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Adsorption of Azo Dyes from Textile Wastewater by *Spirulina Platensis*

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ABSTRACT

Due to the mushrooming of industrial activities nowadays, the released contaminants have posed risks to the stability of ecological system. In particular, the mixture consisting of colourants used in the textile industry and water resources is detrimental to human health. In order to circumvent this problem, strategies such as precipitation, membrane filtering, adsorption and electrochemical procedures have been applied. It is commonly known that adsorption is economical, eco-friendly and easy to operate. In this study, microalg, which is a kind of cyanobacteria (i.e. *Spirulina plantensis*), was used to eliminate azo-dyes from the aqueous solution via adsorption. Microalg was tested at various conditions (i.e. pH, dye concentration, temperature, biomass amount and contact time). The removal percentages of Acid Black 210 and Acid Blue 7 dyes by using microalg biomass at pH=2 were 95.35 % and 92.56 %, respectively. Meanwhile, conditions such as 100 mg/L dye concentration and 0.5 g/L biomass would lead to removal percentages of 98.55 % and 97.05 % for Acid Black 210 (60 minutes contact time) and Acid Blue 7 (75 minutes contact time), respectively. The spectrofotometric measurements show that adsorption method has a great potential for removing colourants in aqueous solutions. It could serve as an alternative method for.

Keywords: *Spirulina platensis*, waste water, azo-dyes, textile industry, adsorption

INTRODUCTION

Nowadays, many synthetic dyes have been extensively applied in many industries such as textiles, rubber, paper, plastics, leather, food, pharmaceuticals, petrochemicals, dyestuffs and cosmetics. The release of significant amounts of synthetic dyes to the environment has been causing many serious environmental and health problems. It has been reported that more than 100,000 types of dyes and pigments (total mass 7x105 tons) are produced annually (Crini, 2006).

Synthetic dyes can be categorized as anionic (direct, acid and reactive dyes), cationic (basic dyes) and non-ionic (dispersive dyes) (Mohan & Karthikeyan, 2004). Reactive dyes are highly water-soluble polyaromatic molecules. The reactive dyes are commonly used in textile dyeing processes. Meanwhile, about 20% - 40 % of these dyes remain in the effluents because the dye molecule might react with hydroxyl ions in the solution (Axelsson *et al*., 2006). These dyes are hardly removed under aerobic conditions. Consequently, they might

be decomposed into carcinogenic aromatic amines under anaerobic conditions (Kaner *et al*., 2010). Obviously, the release of these dyes into the ecological system is highly undesirable. The three common groups of reactive dyes are azo, anthraquinone and phthalocyanine dyes (Greluk & Hubicki, 2013). Among these dyes, azo dyes are organic compounds prepared by coupling a diazonium compound with a phenol or an aromatic amine (Kamboh *et al*., 2011). Azo dyes is the largest and most versatile class of dyes; therefore, they are widely used in industries (Chen *et al*., 2009). In general, during the dyeing processes, approximately 30 % -70 % of azo dyes used are hydrolyzed and mixed with the wastewater (Ambrosio & Campos-Takaki, 2004), which is detrimental to public health (Heiss *et al*., 1992). Hence, effective removal of azo dyes from wastewater is crucial (Liu *et al*., 2013).

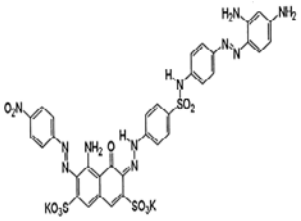
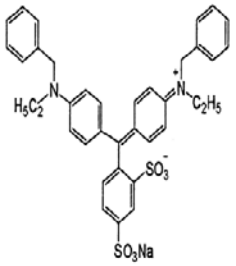
Usually, dye wastewater is treated by flocculation combined with treatment methods such as flotation, electroflocculation, membrane filtration, electrokinetic coagulation, electrochemical destruction, ion-exchange, irradiation, precipitation, ozonation, and katox. This combined technique employs activated carbon and air mixtures, which is generally expensive and ineffective in dye removal (Gupta & Suhas, 2009). A more economical and eco-friendly technique such as adsorption has been proposed (Aksu & Tezer, 2005)by using non-growing or dead microbial mass. It involves a number of metabolism-independent processes (e.g. physical and chemical adsorption, electrostatic interaction, ion exchange, complexation, chelation, and microprecipitation) that occur essentially in the cell wall (Aksu, 2005). Many biosorbents such as fungi, bacteria, chitosan, algae and peat have been used to remove pollutants from aqueous solutions (Aksu, 2005). It is worth to mention here that biosorbents such as Chlorella vulgaris (Aksu & Tezer, 2005), Ulothrix sp. (Dogar *et al*., 2010)and Scolymus hispanicus(Barka *et al*., 2011) have been successfully employed to remove dyes from aqueous solutions. On the other hand, the *Spirulina platensi*s biomass has been commonly used to remove metals such as cadmium, cooper, lead and nickel(Fang *et al*., 2011). Its application in dye removal, however, is very limited. *Spirulina platensis*, which is a member of blue-green algae, is an alternative source of protein, polysaccharide, lipid and vitamin for human(Costa *et al*., 2004). Also, it contains functional groups such as carboxyl, hydroxyl, sulfate, phosphate and other charged groups (Fang *et al*., 2011)which are usuful for dye-binding. This microalgae is abundant and relatively cheap for adsorption process (Celekli *et al*., 2010). In this study, the removal of dyes found in the textile industries will be performed by using *Spirulina platensis*.

MATERIAL AND METHODS

Dyes

Anionic textile dyes, i.e., C.I. Acid Black 210, C.I. Acid Blue 7 were generously supplied by Burboya Bursa for Dyes Manufacturing and Trading Company. The chemical structures of the dyes are shown in Table 1. The stock solutions of the dyes were prepared using distilled water with a concentration of 10,000 mg/L (1 g / 100 mL). The maximum a bsorbans (λmax) of the individual dyes was determined by UV-Visible spectrophotometer. The cyanobacteria (*Spirulina. platensis*) was obtained from Istanbul Spice and Food Industry and Trade Company in the form of powder.

Table 1. The chemical properties of Acid Black 210 and Acid Blue 7 dayes .

C. I. name	Acid Black 210	**C. I. name**	Acid Black 7
Ionization	Acid	**Ionization**	Acid
λmax (nm)	500	**λmax (nm)**	600
Molecular weight	938.02 g/mol	**Molecular weight**	690.81 g/mol
CAS Number	99576-15-5	**CAS Number**	3486-30-4
C. I. number	30027	**C. I. number**	42045
chemical formula	$C_{34}H_{25}K_2N_{11}O_{11}S_3$	**chemical formula**	C37H35N2NaO6S2
Chemical Structure		**Chemical Structure**	

Batch Adsorption Studies

Experiments were conducted with 250 mL Erlenmeyer flasks containing 100 mL of aqueous solution mixed with dyes. Flasks were agitated on a rotary shaker operating at 100 rpm and 25 ºC. The influences of physicochemical variables such as pH (2, 4, 6, 8 and 9, adjusted by the addition of 1 M HCl or 1 M NaOH solutions), initial dye concentration (25, 50, 75, 100 and 125 mg/L) and biomass dosage (0.5, 0.7, 1, 1.4 and 2 g/L) on adsorption were examined after the equilibrium was reached. Finally, specimens were centrifuged for 15 min at a speed of 10000 rpm in order to estimate the dye concentration. The concentrations of the two dyes in the aqueous solution were measured from UV−vis spectra (UV-1201 V, Shimadzu) in order to calculate the maximum absorption. The maximum absorption values of AB 210 and AB 7 dyes are listed in Table 1.

The dye removal can be calculated using Eq.1:

$$\% \text{ Removal} = \frac{(Co - Cf)}{Co} \times 100 \qquad (1)$$

Co: the initial concentration (mg/L) of dyes in solution

Cf: the equilibrium concentration (mg/L) of dyes in solution

RESULTS AND DISCUSSION

Considering the environmental and health risks caused by pollutants in wastewater, a proper treatment method must be devised. Recent studies show that techniques combining microorganisms such as bacteria, fungi and algae with some physical and chemical techniques are efficient in dye adsorption (Vandevivere *et al*., 1998). In this study, *S. platensis* was used as biosorbent. The effects of pH, temperature, dye concentration and contact time on the adsorptions of Acid Black 210 and Acid Blue 7 textile dyes were examined.

Effect of Solution pH

The effect of pH on the adsorption capacity of dyes were studied by preparing samples of dye solution in 100 mL flasks with different pH values of 2, 4, 6, 8 and 9 while keeping other variables constants. The obtained results illustrated in Fig. 1, shows that as pH value increases, the percentage of adsorption activity decreases. The highest dye adsorption for AB 210 and AB 7 was recorded as 95.55 % and 92.56 %, respectively, at pH 2.0. And the lowest dye adsorption activity was observed as 5.07 % and 0 %, respectively, at pH 9. As a result, the optimal pH value for adsorption of dye solutions of AB 210 and AB 7 was found at 2. Under acidic conditions, the surface of *S. platensis* is positively charged as well as the dyes detach in the anionic form ($D\text{-}SO3^{-}$). Therefore, electrostatic interactions amid the dyes sulfonated groups and *S. platensis* surface (positively charged) happened (Dotto *et al*., 2012). The number of sites that are positively charged decreases while the number of sites that are negatively charged increases. This happens when the pH of the system increase. The adsorption of dye anions is not supported or liked by the surface site that is negatively charged. This is due to electrostatic repulsion power. In the same vein, the lower adsorption of acid dyes at alkaline pH takes place owing to the extra hydroxyl ions(Namasivayam & Kavitha, 2002).

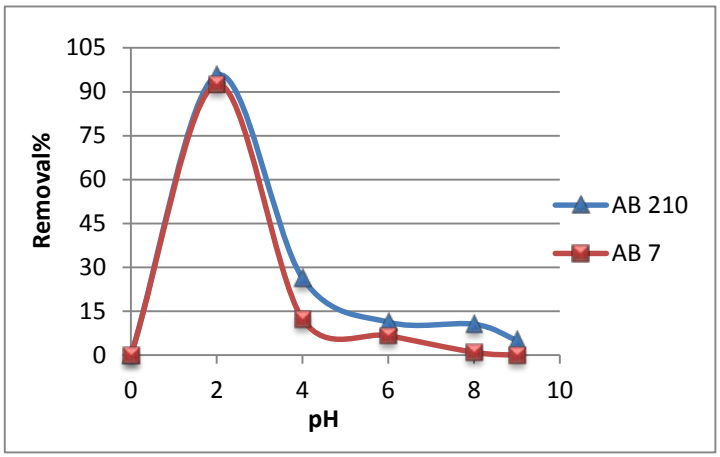


Figure 1. Effect of pH on acidic dyes removal efficiency of *S. platensis* biomass (dye consentration: 100 mg/L; Biomass level: 0,5 g/L; Contact time: 30 min; T = 25 °C)

Effect of Biosorbent Dosage

Biosorbent mass ranging from 0.5 to 2.0 g/L was considered. Here, the pH is 2, the concentrtaions of AB 210 and AB 7 solutions are 100 mg/L, the contact time is 30 min and the operating temperature is 25 °C. The results are shown in Fig. 2. As seen, the adsorption efficiencies of AB 210 and AB 7 dyes decrease from 97.56 % and 88.53 % to 0 %, respectively, as the biosorbent dosage increases from 0.5 to 2 g/L. The decrease in adsorption efficiency at higher biosorbent dosage can be attributed to the adsorption sites that remain unsaturated during the adsorption reaction, whereas the number of sites available for adsorption is increased by increasing the biosorbent dosage (Ratnamala *et al*., 2012). Also, aggregation may occur which would reduce the total biosorbent surface area. This would reduce the amount of dye biosorbed per unit of weight of biomass (Crini & Badot, 2008). Due to the fact that the greatest adsorption capacity observed was 0.5 g/L, this biosorbent dosage was used in subsequent studies.

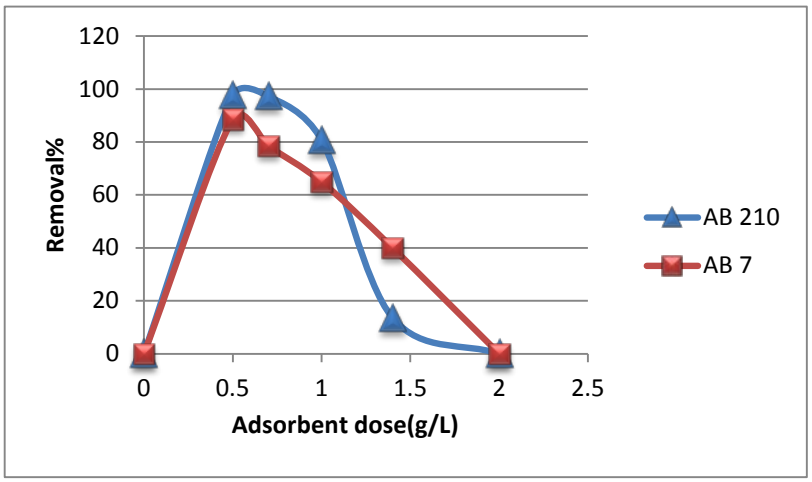


Figure 2. Effect of adsorbent dose on acidic dyes removal efficiency of *S. platensis* biomass (pH: 2; dye consentration: 100 mg/L; Contact time: 30 min; T = 25 °C)

Effect of İnitial Dye Concentration

The influence of dye concentration on the adsorption capacity was studied by experiments carried out with different concentrations of AB 210 and AB 7 from 25 to 200 mg/L. As shown in Fig. 3, the adsorption capacity was increased from % 94,37 to % 97.7 and from % 87,5 to % 91,6 respectively, by increasing the initial dye concentration from 25 to 125 mg/L. This took place due to the concentration gradient, which is the driving force(Crini & Badot, 2008). In addition, the contact of dye and biosorbent can go up in high concentrations of dye(Chen *et al*., 2008).

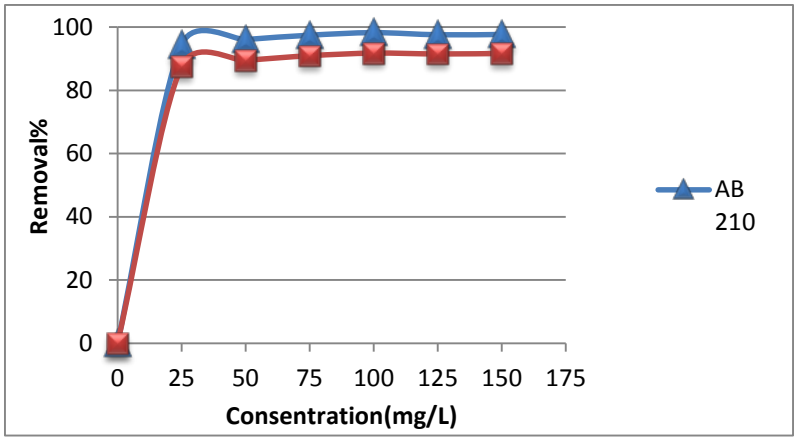


Figure 3. Effect of initial dye consentration on acidic dyes removal efficiency of *S. platensis* biomass (pH: 2; Biomass level: 0,5 g/L; Contact time: 30 min; T = 25 °C)

Effect of Contact Time

In this experiment, the contact time was varied from 15 to 135 minutes. An adsorption rate is typically high within the first 30 minutes and reaches a plateau thereafter. Fig. 3, shows that the dye removal is rapid within the first 15 minutes and it reaches equilibrium after 60 minutes. In a physical adsorption process, most adsorbates are usually adsorbed within a short contact time(Mall *et al*., 2006). At the beginning of adsorption, the dye molecules are adsorbed externally in a rapid manner. When the external surface becomes saturated, the dye molecules are then absorbed into the pores of biomass (Colak *et al*., 2009).

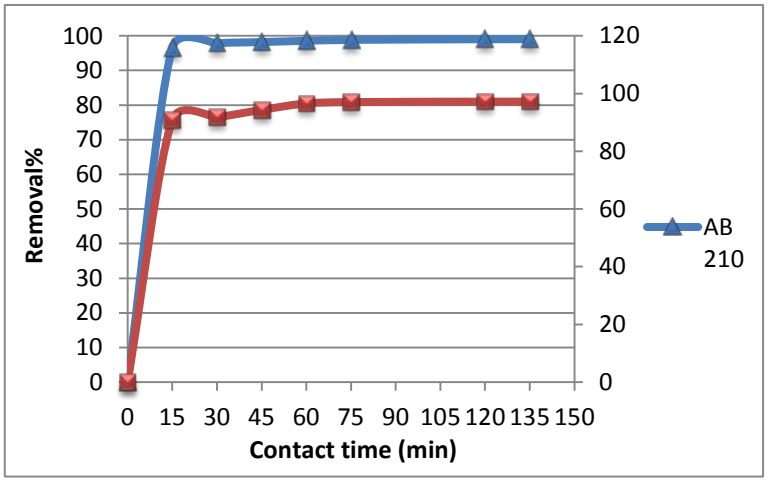


Figure 4. Effect contact time on acidic dyes removal efficiency of *S. platensis* biomass (pH: 2; dye consentration: 100 mg/L; Biomass level : 0,5 g/L; T = 25 °C)

Effect of Temperature

Here, the operating temperatures were fixed at 30°C, 45°C and 60°C. Meanwhile, the experiments were performed at optimum conditions determined earlier. Fig. 5, shows the

effect of temperature on the removals of AB 210 and AB 7. From Fig. 5, as the temperature increases from 30°C to 60°C, the removal efficiencies of AB 210 and AB 7 increase from 97.62% to 98.17% and from 92.61% to 95.01%, respectively. This favourable effect may be due to the increasing mobility of adsorbate molecules and the existence of pores on the surface of adsorbent particles. Similar observations have been reported by(Hussain *et al*., 2009)and the researchers argued that the increase in temperature could enhance the rate of diffusion of the adsorbate molecules.

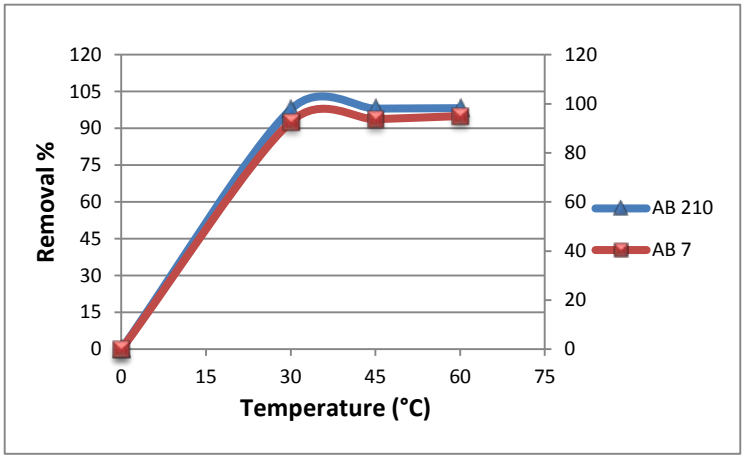


Figure 5. Effect temperatures on acidic dyes removal efficiency of *S. platensis* biomass (pH: 2; dye consentration: 100 mg/L; Biomass level: 0,5 g/L; Contact time: 30 min)

CONCLUSIONS

In this study, the dead *S. platensis* biomass has been used as biosorbent to remove AB 210 and AB7 dyes from aqueous solutions. The effectiveness of the adsorption process has been found to be dependent on conditions such as temperature, contact time, adsorbent dose, solution pH and initial dye concentration. The optimum adsorption conditions have been determined, i.e. pH of 2.0, temperature of 60°C, initial dye concentration of 125 mg/L and biosorbent concentration of 0.5 g/L. *S. platensis* is a suitable adsorbent used for anionic dye removal, as it is abundant and cheap. This study has formulated an effective plan for waste water treatment. However, further work should be performed in order to have a better understanding of dried *S. Platensis* biomass in terms of its binding mechanism. It is concluded that this adsorbent has a great potential for removing dyes from aqueous solutions as it is eco-friendly.

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