parameter Redlich–Peterson equation consists of both features of Langmuir and Freundlich isotherm models [34]. Koble–Corrigan model is also three-parameter equation which has an exponential dependence on concentration in the numerator and denominator. This model is a combination of the Langmuir and Freundlich isotherm type models and is usually used with heterogeneous adsorption surfaces [35].

The values of the parameters and the correlation coefficients, Marquardt's percent standard deviation (MPSD) and the hybrid error function (HYBRID) obtained are listed in Table 2.

The applicability of the isotherm equation to describe the adsorption process was judged by the correlation coefficients,  $R^2$  values. The adsorption isotherm models fitted the data in the order of: Koble–Corrigan > Redlich–Peterson > Freundlich > Langmuir-type(I) > Temkin > Langmuir-type(II) > Dubinin–Radushkevich > Langmuir-type(III&IV) isotherm.

The above order revealed that the equilibrium data are better fitted by the three-parameter models rather than the two-parameter models. The Koble–Corrigan model was found to best represent the equilibrium data, showing that the surface of activated carbon for adsorption of free cyanide may be heterogeneous with a different energy distribution. The Freundlich isotherm model fitted the experimental data better than Langmuir isotherm model, also suggested that the surface of activated carbon for adsorption of cyanide is heterogeneous. Furthermore, multilayer adsorption of cyanide has been proposed by Freundlich isotherm model. Value of  $n > 1$  represents a favorable adsorption condition. Between different linear types of Langmuir model, type(I) best represent the equilibrium data.

In Fig. 1 the prediction of the amount of adsorption at equilibrium by various equilibrium isotherm models was plotted against the experimental values. As shown in Fig. 1, the difference between experimental data and calculated values by Koble–Corrigan isotherm is very low and it is showing that, this isotherm model is the best isotherm for predicting of the amount of cyanide adsorbed by activated carbon at equilibrium. MPSD and HYBRID values (Table 2), also suggesting that Koble–Corrigan isotherm provides a better model of the sorption system.

#### 3.2. Kinetic study

In Fig. 2, the symbols and the lines show the experimental and calculated values of the adsorbed amount of cyanide

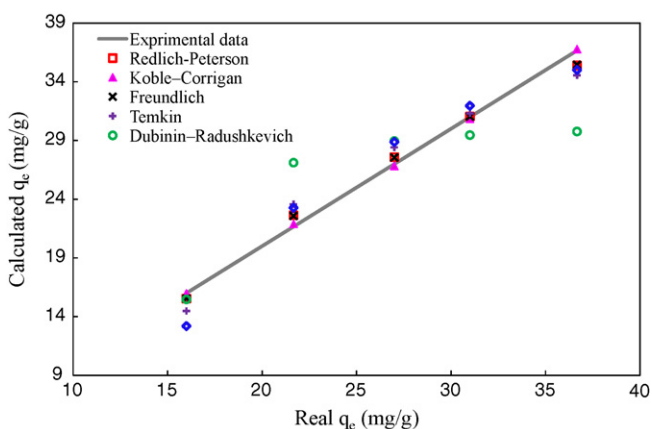
**Table 1**  
Isotherms and their linearized expressions.

Isotherms	Equations	Linear expression	Plot	Parameters	Ref.
Freundlich <sup>b</sup>	$q_e = K_F(C_e)^{1/n}$	$\ln q_e = \ln K_F + n^{-1} \ln C_e$	$\ln q_e$ vs. $\ln C_e$	$K_F = \exp(\text{intercept})$ , $n = (\text{slope})^{-1}$	[21,31,45]
		Type(I) $C_e/q_e = (1/K_L q_m) + (C_e/q_m)$	$(C_e/q_e)$ vs. $C_e$	$q_m = (\text{slope})^{-1}$ , $K_L = \text{slope}/\text{intercept}$	
Langmuir <sup>b</sup>	$q_e = (q_m K_L C_e)/(1 + K_L C_e)$	Type(II) $1/q_e = (1/K_L q_m C_e) + (1/q_m)$	$1/q_e$ vs. $1/C_e$	$q_m = (\text{intercept})^{-1}$ , $K_L = \text{intercept}/\text{slope}$	[28]
		Type(III) $q_e = q_m - (1/K_L)q_e/C_e$	$q_e$ vs. $q_e/C_e$	$q_m = \text{intercept}$ , $K_L = -(\text{slope})^{-1}$	
		Type(IV) $q_e/C_e = K_L q_m - K_L q_e$	$q_e/C_e$ vs. $q_e$	$q_m = -(\text{intercept}/\text{slope})$ , $K_L = -\text{slope}$	
Temkin <sup>b</sup>	$q_e = q_m \ln(K_T C_e)$	$q_e = q_m \ln K_T + q_m \ln C_e$	$q_e$ vs. $\ln C_e$	$q_m = \text{slope}$ , $K_T = \exp(\text{intercept}/\text{slope})$	[31,35,46]
Dubinin–Radushkevich <sup>b</sup>	$q_e = q_m \exp(-D\varepsilon^2)$ that $\varepsilon = RT \ln(1 + C_e^{-1})$	$\ln q_e = \ln q_m - D\varepsilon^2$	$\ln q_e$ vs. $\varepsilon^2$	$q_m = \exp(\text{intercept})$ , $D = -\text{slope}$	[24,31,47]
Redlich–Peterson <sup>c</sup>	$q_e = (A_{RP} C_e)/(1 + B_{RP} C_e^g)$	$\ln[(A_{RP} C_e/q_e) - 1] = g \ln C_e + \ln B_{RP}$	$\ln[(A_{RP} C_e/q_e) - 1]$ vs. $\ln C_e$	$g = \text{slope}$ , $B_{RP} = \exp(\text{intercept})$ , $A_{RP}^a$	[21,34,48]
Koble–Corrigan <sup>c</sup>	$q_e = (A_{KC} C_e^p)/(1 + B_{KC} C_e^p)$	$1/q_e = (1/A_{KC} C_e^p) + (B_{KC}/A_{KC})$	$1/q_e$ vs. $1/C_e^p$	$A_{KC} = (\text{slope})^{-1}$ , $B_{KC} = \text{intercept}/\text{slope}$ $p^a$	[35]

<sup>a</sup> Optimized using a trial and error method.<sup>b</sup> Two-parameter isotherm.<sup>c</sup> Three-parameter isotherm.**Table 2**  
Isotherms parameters by linear regression method for the sorption of cyanide by activated carbon.

Isotherms	R <sup>2</sup>	MPSD	HYBRID	Parameters
Freundlich	0.9902	3.6961	3.4303	$K_F = 3.1393 \text{ mg g}^{-1} (\text{L mg}^{-1})^{1/n}$ ; $n = 2.4938$
Langmuir				
Type(I)	0.9652	12.1201	28.1772	$q_m = 47.62 \text{ mg g}^{-1}$ ; $K_L = 0.007179 \text{ L mg}^{-1}$
Type(II)	0.9410	10.541	32.531	$q_m = 37.9 \text{ mg g}^{-1}$ ; $K_L = 0.00129 \text{ L mg}^{-1}$
Type(III)	0.5902	22.432	129.011	$q_m = 31.102 \text{ mg g}^{-1}$ ; $K_L = 0.01894 \text{ L mg}^{-1}$
Type(IV)	0.5902	87.725	2641.24	$q_m = 34.3 \text{ mg g}^{-1}$ ; $K_L = 0.00112 \text{ L mg}^{-1}$
Temkin	0.9515	8.7449	17.0321	$q_m = 9.766 \text{ mg g}^{-1}$ ; $K_T = 0.0815 \text{ L mg}^{-1}$
Dubinin–Radushkevich	0.7547	18.9112	96.6844	$q_m = 30.08 \text{ mg g}^{-1}$ ; $D = 0.00032 \text{ mol}^2 \text{ kJ}^{-2}$
Redlich–Peterson	0.9946	4.7277	4.2905	$g = 0.626$ ; $B_{RP} = 1.06 (\text{L mg}^{-1})^g$ ; $A_{RP} = 4 \text{ mg g}^{-1} (\text{L mg}^{-1})$
Koble–Corrigan	0.9996	0.9613	0.1522	$A_{KC} = 3.52 \text{ mg g}^{-1} (\text{L mg}^{-1})^p$ ; $B_{KC} = -0.45 (\text{L mg}^{-1})^p$ ; $p = 0.1$

as a function of time at different initial cyanide concentrations, respectively. It can be observed from Fig. 2 (symbols) that the sorption capacity increases with time and at a certain time reaches to a constant value where no more cyanide is removed from the solution. For all initial cyanide concentrations, the most of cyanide is removed within the first 24 h. It should be noticed



**Fig. 1.** The calculated amount of adsorbed cyanide at equilibrium by different isotherm models ( $q_e$ ) vs. experimental  $q_e$  (conditions: sorbent dosage = 1.5 g (500 mL)<sup>-1</sup>; stirring speed = 100 rpm;  $T = 25 \pm 2^\circ \text{C}$ ; pH 10).

that an increase in initial cyanide concentration leads to an increase in the sorption capacity of cyanide by activated carbon. Fig. 3 also shows that an increase in the initial cyanide concentration increases the equilibrium time. This is due to the fact that, at low cyanide concentration, more readily available sorption sites adsorb the cyanide ions, but at higher concentrations, cyanide ions have to diffuse to the inner sites of the activated carbon. It is also noticed that an increase in the initial cyanide concentration leads to an increase in the residual cyanide in solution. It is also noticed that although the adsorbed amount of cyanide increases with an increase in the initial cyanide concentration, but the remaining cyanide concentration in solution is also increases.

The adsorption kinetics of cyanide onto activated carbon was examined with Elovich, fractional power, zero order, first order, pseudo-first order, second order and pseudo-second order kinetic models.

The linear regression method of least squares was used to determine the parameters of the kinetic models. Pseudo-second order kinetic model can be linearized into at least four different types as shown in Table 3. The relative parameters were obtained from the plots between  $[q_t \text{ vs. } \ln t]$ ,  $[\ln q_t \text{ vs. } \ln t]$ ,  $[q_t \text{ vs. } t]$ ,  $[\ln(q_e - q_t) \text{ vs. } t]$ ,  $[q_t^{-1} \text{ vs. } t]$ ,  $[t/q_t \text{ vs. } t]$ ,  $[1/q_t \text{ vs. } 1/t]$ ,  $[q_t \text{ vs. } q_t/t]$  and  $q_t/t \text{ vs. } t]$ , respectively. Linear expression of these kinetic equations and the way to obtain the kinetic parameters are explained in Table 3.



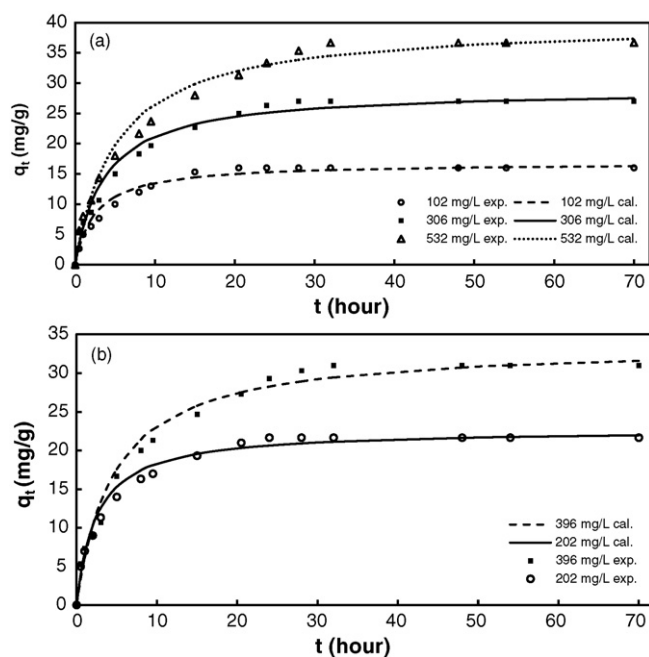
**Table 3**  
Kinetic models and their linearized expressions.

Kinetic models	Equations	Linear expression	Plot	Parameters	Ref.
Elovich	$q_t = \beta \ln(\alpha \beta t)$	$q_t = \beta \ln(\alpha \beta) + \beta \ln t$	$q_t$ vs. $\ln t$	$\beta = \text{slope}$ , $\alpha = (\text{slope})^{-1} \exp(\text{intercept}/\text{slope})$	[21,31]
Fractional power	$q_t = kt^\nu$	$\ln q_t = \ln k + \nu \ln t$	$\ln q_t$ vs. $\ln t$	$k = \exp(\text{intercept})$ , $\nu = \text{slope}$	[31]
Zero order	$q_t = q_e - k_0 t$	$q_t = q_e - k_0 t$	$q_t$ vs. $t$	$q_e = \text{intercept}$ , $k_0 = -(\text{slope})$	[31]
First order	$q_e = q_t \exp(k_1 t)$	$\ln(q_e/q_t) = k_1 t$	$\ln(q_e/q_t)$ vs. $t$	$q_e = \text{intercept}$ , $k_1 = -(\text{slope})$	[31]
Pseudo-first order	$q_t = q_e [1 - \exp(-k_{1p} t)]$	$\ln(q_e - q_t) = \ln q_e - k_{1p} t$	$\ln(q_e - q_t)$ vs. $t$	$q_e = \exp(\text{intercept})$ , $k_{1p} = -(\text{slope})$	[42,43]
Second order	$q_t = q_e / (1 + q_e k_2 t)$	$q_t^{-1} = q_e^{-1} + k_2 t$	$q_t^{-1}$ vs. $t$	$q_e = (\text{intercept})^{-1}$ , $k_2 = \text{slope}$	[31]
Pseudo-second order	$q_t = k_{2p} q_e^2 t / (1 + q_e k_{2p} t)$	Type(I) $t/q_t = 1/k_{2p} q_e^2 + t/q_e$	$t/q_t$ vs. $t$	$q_e = \text{slope}^{-1}$ , $k_{2p} = (\text{slope}^2)/\text{intercept}$	[44]
		Type(II) $1/q_t = (1/k_{2p} q_e^2)(1/t) + (1/q_e)$	$1/q_t$ vs. $1/t$	$q_e = \text{intercept}^{-1}$ , $k_{2p} = (\text{intercept}^2)/\text{slope}$	
		Type(III) $q_t = q_e - (1/k_{2p} q_e) q_t / t$	$q_t$ vs. $q_t/t$	$q_e = \text{intercept}$ , $k_{2p} = -1/(\text{slope} \times \text{intercept})$	
		Type(IV) $q_t/t = k_{2p} q_e^2 - k_{2p} q_e q_t$	$q_t/t$ vs. $q_t$	$q_e = -\text{intercept}/\text{slope}$ , $k_{2p} = (\text{slope}^2)/\text{intercept}$	
Intraparticle diffusion	$q_t = k_p t^{0.5}$	$q_t = k_p t^{0.5}$	$q_t$ vs. $t^{0.5}$	$k_p = \text{slope}$	[22,36]

**Table 4**  
Kinetic models parameters by linear regression method for the sorption of cyanide by activated carbon at 102 mg/L initial cyanide concentration.

Kinetic models	$R^2$	NSD	ARE	Parameters	
Elovich	0.941	9.54	8.01	$\beta = 3.05 \text{ g mg}^{-1}$ ; $\alpha = 1.79 \text{ mg g}^{-1} \text{ h}^{-1}$	
Fractional power	0.893	19.55	14.42	$k = 4.95 \text{ mg g}^{-1} \text{ h}^{-\nu}$ ; $\nu = 0.343$	
Zero order	0.519	58.60	34.38	$q_e = 7.797 \text{ mg g}^{-1}$ ; $k_0 = -0.184 \text{ mg g}^{-1} \text{ h}^{-1}$	
First order	0.418	59.82	37.96	$q_e = 2.046 \text{ mg g}^{-1}$ ; $k_1 = -0.016 \text{ h}^{-1}$	
Pseudo-first order	0.978	43.83	31.46	$q_e = 15.26 \text{ mg g}^{-1}$ ; $k_{1p} = 0.193 \text{ h}^{-1}$	
Second order	0.278	207.1	88.01	$q_e = 6.58 \text{ mg g}^{-1}$ ; $k_2 = -0.002 \text{ g mg}^{-1} \text{ h}^{-1}$	
Pseudo-second order		Type(I)	8.67	6.17	$q_e = 16.95 \text{ mg g}^{-1}$ ; $k_{2p} = 0.0234 \text{ g mg}^{-1} \text{ h}^{-1}$
		Type(II)	7.79	6.15	$q_e = 16.39 \text{ mg g}^{-1}$ ; $k_{2p} = 0.0239 \text{ g mg}^{-1} \text{ h}^{-1}$
		Type(III)	16.74	11.19	$q_e = 16.95 \text{ mg g}^{-1}$ ; $k_{2p} = 0.0213 \text{ g mg}^{-1} \text{ h}^{-1}$
		Type(IV)	35.71	28.69	$q_e = 17.28 \text{ mg g}^{-1}$ ; $k_{2p} = 0.0196 \text{ g mg}^{-1} \text{ h}^{-1}$
Intraparticle diffusion	0.750	44.36	25.22	$k_p = 1.702 \text{ mg g}^{-1} \text{ h}^{-0.5}$	

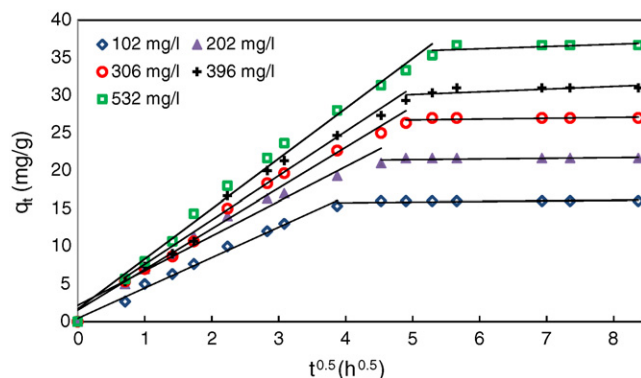
Table 4 presents the values of correlation coefficients ( $R^2$ ), NSD, ARE and constants of different kinetic models for sorption of cyanide onto activated carbon at 102 mg/L initial cyanide concentration.



**Fig. 2.** The adsorbed amount of cyanide as a function of time at different initial cyanide concentrations. (a) 102, 306 and 532 mg/L; (b) 202 and 396 mg/L. Symbols are experimental values (exp.) and lines are the calculated values (cal.) by type(I) of pseudo-second order kinetic model (conditions: sorbent dosage = 1.5 g (500 mL)<sup>-1</sup>; stirring speed = 100 rpm;  $T = 25 \pm 2^\circ\text{C}$ ; pH 10).

Low correlation coefficients (<0.939), high NSD (>16.74%) and ARE (>11.19%) confirm that fractional power, zero order, first order, pseudo-first order, second order, intraparticle diffusion and type(III&IV) of linearized form of pseudo-second order kinetic models do not give a good regression (figures are not shown).

The correlation coefficient, NSD and ARE for the type(I) of linearized form of pseudo-second order equation were 0.998, 8.67% and 6.17%, respectively. Furthermore, the calculated  $q_e$  value through this model is close to the experimental value. This strongly suggests that the sorption of cyanide onto activated carbon is most appropriately represented by a pseudo-second order kinetic model. This model supposes that two reactions either in series or in parallel are occurring, the first one is fast and reaches equilibrium quickly and the second is a slower reaction that can continue for a long period of time [31].



**Fig. 3.** Weber–Morris plots for cyanide adsorption onto activated carbon at different initial concentration (conditions: sorbent dosage = 1.5 g (500 mL)<sup>-1</sup>; stirring speed = 100 rpm;  $T = 25 \pm 2^\circ\text{C}$ ; pH 10).

The correlation coefficient for type(II) of linearized form of pseudo-second order equation is lower than type(I) but calculated values of NSD and ARE are lower than type(I) and furthermore calculated  $q_e$  value is closer to the experimental value (16.39 vs. 16). This indicates that type(II) of linearized form of pseudo-second order equation is more accurate in prediction of  $q_e$  value compared with type(I).

Fig. 2 (lines) shows the calculated values of adsorbed amount of cyanide versus time for the type(I) of linearized form of pseudo-second order kinetic model. These curves indicate that the pseudo-second order kinetic model is consistent with the data at different initial cyanide concentrations.

Since the pseudo-second order model cannot identify the diffusion mechanism, intraparticle diffusion model based on the theory proposed by Weber and Morris was employed to identify the diffusion mechanism. It is assumed that the rate is not limited by mass transfer from the bulk solution to the external surface of adsorbent due to the particles are vigorously agitated during the sorption period [36–39].

Weber and Morris reported that if intraparticle diffusion was dominated in the adsorption process, then a plot of  $t^{0.5}$  versus the adsorption amount would be linear [39–41]. Fig. 3 represents the plot of  $q_t$  versus  $t^{0.5}$  for the initial cyanide concentrations of 102, 202, 306, 396 and 532 mg/L. All plots seem to be nonlinear for the whole sorption period, suggesting that the intraparticle diffusion is not the rate-limiting step for the whole reaction. The data can be better represented by two linear steps with different slopes ( $k_p$ ). Value of  $k_p$  is rate constant for the intraparticle diffusion ( $\text{mg g}^{-1} \text{h}^{-0.5}$ ). It was found that the rate constant increased with initial cyanide concentration. The first steep linear step is due to fast adsorption of cyanide onto activated carbon. Cyanide adsorption slows down in the second stage due to the diffusion of cyanide ions into the inner adsorption sites of the activated carbon.

#### 4. Conclusion

The main conclusions drawn from these studies may be summarized as follows.

- (i) Three-parameter isotherm models fitted the adsorption equilibrium data better than the two-parameter isotherm models and among all of isotherms the adsorption equilibrium data of cyanide were best represented by Koble–Corrigan isotherm model, showing that the surface of activated carbon for adsorption of free cyanide may be heterogeneous with a different energy distribution.
- (ii) The Freundlich isotherm model fitted the equilibrium data better than Langmuir isotherm model, revealing that the adsorption of cyanide onto the activated carbon was multi-layer adsorption. Also, between four different linear types of Langmuir model, type(I) shows better fitting with experimental data.
- (iii) The kinetic data closely follow the pseudo-second order kinetic model.
- (iv) Weber–Morris plots show that the adsorption process of free cyanide is a two step process. In the first step, the adsorption of cyanide is fast while in the second step, cyanide adsorption slows down. Also these plots indicate that the intraparticle diffusion is not the rate-limiting step for the whole reaction.

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