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Study of the adsorption of reactive blue 50 on zero valent iron

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In this study, removal efficiency of the Reactive blue 50 and adsorption mechanism on the zero valent iron were investigated. Reactive blue 50 which is used to wool and cashmere dyeing were selected due its non-biodegradable and metabolic stability. Zero valent iron particle has been synthesized by chemical method. A systematic characterization of zero valent iron was performed using X-ray diffractometer, scanning electron microscope and infrared spectrometer analysis. The optimal condition of adsorption was determined as initial reactive dye 50 concentration of 150 $mg \cdot L^{-1}$, zero valent iron mass of 0.2 g and solution pH of 6.0 at room temperature. At optimal condition, organic dye removal in a real wastewater sample from *Tsombon Knit* LLC was 99.5%.

Keywords: adsorption, reactive dye, zero valent iron

INTRODUCTION

Azo dyes comprise of almost half of global production (700000 t/y) and during dyeing operation process about 20% of them end up in wastewater. In Ulaanbaatar, there are 27 cashmere treatment factories that 340 ton water per day for industrial usage. 11 of them are dyeing factories which conduct bleaching and dyeing process. These factories use acid and reactive dyes such as lanaset yellow, lanasol red, lanasol black etc. One of these organic dye is reactive blue 50 that is 1-amino-4-bromo-9,10-dioxo-9,10-dihydroanthracene-2-sulfonic acid (Fig. 1). It consists of sulfo group containing reactive dyes which have been especially developed for wool dyeing. Its' molecule contains two bromoacrylamide reactive groups which form a covalent bond with the nucleophilic groups of the wool's amino acids during the dyeing process, resulting in outstanding wet fastness properties. However these organic dyes are stable, non-biodegradable, cancerogenic substances and negative impact on environment due to their complex aromatic molecular structure.

There are many physical, chemical and biological methods used for the removal of dye from aqueous solution, including chemical coagulation, flocculation, chemical oxidation, photochemical degradation, membrane filtration, reverse osmosis, and aerobic/ anaerobic degradation. All of these techniques suffer from one or more limitation, and none of them is able to completely remove dyes from wastewater. Thus, there is a need to find alternative methods that are effective in removing dyes from large volumes of effluent. Zero valent iron nanoparticle technology is becoming an increasingly popular choice for treatment of hazardous and toxic wastes, and for remediation of contaminated sites.

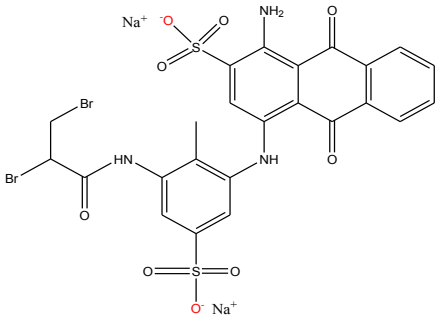

Fig. 1. Chemical structure of reactive blue 50 molecule

For many types of reactive dyes, various adsorbent materials have been investigated as an adsorbent materials. For example, adsorption behavior of reactive dyes (reactive blue 2, reactive red 2, reactive yellow 2) on activated carbon was studied at various experimental conditions. Adsorption of these dyes was fitted with the Langmuir and Freundlich isotherm models and isotherm parameters were calculated [1]. R.Hariharasuthan *et.al*. studied the adsorption of reactive blue 4 onto MgO in Sorel's cement and revealed the experimental data correlated reasonably well with the Langmuir adsorption isotherm due to values of adsorption capacity and separation factor

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[2]. There are some studies on adsorption of reactive blue dyes on various adsorbent materials, almost all of them have studied that experimental data was fitted to the Langmuir isotherm model [3, 4]. Adsorption of different types of organic dye such as basic yellow, vat dye, acid dye and aniline blue dye onto zero valent iron were investigated in the basis of influence of pH, ratio of adsorbent and dye concentration, equilibrium isotherm and kinetics [5-8].

In this study, removal efficiency of reactive blue dye 50 in account of pH, initial concentration, adsorbent mass and the adsorption equilibrium were investigated.

EXPERIMENTAL

Preparation of ZVI: Zero valent iron (ZVI) was synthesized through a chemical reduction method using sodium borohydride as a reducing agent. 2.703 g $FeCl_3 \cdot 6H_2O$ was dissolved in 100 ml distilled water and stirred well. In another beaker 0.6053 g sodium borohydride was dissolved in 100 ml distilled water. The borohydride solution is added drop by drop into iron chloride solution with vigorous hand stirring in excess amount. Ferric iron was reduced and ZVI particles precipitated instantly according to the following reaction:

$$2FeCl_3 + 6NaBH_4 + 18H_2O \rightarrow \downarrow 2Fe^{o}_{(xaT)} + 6B(OH)_3 + 21H_2 + 6NaCl$$

After the first drop of sodium borohydride solution, black solid particles immediately appeared and then the remaining sodium borohydride is added completely to accelerate the reduction reaction.

Then the obtained mixture was conditioned in thermostat to separate the black iron nanoparticles from the liquid phase. The solid particles were washed with 25 ml pure ethanol to remove water. The synthesized nanoparticles were finally dried in oven at 323 K overnight. A scanning electron microscope (SEM) and X-ray diffractometer (XRD) techniques were used to characterize the synthesized ZVI. SEM analysis was done using a Semtrac mini with 30kV and High Vacuum Mode. Particles were poly and randomly distributed [10]. It reveals that ZVI particles were agglomerated due to drying process. Powder XRD analysis was done using XRD Panalytic. XRD of ZVI samples was recorded over a 2θ range of 6-70°. The characteristic broad peak at 2θ of 44.7° indicated that the Fe^{o} and broad peak at 2θ of 35.8° indicated that the FeO and Fe_2O_3 [5, 11].

Adsorption studies: The adsorption experiments were carried out at the desired pH value, contact time, sorbent-zero valent iron mass and initial dye solution concentration level using the necessary sorbent in a 500 ml conical flask containing 250 ml dye solution at room temperature. Zero valent iron mass from 0.1 g to 1 g of dry mass were used while the initial reactive blue 50 concentration varied from 100 $mg \cdot L^{-1}$ to 500 $mg \cdot L^{-1}$ and the pH from 2 to 12. Before analysis, samples of solution were filtered through a filter paper (∅45mm). The solution pH in batch experiments was measured with a pH/conductivity meter (Sanxin 521). The pH was adjusted to the range of 2-12 using 1.0 M NaOH or 1.0 M HCl. Different experimental parameter such as sorbent mass, pH and initial dye concentration were optimized to obtain maximum removal of Reactive blue 50 using ZVI.

The batch sorption experiments were carried out in 300 ml Erlenmeyer flasks where 0.20 g of the adsorbent and 250 mL of the reactive blue 50 solutions (100, 150, 200, 250 $mg \cdot L^{-1}$) were added. The pH of all solutions in contact with adsorbents was found to be 6.0. The Erlenmeyer flasks were subsequently capped and agitated in an isothermal shaker at constant speed and 20°C for 20 minutes to achieve equilibration. The amount of adsorption at equilibrium, qe ($mg \cdot g^{-1}$), was calculated by the following equation:

$$qe = \frac{(C_o - C_e)V}{W} \qquad (1)$$

Where;

C_0 and C_e - dye concentration ($mg \times l^{-1}$) initially and at a given time t recpectively,
V - volume of dye soliution (L);
W - the weight of adsorbent (g).

RESULTS AND DISCUSSION

Optimal condition

Effect of pH on reactive blue 50 sorption: The pH is a very important parameter that affects dye sorption process on zero valent iron [9, 12]. The sorption experiment was carried out for the removal of reactive blue 50 using zero valent iron in the pH range 2.0-12.0. Solution with concentration of 150 $mg \cdot L^{-1}$ of reactive blue 50 and 0.5 g of sorbent mass were used for this study. The results are presented in Figure 2.

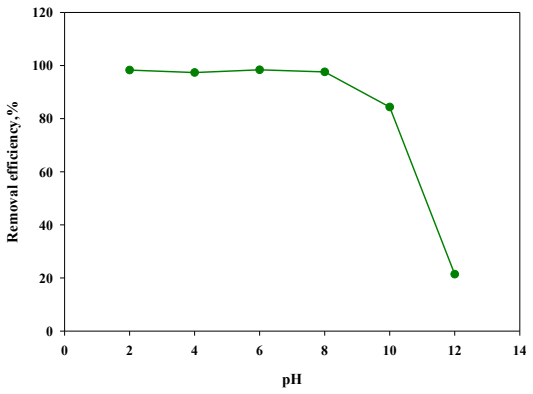

Fig. 2. Effect of pH on the sorption of reactive blue 50 (C_0=150 $mg \cdot L^{-1}$, sorbent mass: 0.5 g)

During the experiments, the removal efficiency was from 98.29% to 21.41% and fas pH increased from 2 to 12. The sorption of reactive blue 50 depends on solution pH, which influences electrostatic binding of ions to corresponding groups. The sorption capacity of reactive blue 50 at low pH is better than that at higher pH. This result attributed to a pH_{ZPC} (zero point charge) of zero valent iron. Li et al. indicated that the pH_{ZPC} of zero valent iron is at around 8.0 [6, 9, 12]. At low pH, the zero valent iron surface has positive charge and reactive blue 50 molecule has negative charge in aquatic dye solution. So the sorption of reactive blue 50 in the iron surface is improved at low pH. The removal efficiency was decreased at higher pH that is related to the formation of corrosion products such as oxide and hydroxide of Fe(II) and Fe (III) [6, 12]. The removal efficiency is higher (98.39%) at pH=6.0, so this result, the optimum pH is 6.0 for sorption of reactive blue 50 in zero valent iron.

Effect of initial concentration on reactive blue 50 sorption: The concentration of dye concentration is a significant factor to be considered for effective sorption process. The effect of reactive blue 50 concentration which was varied from 100 mg·L^{-1} to 500 mg·L^{-1} on the sorption capacity is shown in Figure 3. The sorption capacity decreased as the initial concentration of reactive blue 50 concentration was increased from 100 to 500 mg·L^{-1}.

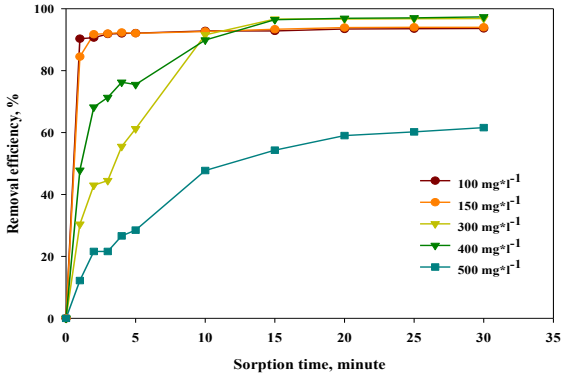

Fig. 3. Relationship between sorption capacity and sorption time (pH=6.0, sorbent mass: 0.2 g, room temperature)

After 5 minute, the sorption capacity was decreased from 92.09% to 93.82% with increasing initial reactive blue 50 of 100 to 500 mg·L^{-1}. However, reactive blue 50 concentration was 100 mg×L^{-1} and 150 mg×L^{-1}, sorption capacity was relatively stabilized. At lower concentrations, reactive blue 50 molecule present in the solution could interact with the binding sites and thus the sorption capacity was higher than those at higher reactive blue 50 concentrations. Lower sorption yield is due to the saturation of sorption sites at higher concentrations [6, 13]. Therefore, 150 mg·L^{-1} for sorption of reactive blue 50 were selected as optimum reactive blue 50 concentration.

Effect of zero valent iron mass on Reactive blue 50 sorption: One of the important factors on sorption process is sorbent mass. The removal efficiency for reactive blue 50 as a function of zero valent iron mass was investigated in the range of 0.1-1.0 g and the results are presented in Figure 4.

During the experimental time, the removal efficiency was increased from 96.6% to 99.6% with increasing

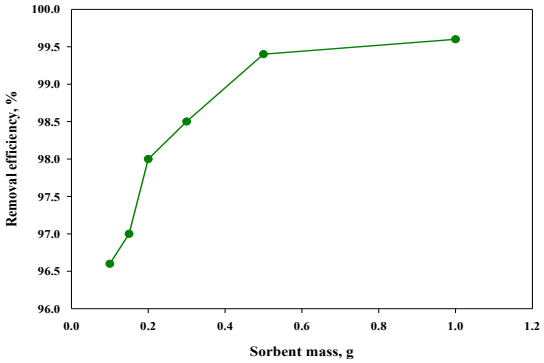

Fig. 4. Effect of sorbent mass on the adsorption of reactive blue 50 onto zero valent iron (C_0=150 mg·L^{-1}, pH=6.0, room temperature)

sorbent mass from 0.1 g to 1.0 g. This result can be explained by the fact that the sorption sites remain unsaturated during the process whereas the number of sites available for sorption sites increases by increasing the sorbent mass [6, 13]. However, the removal efficiency was stabilized with increasing sorbent mass from 0.5 g·L^{-1} to 1.0 g·L^{-1}. It higher sorbent mass, aggregates of sorbent mass can be formed. These may cause interference between binding sites at higher sorbent mass. Therefore, 0.2 g for sorption of reactive blue 50 were selected as optimum zero valent iron mass for further experiments. Therefore, the optimum sorption condition is selected as initial reactive dye 50 concentration of 150 mg·L^{-1}, zero valent iron mass of 0.2 g and solution pH of 6.0 at room temperature. Organic dye of real wastewater sample from "Tsombon Knit" LLC was removed with a percentage 99.5% through sorption by zero valent iron at this condition.

Adsorption isotherms: The experimental data of adsorption equilibrium between the amount of adsorbed dye (q_e) on the ZVI and the concentration of dye in solution (C_e) at optimal condition were used to describe the appropriate isotherm model. The Langmuir and Freundlich isotherm models were used in this paper. The linearity and applicability of the models were evaluated by correlation coefficients.

Freundlich isotherm: Freundlich isotherm model is assuming that the adsorption process takes place on a heterogeneous surface. The Freundlich isotherm is expressed as:

$$q_e = K_F \cdot C_e^{\frac{1}{n}} \quad (2)$$

Where;

q_e - amount of dye adsorbed at equilibrium (mg g^{-1}).

Ce - equilibrium dye concentration in liquid phase (mg·L^1).

K_F - Freundlich constant related to the bond energy and adsorption capacity, n is empirical constant (l·g^{-1}).

1/n indicates the adsorption intensity of the reactive blue dye onto ZVI where 1/n=0 reversible, 1/n<0 unfavorable, 1/n>0 favorable adsoprtion. And also 1/n is a measure of surface heterogeneity then as its value gets closer to zero becomes more heterogeneous [14]. Equation (2) can be arranged to linear form:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (3)$$

To describe the applicability of the Freundlich isotherm model for the reactive blue 50 adsorption on ZVI a linear plot of lnq_e versus lnC_e is plotted and presented in Figure 5 and the calculated parameters are shown in Table 1.

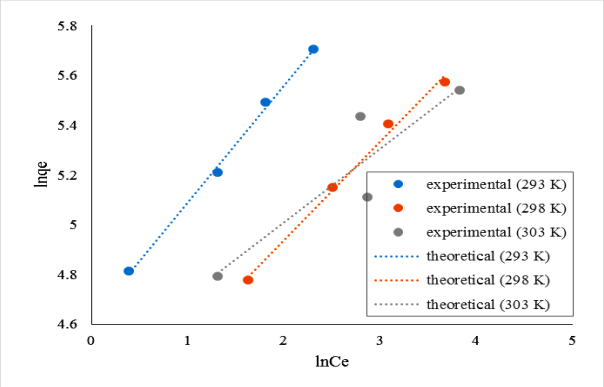

Fig. 5. Linear form of Freundlich isotherm model, experimental condition: pH= 6.0, room temperature 293K

From the experimental results the Freundlich isotherm fits quite well with the experimental data (correlation coefficient R^2> 0.99) at room temperature (20 and 25°C), however at 30°C the Freundlich isotherm fits poor with the experimental data. It is clear that the adsorption of reactive blue 50 onto zero valent iron is favorable because of value of 1/n<0.

Langmuir isotherm: The Langmuir isotherm, one of the first theoretical treatments of non-linear adsorption has been successfully applied to a wide range of data that exhibit limiting or maximum adsorption capacities. The Langmuir isotherm model is used to predict the sorption of aqueous compound onto a solid phase. This model assumes that a monolayer of adsorbed material is adsorbed over a uniform adsorbent surface. The Langmuir isotherm model is assumed that once a dye molecule occupies a site no further adsorption can take place at that site and theoretically a saturation value is reached beyond which no further adsorption can take place.

The distribution of these two phases is controlled by equilibrium constant. The Langmuir isotherm is expressed as:

The parameters q_m (mg·g^{-1}) and K_L (L·mg^{-1}) are the Langmuir constants that relate the maximum

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (4)$$

Where q (mg·g^{-1}) is the adsorbate amount adsorbed on adsorbent at equilibrium and C (mg·L^1) is equilibrium adsorbate concentration in solution.

adsorption capacity and energy of adsorption.

The linear form of the Langmuir isotherm equation (4) is expressed as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (5)$$

From the equation (5) maximum adsorption capacity, q_m and the Langmuir constant can be calculated from the slope ($1/q_m$) and intercept $1/q_m K_L$ for the linear plot C_e/q_e versus C_e. The calculated parameters are presented in Table 1.

The constants evaluated for Langmuir isotherms by regressing the experimental data which is shown in Figure 6 were K_L (Lmg^{1-})=0.245, q_m (mg·g^{1-})=416.67 with correlation coefficient R^2=0.9799 at room temperature.

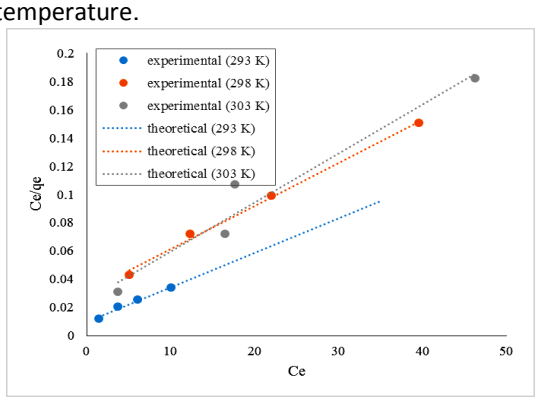

Fig. 6. Linear form of Langmuir isotherm model, experimental condition: pH= 6.0, room temperature 293 K

It is clear that the Langmuir adsorption isotherm is the best model for reactive blue 50 adsorption on to ZVI. From the Table 1 as increasing the temperature maximum adsorption capacity is decreasing due to desorption of reactive blue dye from surface of zero valent iron.

In the Langmuir equation, parameters qm and K_L are used to evaluate dimensionless constant called separation factor or equilibrium parameter (R_L).

$$R_L = \frac{1}{1 + K_L C_0} \quad (6)$$

The value of the separation factor is a measure of adsorption behavior. If R_L>1 the adsorption is

Table 1. Isotherm parameters of adsorption of reactive blue dye on ZVI

Isotherm parameters		**Value**	
Freundlich isotherm model	293 K	298 K	303 K
K_F L·mg^{-1}	101.42	63.16	82.91
1/n	0.4693	0.3957	0.2958
R^2	0.9972	0.9933	0.8223
Langmuir isotherm model	293 K	298 K	303 K
$q_{m,}$ mg·g^{-1}	416.67	322.58	285.71
K_L, L·mg^{-1}	0.245	0.101	0.141
R_L	0.039	0.09	0.06
R^2	0.9799	0.9962	0.9517

unfavorable, R_L=1 the Langmuir isotherm is linear, R_L=0 irreversible. When 0<R_L<1 the adsorption process is favorable [14].

The calculated value of R_L was 0.04 at 20^{o}C that is indicating adsorption of reactive blue 50 on ZVI is favorable. Considering the Langmuir model monolayer of reactive blue 50 molecule was formed over a uniform adsorbent surface by intermolecular bonding.

The correlation coefficients show that the adsorption process could be described by both Langmuir and Freundlich models. The experimental results show that the zero valent iron studied in this work has a very large adsorption capacity.

CONCLUSIONS:

From this study, it is shown that the zero valent iron is efficient adsorbent material for reactive dyes. The optimal condition of batch adsorption process was evaluated as pH=2-8, mass of adsorbent was 0.2 g and temperature of adsorption found 20°C in 150 mg/L concentration of dye solution. At optimal condition, removal of efficiency of dye in real wastewater sample from Tsombon Knit LLC was 99.5%. The correlation coefficients show that the adsorption process could be described by both Langmuir and Freundlich models. The experimental results show that the zero valent iron studied in this work has a very large adsorption capacity. It has been showed that assumed monolayer deposition of dye onto surface of zero valent iron by chemical sorption. It is clear that the surface of natural ores such as zeolite and bentonite can be modified by the zero valent iron due to its high adsorption capacity and high surface area. The modified natural ores presumably have high adsorption capacity and distribution constant.

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