Cyanide removal simulation from wastewater in the presence of titanium dioxide nanoparticles

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Abstract. One of the methods of removing cyanide from wastewater is surface adsorption. We simulated the removal of cyanide from a synthetic wastewater in the presence of Titanium dioxide nano-particles absorbent uses VISUAL MINTEQ 3.1 software. Our aim was to determine the factors affecting the adsorption of cyanide from synthetic wastewater applying simulation. Synthetic wastewater with a concentration of 100 mg/l of potassium cyanide was used for simulation. The amount of titanium dioxide was 1 g/l under the temperature of 25°C. The simulation was performed using an adsorption model of Freundlich and constant capacitance model. The results of simulation indicated that three factors including pH, nanoparticles of titanium dioxide and the primary concentration of cyanide affect the adsorption level of cyanide. The simulation and experimental results had a good agreement. Also by increasing the pH level of adsorption increases 11 units and then almost did not change. An increase in cyanide concentration, the adsorption level was decreased. In simulation process, rising the concentrations of titanium dioxide nanoparticles to 1 g/l, the rate of adsorption was increased and afterward no any change was observed. In all cases, the coefficient of determination between the experimental data and simulation data was above 0.9.

Keywords: cyanide; titanium dioxide nanoparticles adsorption; simulation

1. Introduction

Cyanide is toxic and dangerous which results from carbon-nitrogen triple bond (Dash and Gour 2009). Cyanide is found in various industrial wastewaters such as metal smelting, electroplating, supplying coke and coal, petroleum refining, production of explosives and mining (Khodadadi *et al*. 2009). Besides, cyanide has many applications in the extraction of metallic minerals such as zinc, lead, gold (EPA 2002). It is absorbed rapidly and extensively through oral, inhalation and dermal adsorption and in Short-term exposure leads to increased respiratory rate, increased heart rate and other effects on the nervous system and prolonged exposure causes weight loss, enlargement of the thyroid, nervous system damage and eventually leading to death (Dai *et al*. 2012). The Environmental Protection Agency of America (EPA) and Iran National Standard determined the maximum allowable concentration of cyanide as 1.5 mg/l and 1.13 mg/l for

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drinking and mineral water respectively (Standard 1053 2009, EPA 2002). The World Health Organization (WHO) determined the maximum allowable concentration of cyanide in water at 1.13 mg/l (Dai *et al*. 2012). Due to the toxicity and hazards of cyanide, its control and removal is very important (Majidi 2011). The experimental with cyanide solution is very dangerous due to the high toxicity of this chemical and high volatilization of cyanide at temperature above 40 ℃ and pH below 7 which generate cyanidric acid (Khodadadi *et al*. 2009). Therefore, the simulation aspects of cyanide removal of different environmental condition such as pH, Eh and temperature are very important. Chiang *et al*. (2003) established methods for the treatment of cyanide in wastewater include physical method, such as dilution, filtration, adsorption using activated carbon, chemical methods like alkaline chlorination and oxidation, using hydrogen peroxide and ozone, physicochemical methods, such as ion exchange and electrolysis, and biological method, such as degradation and photocathalyst degradation (Farrokhi *et al*. 2013). One of the removal methods is the surface adsorption. Surface adsorption refers to a process in which a layer at the interface of the two phases enriches by one or more components. Adsorption reactions are very important in many heterogeneous systems and water treatment. So that the ions can be omitted in the aquatic environment using adsorption and desorption reactions performed on the interface of solid and liquid phases. Factors affecting adsorption include the type and physical properties of the adsorbent and the adsorption, mixing of the liquid phase, pH and temperature (Djeribi and Hamdani 2008).

Barakat (2005) investigated the adsorption of copper and cyanide in aqueous solution of titanium dioxide nanoparticles. Dash *et al*. (2009) studied the adsorption of cyanide from wastewater by granular activated carbon. Mousavi and Khosravi (2010) used the activated carbon prepared from pistachio powder to absorb the cyanide from wastewater. Gupta *et al*. (2012) studied the effect of pH, initial concentration of cyanide and adsorbent concentration on cyanide adsorption by as under laboratory conditions. Samiei *et al*. (2012) studied the cyanide adsorption of talc mineral from the gold processing plant dam's wastewater.

The first objective of this study was to simulate the removal of cyanide in the presence of titanium dioxide nano-particles from a synthetic industrial wastewater using the VISUAL MINTEQ 3.1 software. The second aim was to determine factors affecting the adsorption rate using Freundlich adsorption and constant capacitance models.

2. Materials and methods

2.1 Theoretical aspects of the model

The mechanism of adsorption and photocatalytic oxidation of cyanide using TiO_2 has been well documented in the literature The oxidation of cyanide is possible via the reaction of CN^- with surface hydroxyls or holes. According to Domenech and Peral (1998) the initial step of cyanide photocatalytic oxidation is the formation of cyanide radical, which subsequently dimerize to form cyanogen molecule undergoes dismutation under alkali conditions to give cyanide and cyanate. The cyanate produced is further oxidized to give NO_3^- and CO_2. The corresponding reactions are presented as follows

$$CN^{-h^+/OH^\cdot} \rightarrow CN^\cdot \qquad (1)$$

$$2CN^\cdot \rightarrow (CN)_2 \qquad (2)$$

$$(CN)_2 + 2OH^- \rightarrow CN^- + CNO^- + H_2O \tag{3}$$

$$CNO^- + 8OH^- + 8h^+ \rightarrow NO_3^- + CO_2 + 4H_2O \tag{4}$$
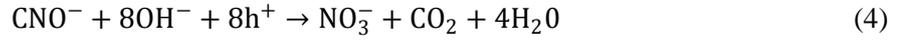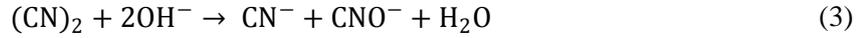
Because of the high possibility of interactions between the ions and inorganic and organic solids in natural systems, the models are used as a tool to quantify and predict the behavior of ions in solution and their interactions with other particles. For this reason, in recent decades, several models have been proposed for the analysis of chemical reactions. Various models are available to explain the ion adsorption data among which Freundlich adsorption models were described (Davoudi 2010).

Freundlich equation has no theoretical foundation and it developed based on complying with experimental data. In the Freundlich equation, the areas of the adsorbent surface are not uniform and they contain different adsorption capacity. Eq. (5) defines the Freundlich equation (Aber *et al*. 2008)

$$\frac{x}{m} = K_f \cdot C_e^{\frac{1}{n}} \tag{5}$$

Where $\frac{x}{m}$ = Amount of adsorbed per unit of adsorbent mass (mg/g)
C_e = Equilibrium concentration of adsorbent in solution (mg/l)
K and n = constants for a given adsorbent and adsorbent at a particular temperature.

In Constant Capacitance Model, a layer with constant capacity is assumed to separate the solution for charged surface sites. Therefore, to interrelate the charge and potential of C_1 parameter is needed. C_1 parameter relates the surface charge $\sigma_d = \sigma_0 = \sigma_s$ to electrostatic potential $\Psi_0 = \Psi_d$ linearly.

$$-\sigma_d = \sigma_d \approx C_1 \times \Psi_0 \tag{6}$$

Since in high ionic power the dual electric layer may act as a capacitor, this model is commonly used for high and constant ionic strengths (above 0.1 molar electrolyte concentrations). If we do not consider the C_1 parameter as an exclusive parameter, this model can be used in systems with varying ionic strengths (Hohl and Stumm 1978)

The assumptions are as follows (Hayes and Leckie 1987):

- The surface sites are amphoteric
- Surface complexes are Monodandit and within the sphere
- One electrostatic exist which is assumed as the surface plate to adsorb H and OH as well as other ions such as K^+, Na^+, CL^- and NO_3^- which follow the surface.
- The model is the 0 charge of the surface species and the constant ionic species in solution.

Because the ionic species are assumed to be constant; activity coefficient of ions in the solution phase can be applied to an equilibrium constant of surface reaction. The above assumptions lead to the expression of activity coefficient of surface species indicated in Eq. (7)

$$\Upsilon_{cc} = \gamma_{cc}^0 \times \exp\left(\frac{z_{cc} \times F \times \Psi_0}{R \times T}\right) \tag{7}$$

Where Υ_{cc} and γ_{cc}^0 = Activity coefficient in the base case model and the desired ionic strength

respectively

z_{cc} = Surface complex capacity
F = Faraday constant (J/volt equiv)
R = the gas constant (J/K.mol)
T = Absolute temperature (K)

Table 1 Cyanide removal percentage in different pH (Ijadpanah-Saravy *et al* . 2014)

Cyanide adsorption	pH
58	5
76	7
91	9
100	12

Table 2 Cyanide removal percentage in different Concentration of Titanium Dioxide Nanoparticles (Ijadpanah-Saravy *et al* . 2014)

Percentage of cyanide adsorption	Concentration of Titanium Dioxide Nanoparticles (g/l)
73	0.5
100	1
91	1.5

The reason for selecting this software is containing various adsorption models, an organic material, a powerful database and acceptable agreement with experimental data. In this simulation, we used the experimental data which were conducted by Ijadpanah-Saravy *et al* . (2014). Tables 1 and 2, indicate his experiment's data. Creating chemical equilibrium (reversible reaction), failure in time mentioning (there are no synthetic reactions) 0-99°C temperature restriction and limited Ionic strength are among the limitation of this software.

In the simulation, we applied the synthetic wastewater with a concentration of 100 mg/l of potassium cyanide, and potassium cyanide containing 60 mg potassium and 40 mg cyanide. The amount of titanium dioxide was 1 g/l under the temperature of 25°C. Titanium dioxide nanoparticles used for modeling include 20% rutile phase with a surface area of 31.37 square meters per gram and the density of 3.89 g/cm^2 and Anatase with a surface area 49.76 m^2/g and the density of 4.259 g/cm^2. All the mentioned specification are according to experiments which was conducted by Ijadpanah-Saravy *et al* . (2014).

3. Results

Based on the purposes of this study, we simulated the adsorption of cyanide at different pH. The results indicated that by increasing the amount of cyanide from 3 to 11 adsorption increases and then declines slightly with increasing pH to 13. The increase of adsorption efficiency by increasing pH may be attributed to the surface increase and expansion of the number of sites available for interaction with cyanide ions. Fig. 1 indicated the effect of pH on the adsorption of cyanide in the presence of titanium dioxide nanoparticles formed on the adsorption model of
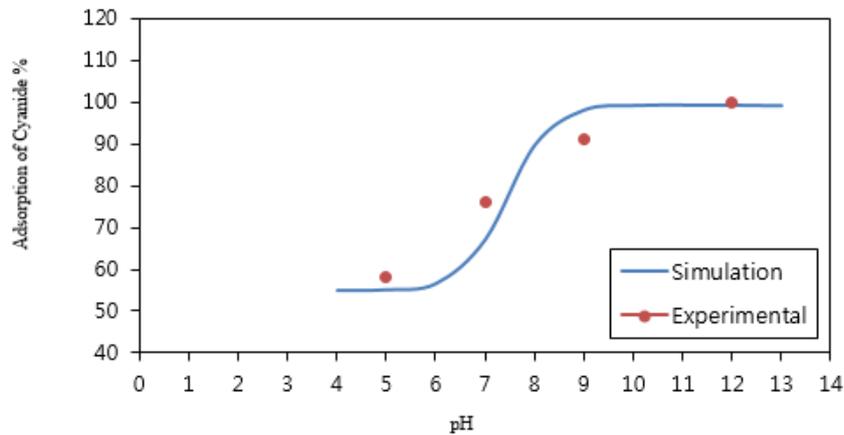
Fig. 1 The effect of pH on the adsorption of cyanide in the presence of titanium dioxide nanoparticles
on Freundlich adsorption model and the Constant Capacitance Model 2-pK CCM

Freundlich and formation of 2-pK CCM adsorption complex. The coefficient of determination (R^2)
between the experimental data and model is 0.96 which confirms the stimulation. Barakat (2005)
presented that with increasing pH to 3 the adsorption by titanium dioxide increases and then
decreases with increasing pH. Dash *et al*. (2009) indicated that by increasing the pH to 9 granular
activated carbon adsorption of cyanide increases and then the adsorption rate decreases. Mousavi
and Khosravi (2010) used the activated carbon prepared from pistachio powder to absorb the
cyanide from wastewater. The results described that with increasing pH from 2 to 10 adsorption of
cyanide increases and then the adsorption rate decreases as pH increases. Gupta *et al*. (2012)
indicated that with increasing pH from 2 to10 adsorption of cyanide increases and then the
adsorption rate decreases as pH increases. Our simulation results were similar to the mentioned
experimental results. The reason which a little description and discussion related to the
experimental results presented was our main objective was simulation and experimental data
belongs to Ijadpanah-Saravy *et al* . (2014).
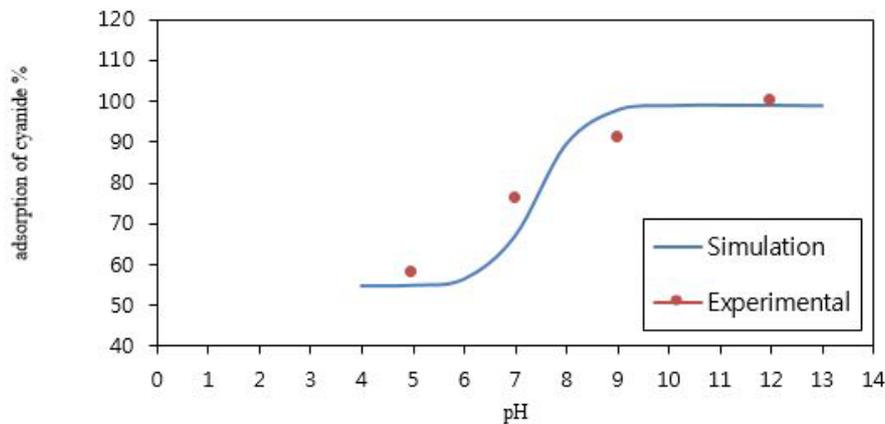
Fig. 2 The effect of concentration of titanium dioxide nanoparticles on the adsorption of cyanide on
Freundlich adsorption model and the Constant Capacitance Model 2-pK CCM

To simulate the effect of titanium dioxide nanoparticles, the amount of the nanoparticles was changed in the range of 0.5 to 1.0 g/l. It is due to the increased number of sites available for adsorption. Model results described that with increasing nanoparticle concentration from 0.5 to 1 g/l adsorption increased and after that by increasing the concentration in 1.5 g/l the adsorption remained unchanged. Fig. 2 presents the adsorption of cyanide at different concentrations of titanium dioxide nanoparticles and Freundlich adsorption model and the Constant Capacitance Model 2-pK CCM. The coefficient of determination (R^2) between the experimental data and model prediction is 0.96 which confirms the stimulation. Mousavi and Khosravi (2010) showed that with increasing absorbent concentration from 0.5 to 1 g/l adsorption increases and after that by increasing the concentration into 2.5 g/l the adsorption remained unchanged. Gupta *et al*. (2012) indicated that with increasing absorbent concentration of 3 g/, adsorption increased and after that by increasing the concentration the adsorption changes a little and then becomes constant.

After that, the initial concentration of cyanide was increased from 50 to 500 g/l. Results indicated that with increasing the cyanide concentration adsorption decreases. The decrease of cyanide adsorption as a function of its concentration may be justified by the restriction of the sites in hand in CN adsorption with the increase of cyanide in solution for a constant mass of adsorbent. The data of Ijadpanah-Saravy *et al* . (2014) experiments indicated that with the decline of the initial concentration of cyanide its removal process increased. So that with 300 milligrams per liter and higher concentrations the complete removal did not complete within 180 min, but in 200, 100 and 20 mg/l the complete removal happened in 150, 120 and 60 minutes respectively. Considering the simulation software does not consider the past time of the process and considers the problem in chemical equilibrium the experimental results are not mentioned in Fig. 3. This is due to the difference between the laboratory and simulation situation. Dash *et al*. (2009) indicated that with increasing the initial concentration of cyanide from 50 to 400 mg/l the cyanide adsorption decreases. Mousavi and Khosravi (2010) described that by increasing the initial concentration of cyanide the cyanide removal efficiency decreased. Fig. 3 represents the adsorption of cyanide in various initial concentrations on Freundlich adsorption model and the Constant Capacitance Model 2-pK CCM.
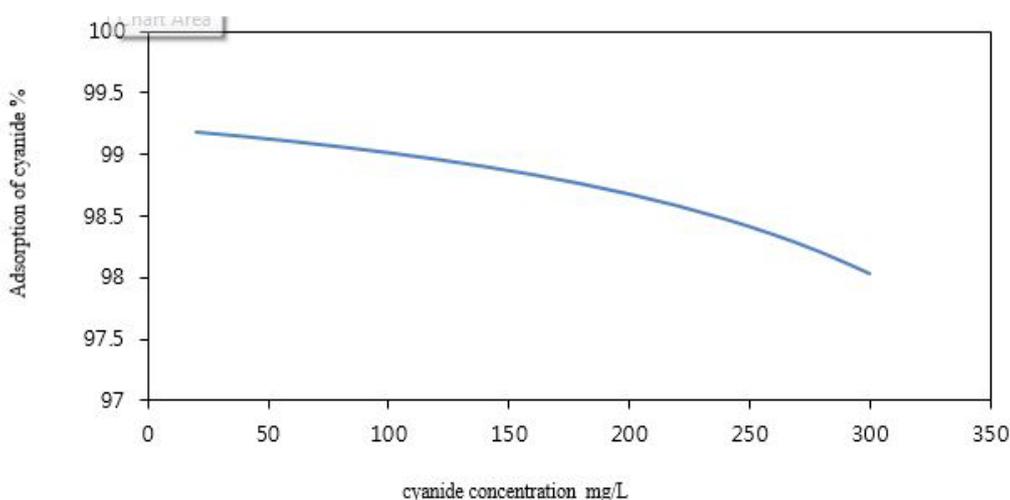
Fig. 3 Adsorption of cyanide in various initial concentrations in Freundlich adsorption model and the Constant Capacitance Model 2-pK CCM

4. Conclusions

The results of simulation of cyanide adsorption in the presence of titanium dioxide nano-particles of the synthetic wastewater using the VISUAL MINTEQ 3.1 software are as follows:

- The simulation results using VISUAL MINTEQ 3.1 software using the Freundlich adsorption and the Constant Capacitance Model 2-pK CCM were consistent with laboratory works.
- In analyzing the effect of nanoparticles of titanium dioxide concentration and pH value, the coefficient of determination between experimental data and simulation was above 0.9 which indicates the acceptability of simulation.
- With the increase of pH up to 11 the cyanide removal efficiency increased and then became constant which is in line with laboratory experiments.
- The highest adsorption happened at pH values of 11.
- By increasing the titanium dioxide nanoparticles concentration up to 1 g/l the adsorption capacity increased and then became constant which is in line with laboratory experiments.
- With the increase of the initial cyanide concentration the adsorption decreases.
- Based on the experimental results and simulation of cyanide removal it can be stated that titanium dioxide nanoparticles have a high performance in cyanide adsorption.
- Using VISUAL MINTEQ 3.1 software in simulation of cyanide adsorption in the presence of titanium dioxide nanoparticles from wastewater has convincing results.

Acknowledgments

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