STUDY OF Fe (III) IMPREGNATED CHITOSAN AS ADSORBENT OF CARMINE DYES

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ABSTRACT

One method to reduce carmine dyes concentration in aqueous solution is adsorption using chitosan. Impregnation of Fe(III) onto chitosan could enrich the surface textures and enhance the active sites of adsorbent. The aims of this research were to investigate the effect of impregnated Fe(III) ion onto chitosan toward carmine dyes adsorption, to determine the characteristic of carmine dyes adsorption including pH, agitation time, and to determine the adsorption capacity of the adsorbent. The amount of adsorbed carmine dye in aqueous phase was measured based on the different between concentration before and after adsorption process using UV-Vis spectroscopy. Determination of the optimum condition was conducted on 10ppm carmine dyes, 125rpm and 0.5g adsorbent. The result shows that concentrations of Fe(III) ion impregnated onto chitosan influence the adsorption of carmine dyes, with the optimum Fe(III) concentration of 15ppm. In overall, the optimum conditions were reached at pH of 8, aging time of 4 hours with adsorption capacity of 0.116 mg/g.

Key words: Adsorption, chitosan, impregnation, carmine dye, Fe(III) ions.

INTRODUCTION

Dyes from textile industries are known for its contributions in the environmental pollution. Dyes are designed to be resistant from environmental effects, i.e. pH, light, microorganism, hence their presences in the aqueous systems are unexpected, disturbed esthetically, and carcinogenic (Albanis, et al., 2000). At certain level, dyes could decrease the sunlight transmission in aqueous system which might affect the photosynthesis (Longhinnotti, et al., 1998). Liquid waste of textile industries, which is mostly contain many dyes, has high organic compounds, high colour intensity, and wide range of pH; in fact it can be very basic. The dyes concentrations could reach up to 7700 – 13100 mg/L (Anonymous, 1996).

One type of dyes is carmine which is an anionic dye that has carboxylate functional groups. Carmine is commonly used dyes in several textile industries in East Java, Indonesia (Setianingsih, 2006). The reduction of carmine concentration in liquid waste is commonly based on adsorption due to stability, effectiveness and low cost. There are two mechanisms which possibly responsible on the removal of carmine in waste which is adsorption and ion exchange. The adsorption itself is influenced by several factors i.e. adsorbent – dyes interactions, size and surface area of adsorbent, temperature, pH and adsorption time (Allen and Koumanova, 2005).

Several type of adsorbent have been tested and investigated toward anionic dyes adsorption, such as Acid red L, in which chitosan is likely emerged and posses greater adsorption capacity compare to chitin (Lazlo, 1994) or activated carbon due to less chemical interactions between the anionic dyes and the adsorbent (Nakamura, et al., 2003). Moreover, chitosan is commonly prepared from chitin which previously isolated from shrimps, crabs, or snail’s shell (Kim, 2010), non toxic materials and could be used as an antibacterial (Vasireddy, 2005), therefore it is environmentally friendly.

Although chitosan is very potential to be used as anionic dye-adsorbent, its low capacity is being a big concern among scientists. For example, adsorption capacity for Acid red L was only 0.45 mol/Kg, while for Acid red 25 was only 0.032 mol/Kg (Lazlo, 1994). It is reasonable since the adsorption was mostly done at pH above its pKa in order to prevent dissolution of chitosan. Chitosan is miscible in acid due to protonation of amine at pH below pKa, hence most of the adsorption mechanism are held by hydrogen bonds and other Van der Walls interactions (Kim, 2010).

The adsorption capacity of chitosan is predicted increase by impregnation of iron(III) ions on the chitosan’s surface. As reported by Vasireddy (2005), Fe(III) impregnated chitosan could adsorb arsenate and arsenite...
anions at pH of 5.8 – 8.8 constantly for about 98%. Moreover, Burke (2000) suggest that Fe(III) ions were attached to chitosan’s surface by forming complex compound in which Fe(III) act as the metal centre while the ligands were amine and R-O-R of chitosan, instead of anions of the Fe(III) salt (Shriver, et. al, 1990). Therefore, Vasireddy choose Fe(III) nitrate due to high affinity of arsenate and arsenite anions compare to nitrate hence it will facilitate the anion exchange effectively.

The research on Fe(III) impregnated chitosan ability toward anionic dyes adsorption is still needed in order to increase the properties and ability of the adsorbent. Although Burke (2000) had gain the maximum amount of Fe(III) that can be impregnated onto chitosan, it is predicted that the adsorption capacity is not proportionally correlated with the amount of impregnated Fe(III).

Owen and Brooker (1991) stated that -RCOO⁻ ligand affinity toward Fe(III) is greater than OH⁻ and R-O-R due to smaller donor force of π ligand. This will be very useful for the adsorption at either hydrolysed Fe(III) or in basic solution. Unlike Vasireddy (2005) that using Fe(III) nitrate, this research try to study the use of Fe(III) chloride since the ligand affinity toward Fe(III) of -RCOO⁻ is bigger than Cl⁻. Although Vasireddy had investigate the pH influence toward anion adsorption by Fe(III) impregnated chitosan, the properties of carmine is quite different to arsenate or arsenite anions. This is simply because different pH could effect the whole structure or functional group presence on the chitosan’s surface. Therefore, in this case, the study of pH was also need to be explored. The pH range that was used are 5 to 11, due to most of the dyes waste are basic, while at pH below 4, chitosan will effectively re-dissolved.

Materials and Methods

Laboratory reagents were used without further purification and obtained from standard commercial suppliers, which are Fe(III) chloride, NaOH, and HCl. Mean while, chitosan were previously made of deacetylation of chitin from isolation of Pongous monodon shrimp’s shell. The carmine dyes were collected from local textile industry in East Java, Indonesia.

The instrumentations which are used an 8400S infrared spectroscopy (FT-IR), a 1601 UV spectroscopy (UV-Vis), and an AA600 atomic adsorption spectroscopy (AAS).

The method are explained as follows: preparation of Fe(III)-impregnated chitosan, determination of optimum Fe(III) concentration, pH, and adsorption capacity of impregnated chitosan toward its ability in adsorbing carmine dye.

Preparation Of Fe(III)-Impregnated Chitosan:

Fe(III)-impregnated chitosan was made based on a method mentioned by Burke (2000). A 50 g of chitosan was added with 100mL of Fe(III) solution with concentration of 0.1; 0.5; 1.0; 5.0; 10.0; 15.0; 20.0, dan 30.0 ppm in a conical flask. The mixture was then shaked electrically for 64 hours at 150rpm. After that, the solution was filtered off and the residue of chitosan then dried in an oven at 50°C until reached constant mass.

Determination Of Optimum Fe(III) Concentration Of Impregnated Chitosan:

The determination of optimum Fe(III) concentration of impregnated chitosan toward its ability in adsorbing carmine dye was conducted based on a method explained by Setianingsih (2006), but using different adsorbent. A 25 mL of carmine solution 10ppm at pH of 6 was placed in a conical flask and added with 0.1g of various concentration of Fe(III)-impregnated chitosan. The solution was then shaked electrically for 4 hours at 150rpm. Next, the filtrate was taken and analyzed with UV-Vis spectroscopy to determine the concentration of carmine after adsorption. The highest carmine dyes adsorption ability (%) of impregnated chitosan at certain concentration of Fe(III) is considered as the optimum condition.

Determination Of Optimum Ph Of Impregnated Chitosan:

The determination of optimum pH of impregnated chitosan toward its ability in adsorbing carmine dye was conducted based on similar method explained on previous paragraph, at optimum Fe(III) concentration in various pH of 5, 6, 7, 8, 9, 10, and 11. The pH was set by adding aquadest, HCl 0.1M or NaOH 0.1M. In this section, the Fe(III) concentration which released in the filtrate due to pH setting was also determined.

Determination Of Adsorption Capacity

Before the adsorption capacity was determined, we firstly determine time to reach the adsorption equilibrium at optimum Fe(III) concentration, optimum pH and various shaking time, in which horizontal curve of equilibrium is achieved. The adsorption capacity was then determined from the horizontal curve made as
explained above but in condition of optimum Fe(III) concentration, optimum pH, adsorption equilibrium time, in various carmine dye concentrations of 2, 3, 5, 7, and 10ppm.

**Result and Discussion**

Batch method was used to measure the adsorption ability of Fe(III) impregnated-chitosan toward carmine dyes. The amount of adsorbed Fe(III) at different concentration of Fe(III) is given in Figure 1.

Based on Figure 1, the adsorption process of Fe(III) onto chitosan was influenced by Fe(III) concentration used. At low concentration, all of Fe(III) can be adsorbed by chitosan, while at Fe(III) concentration above 20 mg/L, less Fe(III) were adsorbed. Hence, the next step in this research, Fe(III) concentration of 5 – 20 mg/L was used to impregnation onto chitosan.

![Fig. 1: The amount of adsorbed Fe (III) onto chitosan at different concentration of Fe (III).](image)

**Determination Of Optimum Fe(III) Concentration Of Impregnated Chitosan:**

The amount of carmine dyes which was absorbed by Fe(III) impregnated-chitosan at various concentration is given in Figure 2.

Figure 2 illustrate that the percentage of carmine dyes adsorption was affected by concentration of Fe(III) impregnated-chitosan. Un-impregnated chitosan have low level adsorption because at pH 6, only hydrogen bonds and other Van der Walls forces were involve in the adsorption. Meanwhile the impregnated chitosan has higher adsorption since the ionic interaction between carmine dyes with the adsorbent start to happen. The increasing percentage of carmine dyes adsorption at pH 6 was caused by the present of Fe(III) on chitosan. The adsorption was steadily increase until Fe(III) concentration of 15ppm. Above that concentration, the adsorption start to decline due to too many Fe(III) on the surface which might cover the active sites on the chitosan’s surface. Fe(III) concentration of 15 ppm was then used in the next step.

![Fig. 2: The amount of carmine dyes which was absorbed by Fe(III) impregnated-chitosan at various concentration](image)
Determination Of Optimum Ph Of Impregnated Chitosan:

The amount of carmine dyes which was absorbed by Fe(III) impregnated-chitosan at various pH is given in Figure 3.

![Graph showing adsorption of carmine dyes at various pH](image1)

**Fig. 3:** The amount of carmine dyes which was absorbed by Fe(III) impregnated-chitosan at various pH.

Figure 3 illustrate that at pH of 5-8, the percentage of adsorbed carmine dyes was increasing steeply. At pH higher than 8, the adsorption of carmine dyes was decreasing gradually. At pH 5-8, the adsorption process involve electrostatic mechanism, in which ligand affinity of –RCOO⁻ from dyes with Fe(III) was getting higher than OH⁻ from dyes with Fe(III). The decline adsorption at pH above 8 is due to too many OH⁻ in the solution which might cover the active sites on the chitosan surface. Moreover, deprotonation of OH could probably contribute to the steric hindrance for carmine. Fe(III) concentration of 15 ppm and pH of 8 were then used in the next step.

Determination Of Adsorption Capacity

Determination of adsorption time equilibrium was done before determination of adsorption capacity, which presented in Figure 4. Aging time was firstly determined in order to obtain time that needed to reach optimum adsorption.

![Graph showing adsorption of carmine dyes at various aging time](image2)

**Fig. 4:** The amount of carmine dyes which was absorbed by Fe(III) impregnated-chitosan at various aging time.

Figure 4 shows that the adsorption percentage was increasing steadily from 1 to 4 hours but then directly decreasing steeply. It is assumed that 4 hours is the time that needed to reach adsorption equilibrium. Above 4 hours, it is predicted that chitosan start to swell, which is commonly occur in organic polymers.

The adsorption capacity (mg/g) of Fe(III) impregnated chitosan toward carmine was investigated by measuring the amount of carmine dyes that absorbed by Fe(III) impregnated-chitosan at various concentration of carmine. The result is presented in Figure 5.
Fig. 5: The amount of carmine dyes which was absorbed by Fe(III) impregnated-chitosan at various concentration of carmine

Figure 5 shows that adsorption of carmine was gradually increase as the carmine concentration is getting higher. The highest point was reached at 5 mg/L with adsorption capacity of 0.116 mg/g. After that, the adsorption was remain steady. The graph also demonstrate Langmuir Isotherm characteristic, in which L curve similar to hyperball rectangular was obtained by plotting the amount of adsorbed carmine versus the amount of un-adsorbed carmine in the solution.

Conclusion:

The amount of Fe(III) in Fe(III) impregnated-chitosan affect the adsorption of carmine dye, in which optimum Fe(III) concentration was obtained at 15 ppm. The adsorption gave optimum adsorption at pH of 8 and aging time of 4 hours. The adsorption capacity of 15 ppm Fe(III) impregnated-chitosan at optimum condition was 0.116 mg/g.

References


