A COMPARATIVE STUDY ON THE REMOVAL OF REMAZOL GOLDEN YELLOW 6 DYE BY MIXED CULTURE OF DEAD FUNGAL BIOMASS AND ACTIVATED CARBON

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Abstract

Remazol Golden Yellow 6 is a vinyl sulfone reactive dye with an azo-based chromophore, which produces a coloured wastewater that is difficult to treat by biological treatment. Physical adsorption of coloured wastewaters with activated carbon although effective is economically expensive. It is therefore necessary to find effective and economic alternatives for absorbant, such as microorganisms. The biosorption capacity of a mixed culture of dead fungi biomass (*Aspergillus sp*., *Penicillium sp*., and *Saccharomyces sp.*) for Remazol Golden Yellow 6 was examined as a function of initial pH and initial dye concentration. The results were compared to the adsorption capacity of a commercial activated carbon. Optimum initial biosorption pH was determined as 1. The percent dye removal of 0.5 g biomass with initial dye concentrations of 60 mg/l, 80 mg/l and 100 mg/l were 90.3%, 93.6% and 97.6% respectively with equilibrium established within 75, 125 and 150 minutes. In comparison, dye removal with granular activated carbon for the same dye concentrations were respectively 32.1%, 36.4% and 37.8 % with equilibrium time at 275, 400 and 475 minutes.

Keywords: activated carbon, biosorption, fungi, textile dye

1. Introduction

Remazol Golden Yellow, a vinyl sulfone reactive dye with an azo-based chromophore (Figure 1), is widely used in the batik industry of Pekalongan. The textile industry favours the use of reactive dyes because of their bright colors, as well as colour-fast and water-resistant characteristics. However, 10-50% of the dyes are not fixed by the textile cloth and are eventually discharged with the effluents (O'Neill *et al.*, 1999). Coloured wastewater is undesirable as a part from being aesthetically displeasing, it enables to inhibit photosynthetic activity and demonstrate toxic effects to aquatic organisms. Hence, the colour should be removed before discharging the wastewater into the environment. However, azo dyes are often difficult to treat by biological treatment because of its complex structure.

Conventional physical and chemical treatments of dye wastewater include flocculation, precipitation, ion-exchange and adsorption. Adsorption with activated carbon is known to be effective, but requires regeneration besides the activated carbon is also expensive. Accordingly, there is a need to find inexpensive and efficient alternative materials, such as agricultural by-products. The use of microorganisms also offers another potential alternative to the existing adsorption methods.

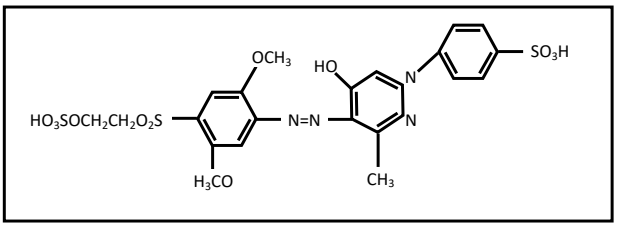

Figure 1. Remazol Golden Yellow 6

Biosorption, is the uptake of pollutants from aqueous solutions by the use of either living or dead microorganisms. It is usually rapid and efficient. A wide range of microorganisms, including fungi and yeasts, has been reported to be capable of removing dyes by biosorption.

In recent years, there have been some studies carried out using dead fungal biomass, such as *Aspergillus niger* (Fu and Viraraghavan, 2002). Compared with commercial activated carbon, dead *Aspergillus niger* biomass shows promise as an effective sorbent for dye removal. In addition, the biosorption capacity could be improved by conducting some pretreatment, such as autoclaving. The ability of yeasts as an adsorbent to remove dyes has been reported by Aksu and Dönmez (2003) and Aksu (2003).

In this study, the dead fungal biomass prepared from a mixed culture of *Aspergillus sp*., *Penicillium sp*., and *Saccharomyces sp.* was used as a biosorbent to remove Remazol Golden Yellow 6. This mixed culture was isolated from the sludge collector of a textile wastewater treatment plant in Bandung. The dye removal behavior of the dead fungal biomass was compared with a commercial granular activated carbon.

2. MATERIALS AND METHODS

Preparation of The Dye Solutions

Remazol Golden Yellow 6 dye stock solution of 1000 mg/L was prepared by dissolving 1 g powder dye in 1 L distilled water. Subsequent dye concentrations of 60, 80 and 100 mg/L were prepared from the stock solutions with distilled water.

Preparation of The Fungal Biomass And Activated Carbon for Sorption Experiments

The mixed fungal culture was grown at 30°C on Potato Dextrose Agar slant (200 g potato, 10 g dextrose, 15 g agar and 1 lt distilled water). After 4 days incubation, mycelial suspensions were prepared and used for the cultivation of fungal pellets. The mycelial suspensions (10% v/v) were inoculated into 250-ml Erlenmeyer flasks containing Potato Dextrose Medium at pH 4.

Fungal pellets were formed after 4 days incubation at room temperature and 125 rpm agitation. The flasks were then sterilized at 121° C for 30 minutes. The dead pellets were filtered, washed with distilled water, dried at 65° C for 2 days and then ground in a pestle (50 mesh particle size). The powder biomass was used in the sorption experiments.

Commercial granular activated carbon was obtained from PT Brataco Chemika, Indonesia. The activated carbon was ground in a pestle to give a powder of 50 mesh particle size (the same as the dead fungal biomass), then rinsed with distilled water and dried overnight at 105°. As with the powder fungal biomass, the ground activated carbon was used in the sorption experiments.

Analysis on Characteristics of The Biosorbent and Activated Carbon

The granular activated carbon and dead fungal biomass were analysed with respect to their water content, ash content and carbon content. Pore analyses of the adsorbents were also conducted by Scanning Electron Microscope Jeol T 330A.

Batch Sorption Experiments

The experiments were conducted in 250 ml Erlenmeyer flasks, where 0.5 g sorbant was mixed with 75 ml of Remazol Golden Yellow dye solutions of various concentrations (60, 80 and 100 mg/L). The flasks were agitated on a shaker at 125 rpm to ensure that equilibrium was reached. At pre-determined time intervals, samples (10ml) were taken to analyse the residual dye concentration in the sample. Before analysis, the samples were centrifuged at 2000 rpm for 10 minutes and the supernatant liquid analysed for the remaining dye concentration.

The biosorption of Remazol Golden Yellow 6 to the oven dried dead fungal biomass was investigated as a function of initial pH, time and initial dye concentrations. The time needed to attained equilibrium was established and compared against the adsorption performance of granular activated carbon. All the experiments were run in triplicate.

Measurement of Dye Concentration

Concentration of Remazol Golden Yellow 6 dye in the samples was measured by spectrophotometry with a Spectronic 20D, Milton Roy Company, USA. The absorbance of the colour of Remazol Golden Yellow 6 was read at 405 nm.

3. RESULTS AND DISCUSSION

Characteristics of The Biosorbent And Granular Activated Carbon

The biosorbent and granular activated carbon were analysed for their water, ash and carbon contents. The results are presented in Table 1 below. As can be seen from Table 1, the dried fungal biomass exhibited higher content of fixed carbon and lower content of ash when compared to the granular activated carbon. The water content of the two different materials was relatively comparable. As adsorption of the dye is by the carbonaceous material, the higher fixed carbon content should result in better dye removal.

Figure 2 below presents scanning microsopy images of the dead fungal biomass and the granular activated carbon. As shown in Figure 2, the number of pores of the dead fungal biomass is greater than that of the activated carbon that could increase the surface area ratio for adsorption processes. However, the pore size of the dead fungal biomass is larger than the pore size of the activated carbon. At 2000x magnification, pore walls of the activated carbon are thicker than that of the dead fungal biomass. In general, the smaller pores provide greater surface areas for adsorption.

Table 1. Properties of Oven Dried Fungal Biomass and Commercial Granular Activated Carbon

Parameter	Oven dried fungal biomass	Activated carbon
Water (%)	10.54	11.19
Ash (%)	0.96	1.10
Fixed Carbon (%)	82.84	16.58

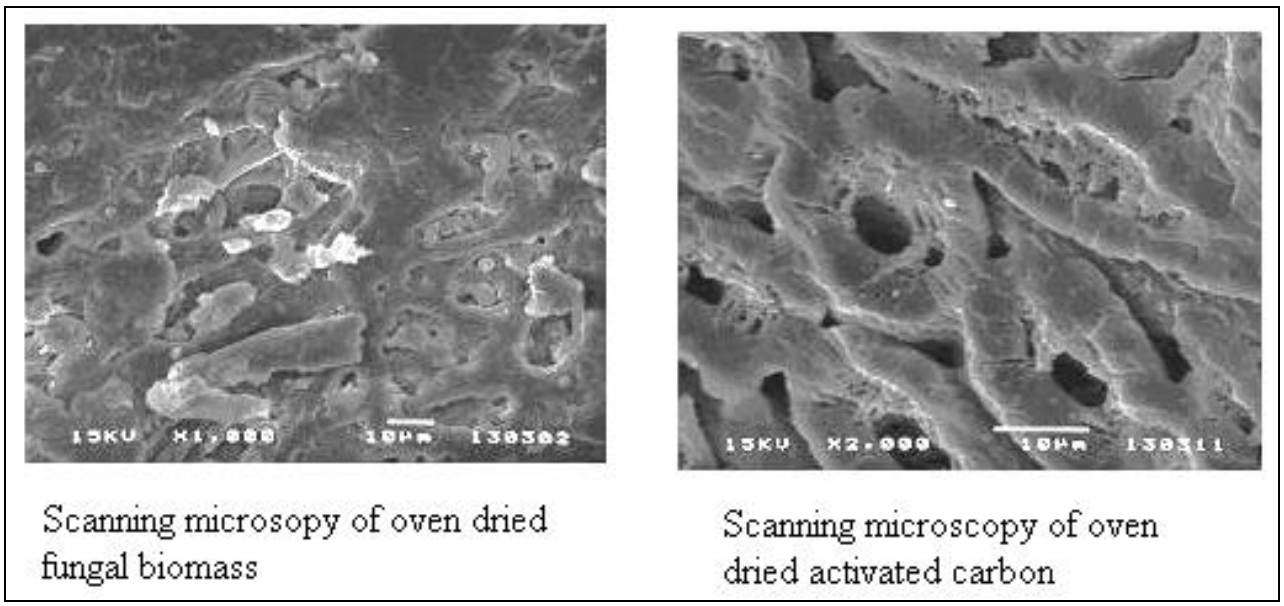

Figure 2. Scanning Electron Microscopy of Oven Dried Fungal Biomass And Activated Carbon

Effect of initial pH on dye sorption

The pH value significantly affects dye biosorption. The variations in dye sorption by fungal biosorbent and activated carbon at different pH values and different initial dye concentrations are shown in Figure 3 and Figure 4. Biosorption with fungal biomass for all dye concentrations under study was maximum at pH 1 then declined with the increase in pH.

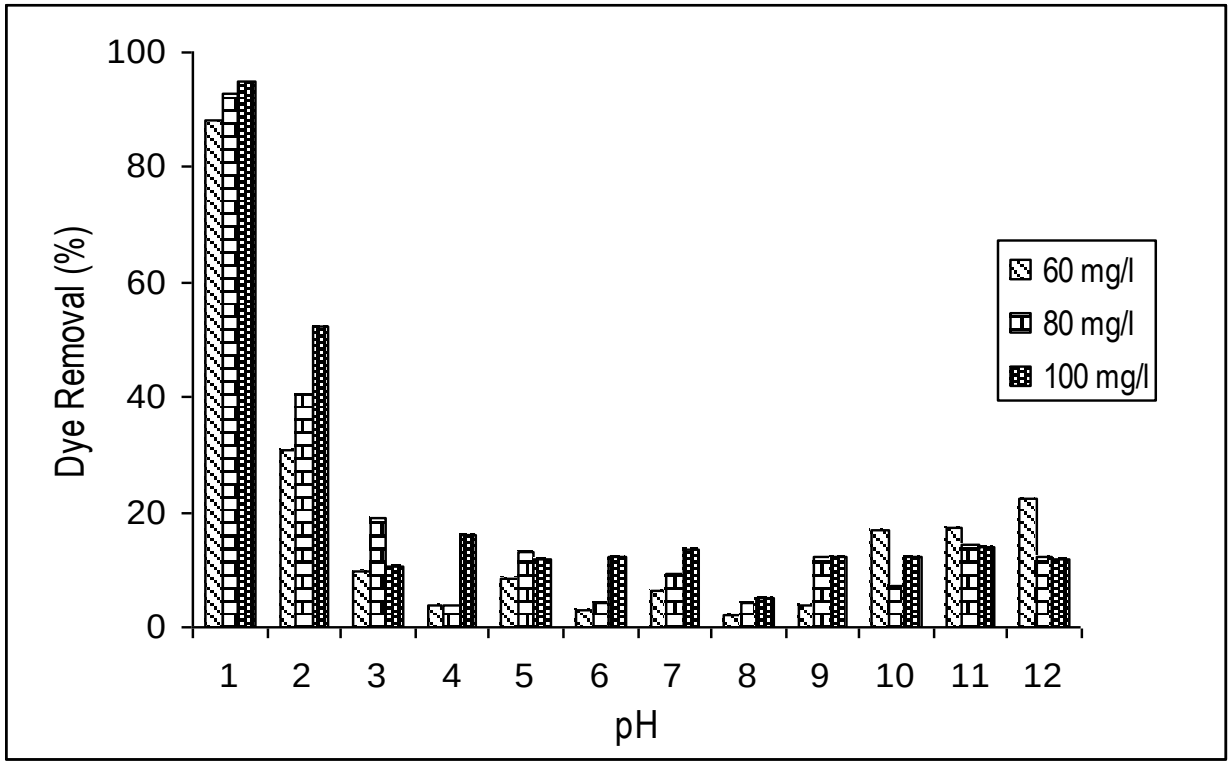

Figure 3. Biosorption at Various pH Values

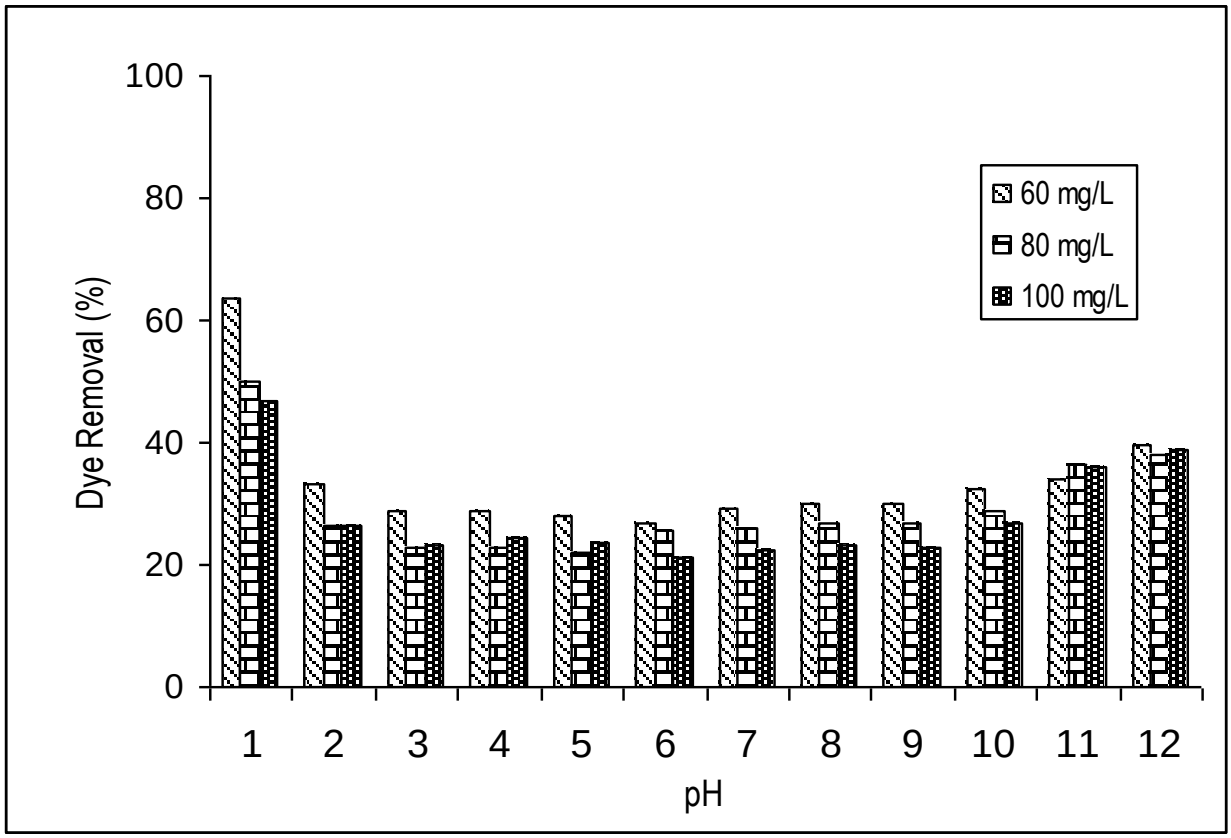

Figure 4. Adsorption With Activated Carbon at Various pH Values

Remazol Golden Yellow 6 has an azo-based chromophore combined with a vinyl sulfone reactive group. The reactive groups of reactive dyes interact with the active group on the cell surface of a fungi, such as chitin, acidic polysaccharides, lipids, amino acids and other cellular components of the microorganism (Aksu and Tezer, 2000). In addition, lower pH levels result in high concentrations of protons in the solution causing the biomass to become protonated and acquiring a net positive charge (O'Mahoney, Guibal and Tobin, 2002). Hence, under low pH levels better electrostatic attractions could occur between the positively charged biomass surface and negatively charged dye anions resulting in better colour removal.

Figure 4 shows that maximum dye adsorption with activated carbon also occurred at pH 1 and then declined at higher pH values. As with the fungal biomass, low pH values caused the surface of the activated carbon to acquire positive charges. Hence, better electrostatic attractions occurred between the positively charged carbon surfaces and negatively charged dye anions causing maximum dye adsorption.

Control experiments were also carried out where dye solutions of various concentrations were adjusted to initial pH values of 1 to determine whether any dye removal would occur if no adsorbent was present. As shown in Figure 5, in the control experiments only low amounts of dye removal was obtained, these being less than 1.5% for initial dye concentrations of 60 mg/L and 80 mg/L and less than 8% for initial dye concentration of 100 mg/L. Whereas, in the presence of fungal biosorbent more than 90% dye was removed at equilibrium (Table 4).

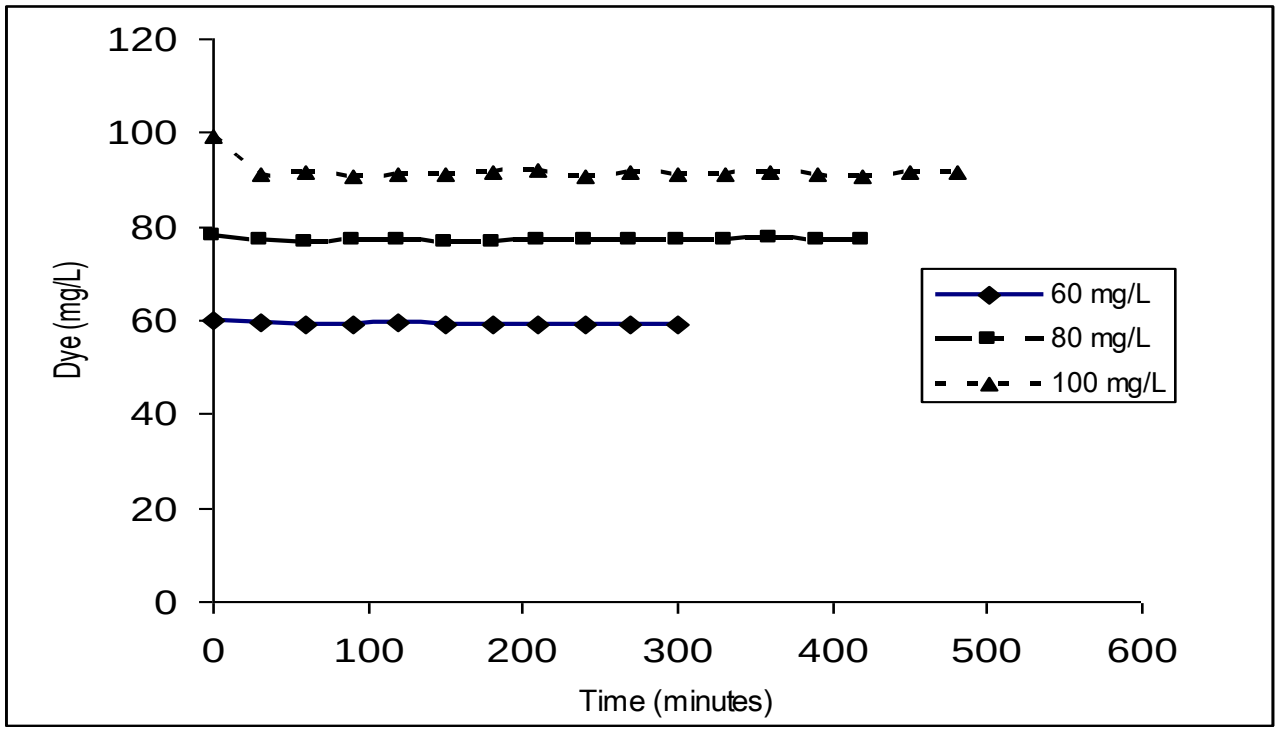

Figure 5. Control Experiments at pH 1 without Sorbent

Table 2 presents the percent colour removal by both dead fungal biomass and activated carbon with a solution that had an initial pH of 1 after 24 hours contact time. With dye concentrations of 80 and 100 mg/L, the dead fungal biomass demonstrated more than 1.5 time better percent colour removal than the activated carbon. The biosorbent also

demonstrated higher dye sorption capacity (mg/g). As the fungal biomass had higher carbon content (Table 1) this could account for why it showed better percent colour removal in comparison to activated carbon. Moreover, in the biosorption experiments the percent colour removed and amount of dye adsorbed increased with increase in initial dye concentrations. Whereas, with the activated carbon, increasing the initial dye concentration resulted in decreasing the colour removal efficiency, which is attributed to the saturation of the sorption sites after 24 hours contact time.

Table 2. Sorption by Dead Fungal Biomass and Activated Carbon after 24 Hours Contact Time, at pH=1

Dye Concentration (mg/l)	Dead Fungal Biomass		Activated Carbon	
	Removal (%)	X/M (mg/gr)*	% Removal	X/M (mg/gr)*
60	88.1	7.93	63.8	5.74
80	93.03	10.89	49.9	5.71
100	94.9	14.24	47.1	7.06

*X/M = amount of dye adsorbed per unit weight of adsorbent

Effect of Initial Dye Concentrations on Dye Sorption

Initial dye concentration provides an important driving force to overcome mass transfer resistance of the dye between the aqueous and solid phases (Aksu and Dönmez, 2003). Accordingly, a higher initial dye concentration should enhance the sorption process. In this study, the effect of initial dye concentration on the percent dye removal and sorption capacity (mg/g) of the fungal biomass as well as activated carbon was investigated at initial dye concentrations of 60, 80 and 100 mg/L with the initial pH value of 1. The results are presented in Tables 3 and 4, whereas Figures 6 and 7 show dye removal as a function of time by the fungal biomass and activated carbon respectively.

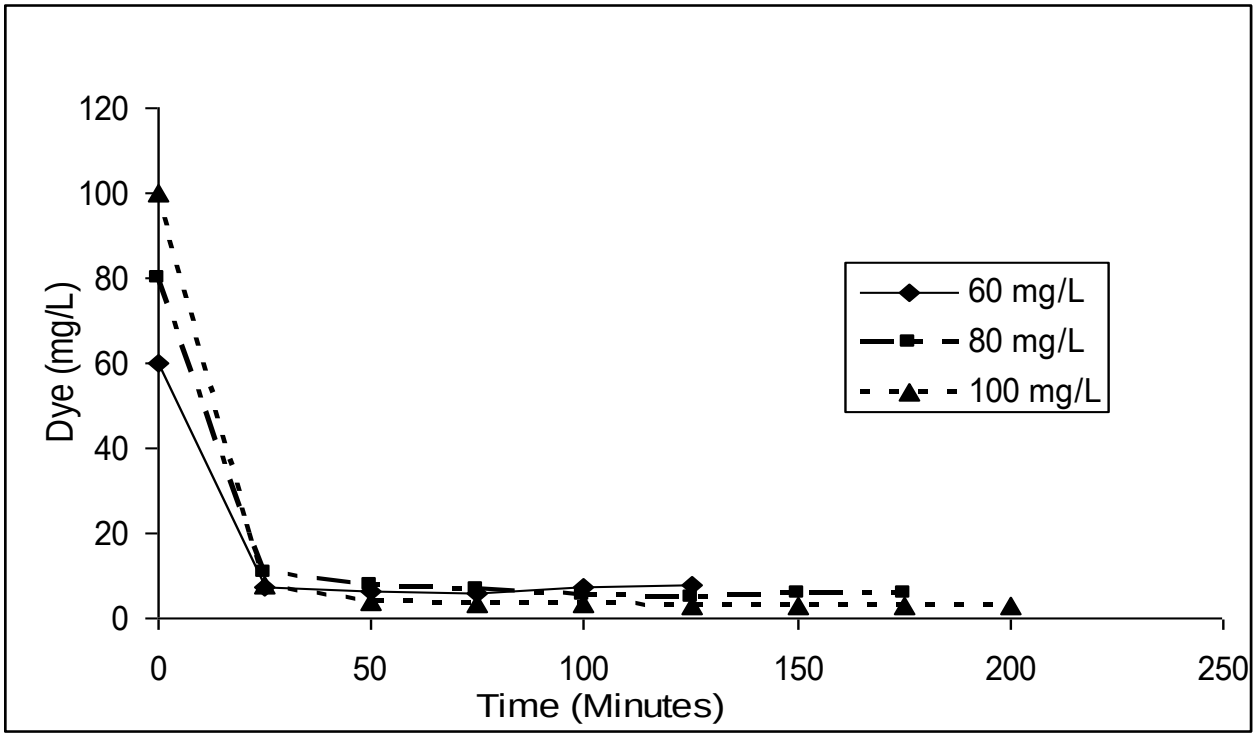

Figure 6. Biosorption at Various Dye Concentrations

As shown in Figure 6, equilibrium using fungal biomass biosorbent with initial dye concentrations of 60, 80 and 100 mg/L was established in 75, 125 and 150 minutes respectively. Both the percent colour removal and sorption capacity of the fungal biomass increased with increasing initial dye concentrations (Table 4). In comparison, the time required to established equilibrium when using activated carbon as the sorbent was longer, i.e. 275, 400 and 475 minutes respectively (Figure 7). This is attributed to the fact that activated carbon is composed of a porous structure with a large internal surface area. There are three consecutive mass transport steps that are associated with the adsorption of solute from solution by a porous sorbent. First, the sorbate has to migrate through the solution to the exterior surface of the sorbent particles by film diffusion, which is followed by solute movement from the particle surface into the interior site by pore diffusion and finally the adsorbate has to be adsorbed into the active sites at the interior of the adsorbent. Such a process usually takes relatively long contact times (Malik, 2004).

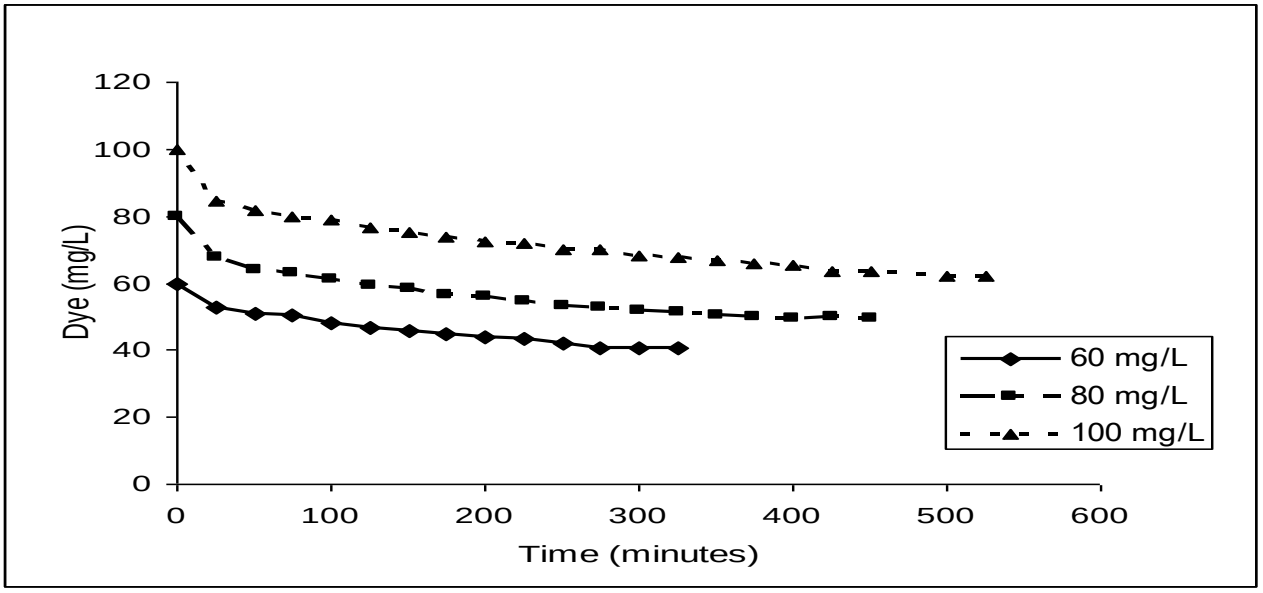

Figure 7. Adsorption with Activated Carbon at Various Dye Concentrations

Table 3. Sorption of Dye During First 25 Minutes Contact Time

Dye Concentration (mg/L)	Fungal Biomass		Activated Carbon	
	% dye removal	X/M (mg/g)	% dye removal	X/M (mg/g)
60	87.6	7.88	12.1	1.1
80	86.7	10.4	13.6	1.88
100	92.4	13.86	15.5	2.31

Figure 6 and Table 3 show that a large amount of dye was removed by the fungal biomass in the first 25 minutes of contact time, followed by a more gradual process until equilibrium was attained. At 60 mg/L, 80 mg/L and 100 mg/L initial dye concentrations, the percent dye removal demonstrated by the fungal biomass within 25 minutes contact time was 87.6%, 86.7% and 92.4% respectively. According to Aksu and Tezer (2000), short times coupled with high dye removals indicate a high degree of affinity for a dye, which points toward chemisorption. After the equilibrium time, no more dye was removed suggesting that available sites on the biosorbent are the limiting factor for biosorption to occur. In comparison, when using activated carbon as the sorbent, percent dye removal within 25 minutes contact time was only 12.1%, 13.6% and 15.5% respectively for initial dye concentrations of 60 mg/L, 80 mg/L and 100 mg/L (Table 3).

After equilibrium was established the fungal biomass was capable of removing more than

90% of all dye concentrations investigated (Table 4). This suggests that the adsorbent capacities of the fungal biosorbent were effectively utilized in solutions of the various dye concentrations. In comparison, at equilibrium the percent dye removed by activated carbon was only 32.1%, 36.4% and 37.8% for initial dye concentrations of 60 mg/L, 80 mg/L and 100 mg/L respectively. Accordingly, the percent dye removed with fungal biosorbent was greater by more than 2.5 times. The amount of dye adsorbed (mg/g) at equilibrium by the fungal biomass was also more than 2.5 times greater.

Table 4. Sorption of Dye at Equilibrium

Dye Concentration (mg/L)	Fungal biomass		Activated Carbon	
	% dye removal	X/M (mg/g)	% dye removal	X/M (mg/g)
60	90.3	8.13	32.1	2.89
80	93.6	11.25	36.4	4.55
100	97.1	14.57	37.8	5.67

5. CONCLUSIONS

The ability of oven dried mixed fungal culture of *Aspergillus sp*., *Penicillium sp*., and *Saccharomyces sp.* to adsorb dye was compared against a commercial granular activated carbon. The biosorbent was found to be capable of removing Remazol Golden Yellow 6 from an aqueous solution. Compared with the commercial granular activated carbon used in the study, the biosorbent demonstrated better percent dye removal and dye sorption (mg/g) for various initial dye concentrations. Chemical analysis of the oven dried fungal biosorbent and commercial activated carbon used in the study indicated that the biosorbent had a higher fixed carbon content. Initial pH of the dye solution affected dye sorption, as at low pH values the biomass becomes protonated. The effective initial pH for Remazol Golden Yellow was 1.

Initial dye concentration also affected dye sorption, where percent dye removal and sorption capacity of the biosorbent increased with increasing dye concentrations, i.e. 90.3%, 93.6% and 97.1% for initial dye concentrations of 60 mg/L, 80 mg/L and 100 mg/L respectively. A comparison of the percent dye removal by the biosorbent with a commercial granular activated carbon showed that the biosorbent was more effective. It may be concluded that dried mixed fungal biomass could potentially be used as an alternative to commercial activated carbon for the removal of vinyl-sulfone azo based reactive dye from wastewater.

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