

The Effect of pH and Temperature on the Dye Sorption of Wool Powders

G. Wen, P. G. Cookson, X. Liu, X. G. Wang

Centre for Material and Fibre Innovation, Institute for Technology Research and Innovation, Deakin University, Geelong 3217, Victoria, Australia

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ABSTRACT: The sorption behavior of wool powders for three acid dyes (C. I. Acid Red 88, C. I. Acid Red 13 and C. I. Acid Red 18) and a basic dye (methylene blue) was investigated as a function of pH and temperature. The sorption capacity of wool powders depends on the pH of dye solution. The maximum uptake of acid dyes and methylene blue by wool powders occurred at pH 2.5 and pH 7.5, respectively. The effect of pH on the sorption of the hydrophilic dyes (C. I. Acid Red 13 and C. I. Acid Red 18) was more significant than that of the uptake of the hydrophobic dye (C. I. Acid Red 88). Increasing tempera-

ture enhanced the dye sorption ability of coarse wool powders, but did not impact that of fine wool powders. The dye-absorption models of wool powders agree with the Langmuir isotherm. Comparison to activated charcoal and other sorbents indicates that fine wool powders have excellent dye sorption capacity even at room temperature, and may be used as a potential sorbent. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 2216–2226, 2010

Key words: wool powder; dye sorption; pH; temperature; adsorption isotherm; activated charcoal

INTRODUCTION

Sorption techniques are considered to be useful for treating industrial effluents because of their simplicity, efficiency, and selectivity.¹ Activated charcoal is widely used as an efficient adsorbent for decolorization of industrial wastewater. Recently, there has been an increasing interest in developing various alternate sorbents to remove color.^{2–4} The possibility of using wool fiber as a potential sorbent to remove dyes from dyehouse effluent has been demonstrated.^{5–7} In a recent study,⁸ it was found that the reactivity of wool, in the form of powder, was remarkably enhanced owing to the disruption of cuticle cells. The uptake of dye by wool powder was rapid in situations where there was virtually no uptake by the original wool fiber at room temperature. The rate and extent of dye uptake of the fine powders were comparable to that obtained with activated charcoal, even though the surface area of the charcoal was 100 times greater. These results suggest that the use of wool powder as a sorbent to remove dyes from industrial wastewater may be feasible.

Many parameters, such as contact time, pH value, temperature, and concentration of the sorbate, play

critical roles in a batch sorption process.^{5,9} The dye uptake of wool powders in the preliminary study,⁸ however, was only conducted under the limited conditions, viz. initial dye concentration of 1.5 g/L, pH 4.5, and 25°C. Hence this study was carried out to examine the influence of pH values and temperature of dye solutions, with various initial dye concentrations, on the dye sorption capacity of wool powders. Comparisons were made with activated charcoal under the optimum conditions. The isotherm adsorption of wool powders was studied using Langmuir and Freundlich isotherms. These results would provide useful information for the potential application of wool powders in the treatment of wastewater.

EXPERIMENTAL

Materials and chemicals

Four wool powders, namely WP-1, WP-2, WP-3, and WP-4, were used as sorbents in this study. The production procedure and characterization of these wool powders were described elsewhere.⁸ Their related properties are summarized in Table I.

Activated charcoal (untreated powder, No.C-5260, Sigma®), with a BET surface area of 858 m²/g, was used as a control.

Three acid dyes, C. I. Acid Red 88, C. I. Acid Red 13, and C. I. Acid Red 18, as well as a basic dye, methylene blue (C. I. basic blue 9), were used as sorbates without further purification. Their chemical structures and relative molecular masses are given in Figure 1.

Correspondence to: X. G. Wang (xwang@deakin.edu.au).

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TABLE I
Properties of Wool Powders

Wool powder	Particle size (μm)	BET surface area (m^2/g)	Morphology	Chemical treatment
WP-1	About 500 μm in length	0.94	intact fiber snippets	Un-chemical treated
WP-2	About 150 μm in length	1.81	considerable fibrous material	
WP-3	Mean particle size of 6.2 μm (on a volume basis)	5.91	small fibrous particles with the disruption of outer cuticle layer and the exposure of inner cortex	
WP-4	Mean particle size of 4.5 μm (on a volume basis)	6.13	similar morphology as WP-3, but generally smaller	Chlorinated with the sodium salt of dichloroisocyanuric acid (4%)

Dye stock solutions (10 g/L) were prepared in distilled water. Buffers were made up of citric acid/di-sodium hydrogen phosphate (anhydrous) (pH 2.5 to pH 7.5) and ammonium sulfate/ammonia solution (30%) (pH 10) in distilled water. Albegal FFA (Ciba) was used as a wetting agent.

Zeta potential measurement

The ζ -potentials of wool powders and activated charcoal were determined by measuring their electrophoretic mobility in the suspension at 25°C using a Zetasizer Nano ZS (Malvern Instruments, UK), after equilibrating wool powders or activated charcoal (0.1 g) into buffers (20 mL) varying from pH 2.5 to pH 10 for 4 h. The pH values of buffer solutions were precisely determined using an HI 9025 micro-computer pH meter (HANNA instruments). The ζ -potential data reported are the average of three measurements of each fresh solution.

Dye uptake

Dye sorption was carried out using a batch technique. The dye uptake of wool powders in the previous study⁸ indicated that the dye sorption equilibrium for wool powders could be established after a contact time of 2 h, so the sorption time was set at 2 h in this study. The liquor-to-wool ratio was 200 : 1. The typical procedure is described as follows:

One gram of wool powder or activated charcoal was stirred in a solution containing 5 mL of Albegal FFA (10 g/L) and the required volume of buffer for 15 min at the required temperature in a shaking water bath (Stuart®, SBS40), and the appropriate volume of dye stock solution (10 g/L) was then added. After stirring for 2 h, the slurry was filtered through a filter paper (Whatman® Glass Microfibre Filters, Cat No 1825,047).

The amount of dye in the filtrate was determined using a CARY-3 UV-visible spectrophotometer at

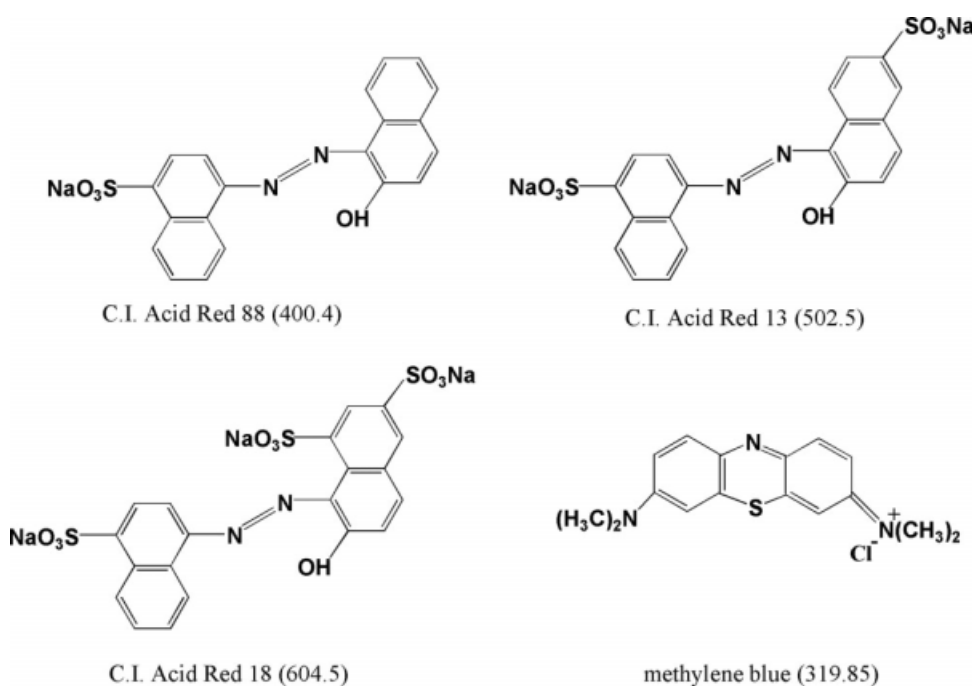


Figure 1 Structures of the related dyes.

λ_{\max} . The values of λ_{\max} for C. I. Acid Red 88, C. I. Acid Red 13, C. I. Acid Red 18, and methylene blue are 505 nm, 506 nm, 507 nm, and 664 nm, respectively. The dye uptake and the amount of sorbed dye on the sorbent (q_e) were calculated by the following equations, respectively:

$$\text{Dye uptake (\%)} = \left(1 - \frac{C_t}{C_0}\right) \times 100 \quad (1)$$

$$\text{Amount of sorbed dye } (q_e) \text{ (mg/g)} = \frac{(C_0 - C_t) \times V}{M} \quad (2)$$

where C_0 is the initial concentration of dye solution (g/L)

C_t is the final concentration of dye solution at a contact time of 2 h (g/L)

V is the volume of the dye solution (mL)

M is the mass of the sorbent (g)

RESULTS AND DISCUSSION

Effect of pH on the dye sorption of wool powders

Surface charge of wool powders and activated charcoal

When a solid is immersed in a solution, an electric double layer on the surface of the solid results in a zeta potential that provides the information about the electrokinetic surface charge of the material.¹⁰ The mechanism for dye sorption of wool and activated charcoal involves electrostatic force between the charged substrates and the ionized dye.^{11,12} Therefore, to study the interactions between the sorbents and the dyes, the surface charges on the wool powders and charcoal were investigated by measuring their zeta potentials at various pH values.

Zeta potentials for WP-3, WP-4, as well as activated charcoal, as a function of pH are shown in Figure 2. It was impossible to measure the zeta potentials of WP-1 and WP-2 because of their rapid settling from suspension due to the large particle sizes.

Figure 2 shows that the isoelectric points (IEP), which is defined as the pH value where the zeta potential equals zero, are pH 4.1 and pH 3.7 for WP-3 and WP-4, respectively. For both WP-3 and WP-4, the number of positive surface charges (pH < IEP) decreased, and the amount of negative surface charges (pH > IEP) increased with the rise in pH values. The result for un-chemical treated wool pow-

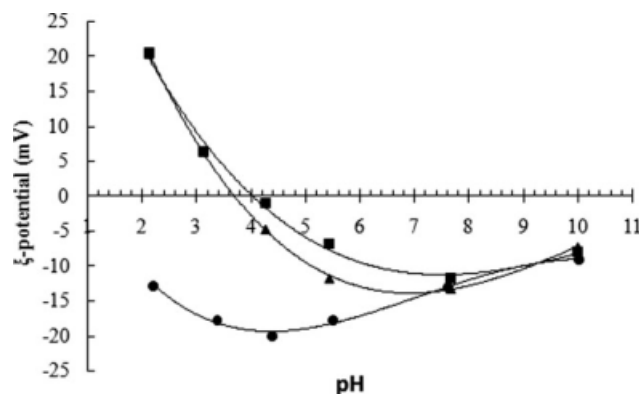


Figure 2 ζ -potentials of WP-3 (■), WP-4 (▲) and activated charcoal (●).

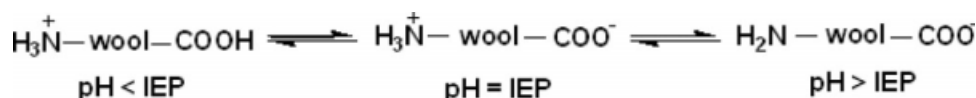
der, WP-3, is very similar to that for native wool fiber,¹² while zeta potential for chlorinated wool powder, WP-4, is different from that for chlorinated wool fiber, which has negative potentials over the whole pH values.^{13,14} This is not surprising because zeta potential depends on not only the surface of wool but also the polar medium in which the wool is immersed,¹³ as well as the methods for zeta potential measurement.^{15,16}

The surface charge of wool powders can be related to the ionization of wool at various pH values, as shown in Scheme 1.¹⁷

At the IEP, untreated wool carries no net charge because of the equal numbers of positively charged ammonium groups and negatively charged carboxyl anions. In the case of pH values below the IEP (pH < IEP), carboxyl anions combining with hydrogen ions are in the form of carboxylic acid groups. Positively charged ammonium groups are considered to be 'dye sites' for acid dyes.^{12,18} For pH value higher than the IEP (pH > IEP), on the other hand, wool carries negative charges because of the abstraction of hydrogen ions from the positively charged ammonium groups. The carboxyl groups present in a sorbent are thought to be mainly responsible for sorption of basic dyes.¹⁹

In comparison with WP-3, the slightly negatively charged surface of WP-4 over the entire pH range could be due to its relatively high concentration of cysteic acid groups as a consequence of chlorination treatment of wool during the powdering process.⁸

The activated charcoal used in this study carried negative charges over the whole pH values under the investigated conditions. The chemical groups in charcoal depend on the raw material employed and



Scheme 1

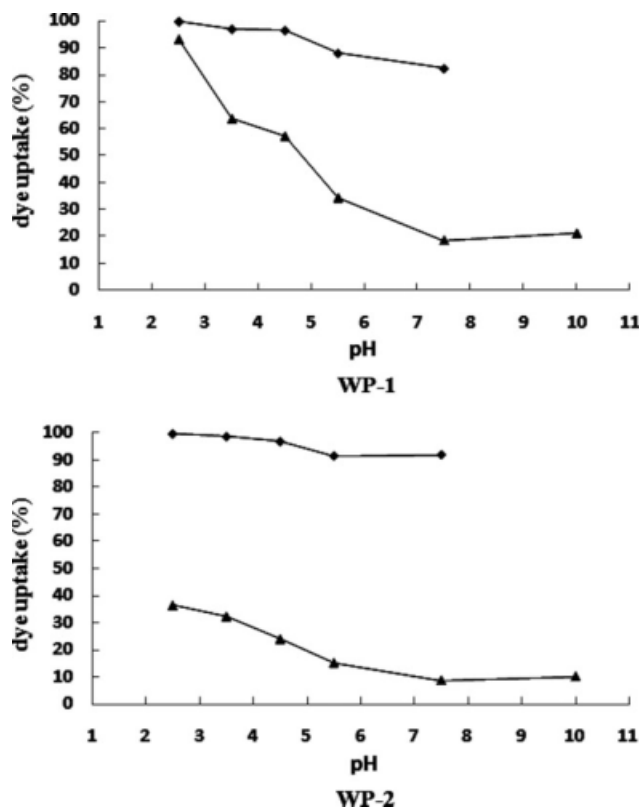


Figure 3 Effect of pH on acid dye sorption of WP-1 and WP-2: C. I. Acid Red 88 (◆), C. I. Acid Red 13 (▲), dye concentration of 0.1 g/L for WP-1, and 0.25 g/L for WP-2, 25°C, 2 h.

the carbonization process.²⁰ The magnitude of the negative surface charges on the charcoal reached the maximum at pH 4.2.

Dye uptake of wool powders at various pH values

The pH value of the dye solution plays a significant role in dye sorption of wool because it affects the degree of ionization and the surface properties of wool in solution, as shown in Figure 2. Therefore, the effect of pH on dye sorption was studied in the range of pH 2.5–10. Uptake of C. I. Acid Red 88 at pH 10 was not determined because the dye solution was cloudy; this was likely to be caused by aggregation of the dye in the buffer solution.

To observe the difference in the dye uptake over the entire pH range, the appropriate initial dye concentration had to be selected for each wool powder. The relatively low dye concentration (0.1 g/L) was used for WP-1, because the sorption capacity of WP-1 is low, and the use of higher dye concentrations leads to very little percentage of dye uptake over the whole pH range. The relatively high dye concentration (1.5 g/L) was set for WP-3, WP-4, and activated charcoal, because of their high dye sorption abilities, with virtually 100% of dye sorbed at each pH value

at lower dye concentrations. A dye concentration of 0.25 g/L was used for WP-2 due to its intermediate sorption ability.

The relationships between the uptake of acid dyes by different wool powders and the pH of dye solution are shown in Figures 3 and 4. As the pH value was increased, the uptake of C. I. Acid Red 88 by all wool powders slightly decreased, while the uptake of C. I. Acid Red 13 and C. I. Acid Red 18 fell off dramatically.

Acid dyes consist of a chromophore (aromatic structure) that is solubilised by one or more sulphonic acid groups. Binding of acid dyes to wool involves a number of forces and interactions, including electrostatic forces between the anionic sulphonate groups (SO_3^-) of dye and the charged wool, hydrophobic interactions between the hydrophobic parts of the dye and hydrophobic groups in wool, and hydrogen bonding.²¹ As the pH value of dye solution was raised from pH 2.5 to pH 10, the surface charge of wool varied from being positive (pH < IEP) to being negative (pH > IEP). As a consequence, the electrostatic forces between the charged wool and the negatively charged acid dyes changed from attractive forces (pH < IEP) to repulsive forces (pH > IEP). This change in the electrostatic force

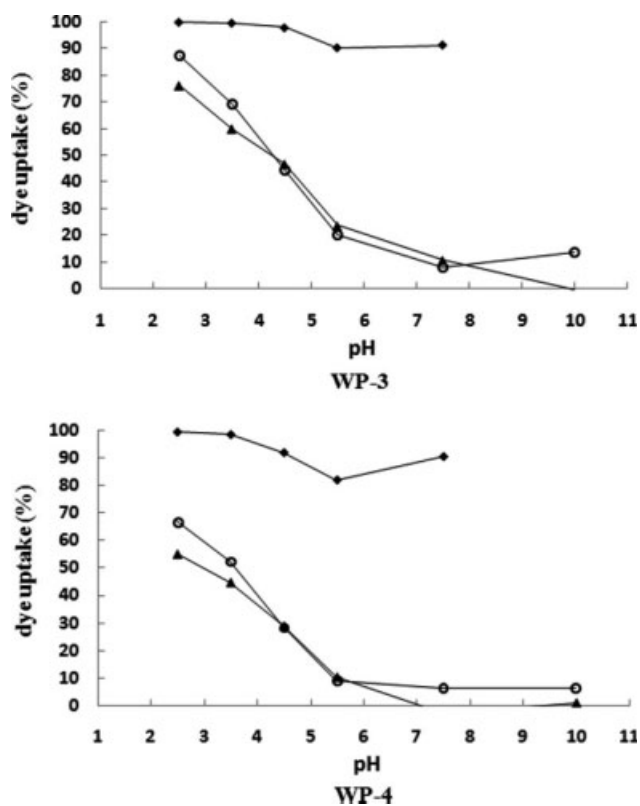


Figure 4 Effect of pH on acid dye sorption of WP-3 and WP-4: C. I. Acid Red 88 (◆), C. I. Acid Red 13 (▲), C. I. Acid Red 18 (○), dye concentration of 1.5 g/L, 25°C, and 2 h.

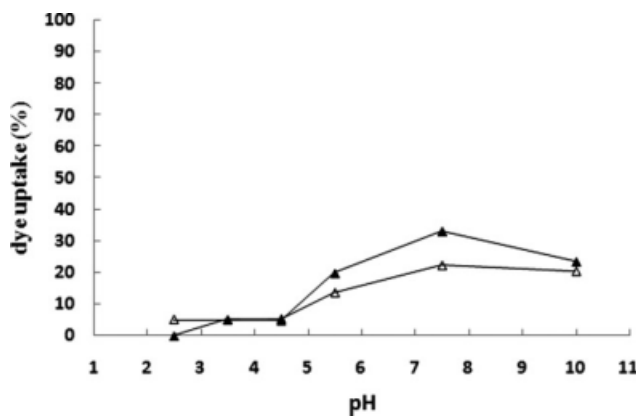


Figure 5 Effect of pH on sorption of methylene blue by WP-3 (Δ) and WP-4 (\blacktriangle): dye concentration of 1.5 g/L, 25°C, and 2 h.

reduced the uptake of acid dyes by wool with increasing the pH value.

Based on the same aromatic structure, C. I. Acid Red 88 has one sulphonate group, while C. I. Acid Red 13 and C. I. Acid Red 18 have two and three sulphonate groups, respectively. There was no significant difference in the uptake of C. I. Acid Red 88 by wool at each pH value. It could be deduced that the hydrophobic aromatic parts of C. I. Acid Red 88 through the hydrophobic interactions, rather than its sulphonate groups via electrostatic forces, are primarily responsible for its binding on wool at all pH values. However, the significant decline in the uptake of C. I. Acid Red 13 and C. I. Acid Red 18 with increasing pH value reveals that the electrostatic forces play a more important role than the other interactions in the uptake of these two acid dyes by wool. This result could be attributed to the increased number of negative sulphonate groups in C. I. Acid Red 13 and C. I. Acid Red 18.

The dependence of sorption of basic methylene blue by WP-3 and WP-4 on the pH of dye solution is shown in Figure 5. Basic dyes exist in the form of positively charged ions in an aqueous solution. At pH values above the IEP, the electrostatic attractive forces between the negative surface charges of wool (such as deprotonated carboxylic acid groups) and the positively charged methylene blue contribute to dye uptake by wool. At pH values below the IEP, the positively charged surface of wool does not favor the sorption of dye cations because of the electrostatic repulsion, so a low uptake of the basic dye was observed at low pH values. The highest uptake of methylene blue occurred at pH 7.5 under the investigated conditions, which could be due to the maximum amount of negative surface charges of wool at this pH value (Fig. 2). Other interactions, such as the hydrophobic interactions and hydrogen

bonding, are also responsible for the binding of the basic dye to wool.

The uptake of C. I. Acid Red 88 and methylene blue by activated charcoal at various pH values is shown in Figure 6. The sorption of dyes by activated charcoal involves electrostatic and dispersion forces.¹¹ Although the electrostatic repulsion between the negatively charged charcoal and anionic C. I. Acid Red 88 repelled the dye sorption, C. I. Acid Red 88 was taken up by activated charcoal via the relatively short range dispersion forces between the charcoal surface and the dye. The highest uptake of C. I. Acid Red 88 (~100%) took place at pH 7.5, at which the amount of negative surface charges on charcoal is the minimum in the tested range of pH 2.5–7.5 (Fig. 2).

In the case of the basic methylene blue, both the electrostatic attractive forces between the negatively charged charcoal and the cationic dye, and the dispersion forces are responsible for its uptake by activated charcoal. The maximum sorption of methylene blue (85%) by charcoal occurred at pH 5.5.

The pH values for the maximum dye uptake were used in the subsequent investigations, viz. for acid dyes, pH 2.5 was used for wool powders, and pH 7.5 for activated charcoal; for the methylene blue, pH 7.5 was used for wool powders, and pH 5.5 for charcoal.

Dye sorption of wool powders at different temperatures

Dye uptake at 25°C

The sorption behavior of wool powders at 25°C was investigated using the uptake of C. I. Acid Red 88, C. I. Acid Red 18 and methylene blue at the selected pH values for 2 h. The different initial dye concentrations were selected for wool powders to take into account their different dye sorption capacities. The

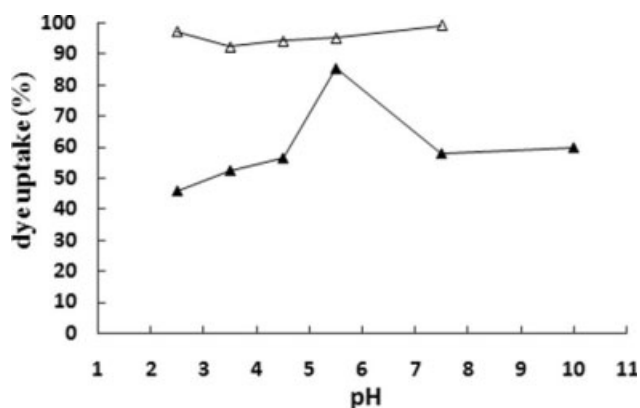


Figure 6 Effect of pH on the dye adsorption of activated charcoal: C. I. Acid Red 88 (Δ) and methylene blue (\blacktriangle): 25°C and 2 h.

small amounts of dye in initial solutions, between 0.5 g/L and 1.75 g/L at intervals of 0.25 g/L, were selected for WP-1 and WP-2 because of their relatively low dye uptake ability. The relatively high initial dye concentrations, ranging from 1.5 g/L to 4.0 g/L at intervals of 0.5 g/L, were used for WP-3 and WP-4 because of their high sorption capacity. The sorption of C. I. Acid Red 88 by activated charcoal at pH 7.5, as a comparison, was carried out under the same conditions as that for WP-3 and WP-4.

The dye sorption of wool powders at 25°C was exhibited by plotting the amount of sorbed dye (q_e) against equilibrium concentration (C_e) in Figure 7. It suggests that sorption capacity of wool powders is dependent on particle size, chemical treatment of the wool and the nature of the dyes.

Figure 7 shows that the finer the wool particle, the greater is the dye sorption capacity. For example, as the particle size was decreased from 500 μm for WP-1 to 5 μm for WP-3, the amount of sorbed C. I. Acid Red 18 increased from 80 mg/g by WP-1 to 300 mg/g by WP-3. Similar results were also found in our previous study.⁸ The higher dye sorption of fine wool powder can be related to its increased surface area and disrupted surface structure. The finer the wool powder, the greater is its surface area, e.g. 0.94 m^2/g for WP-1 and 6.13 m^2/g for WP-4. As a result, more active sites were exposed on the surface of the fine wool powder to interact with dye molecules, leading to the enhanced dye sorption of the fine wool powder. In addition, the outer cuticle cells of fine wool powders, WP-3 and WP-4, were disrupted by mechanical milling, so dyes more easily penetrated into the interior of fine wool powders because of the absence of the cuticle cells, which act as a barrier for the dye diffusion. The detailed explanation has been given in a previous study.⁸

The sorption capacity of WP-4 for acid dyes was lower than that of WP-3, but for basic methylene blue, it was the opposite. Because WP-4 was chlorinated with sodium salt of dichloroisocyanuric acid (DCCA) during its production, the formation of cysteic acid groups as a result of oxidation of the wool, introduced more negative surface charge to WP-4. It can be seen from Figure 2 that, in comparison to WP-3, WP-4 is comparatively less positive at pH 2.5 and more negative at pH 7.5. Thus, the electrostatic attractive forces between the positively charged WP-4 and anionic acid dyes at pH 2.5 are relatively weaker, resulting in the lower uptake of acid dyes of WP-4 than that of WP-3 (such as C. I. Acid Red 18 in Fig. 7); the electrostatic force between the negatively charged WP-4 and the basic methylene blue at pH 7.5 are slightly stronger, leading to its higher uptake of the basic dye (see methylene blue in Fig. 7).

The nature of the dyes impacts on their sorption by wool powders. It was found that the amount of

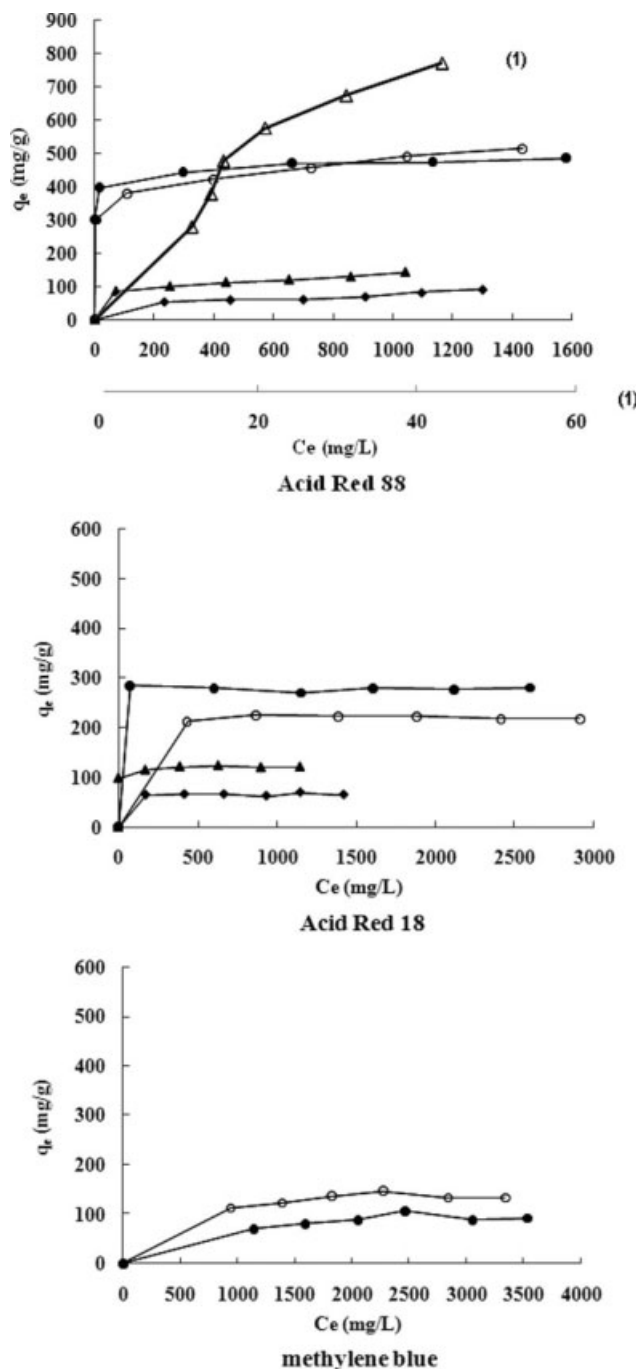


Figure 7 Dye sorption behavior of WP-1 (\blacklozenge), WP-2 (\blacktriangle), WP-3 (\bullet), WP-4 (\circ), and activated charcoal (Δ): 25°C, 2 h.

sorbed hydrophobic acid dye (C. I. Acid Red 88) is more than that of the hydrophilic acid dye (C. I. Acid Red 18), and the uptake of acid dyes is higher than that of the basic dye. For example, the sorption capacities of WP-3 for C. I. Acid Red 88, C. I. Acid Red 18, and methylene blue are approximately 480 mg/g, 300 mg/g, and 100 mg/g at equilibrium, respectively. The difference in the acid dye uptake behavior is explicable in terms of the hydrophobic/

hydrophilic character of a dye. The more hydrophobic a dye, the higher is the substantivity of the dye for wool. The hydrophobic property of an acid dye can be quantitatively characterized by measuring its hydrophobic/hydrophilic ratio in a butan-1-ol/water (50/50) system. The higher the ratio, the more hydrophobic is the dye. Although the structures of these two acid dyes are similar, C. I. Acid Red 88, with a hydrophobic/hydrophilic ratio of 58.4, is more hydrophobic than C. I. Acid Red 18 that has a hydrophobic/hydrophilic ratio of 0.04, essentially because the former has one sulphonate group while the latter has three sulphonate groups.⁸ The comparatively high uptake of C. I. Acid Red 88 is because of its rather hydrophobic property and small relative molecular mass. In the case of cationic methylene blue, the carboxylate groups on wool could be responsible for its binding through electrostatic interactions. The reason for its lower uptake than acid dyes' is not quite clear, but is likely due to its different chemical structure.

In a previous study,⁸ sorption of C. I. Acid Red 88 (1.0 g/L) by wool powders and activated charcoal was conducted only at pH 4.5, at which dye sorption capacities of both wool powders and activated charcoal are not the maximum (see Figs. 4 and 6), the rate and extent of dye uptake by WP-3 and WP-4 were comparable to that by activated charcoal, viz. 100% of dye was taken up by both wool powders (WP-3 and WP-4) and activated charcoal. In this study, the dye (C. I. Acid Red 88) was sorbed under the optimum pH values, viz. pH 2.5 for wool powders, and pH 7.5 for activated charcoal, and fine wool powders (WP-3 and WP-4) still possess comparatively high dye sorption capacity (~500 mg/g), i.e. about 60% of that of activated charcoal (800 mg/g) (C. I. Acid Red 88 in Fig. 7).

Dye uptake at 50°C

Dye sorption behavior of wool powders at a high temperature (50°C) was investigated using C. I. Acid Red 88 and methylene blue. The initial dye concentrations and pH values were the same as that at 25°C, and the results are given in Figure 8.

Compared with the results in Figure 7, increasing dyeing temperature can enhance the dye sorption abilities of large wool particles, WP-1 and WP-2. The amount of sorbed C. I. Acid Red 88 by WP-1 and WP-2 was raised to around 190 mg/g at 50°C from less than 100 mg/g at 25°C. However, there was no significant increase in the sorption of both C. I. Acid Red 88 and methylene blue by WP-3 and WP-4 with increasing temperature.

The increased dye sorption ability of large wool powders, WP-1 and WP-2, with increasing dyeing temperature could be related to the structure of

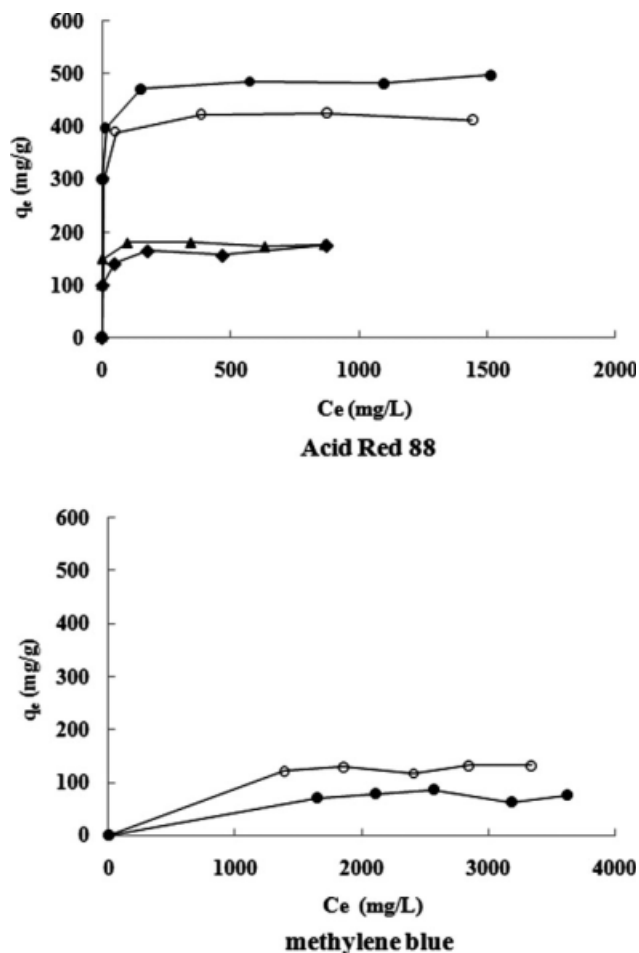


Figure 8 Dye sorption behaviors of WP-1 (◆), WP-2 (▲), WP-3 (●) and WP-4 (○): 50°C, 2 h.

wool and the swelling of wool in water. Wool is an organic polymer. The macromolecules in wool are attached to each other through many bonds, such as hydrogen bonds and van der Waals forces. When wool is immersed in water, water molecules can enter the amorphous regions in between the long chain macromolecules of wool. As a result, some bonds between the macromolecules are broken, resulting in the movement of the macromolecules. The enlarged porous structure of wool allows the large dye molecules to diffuse into the interior of wool. As the dyeing temperature is increased, the movement of the macromolecules increases and the structure of wool opens up more. Thus the penetration of dye became easier, leading to an increased dye sorption of WP-1 and WP-2 at 50°C. In addition, the breakage of the bonds between the macromolecules, as a result of swelling of wool in water, could provide more additional active sites for dye binding, which can also enhance the amount of sorbed dye on wool.^{6,21}

The impact of temperature on dye sorption of finer wool powders, WP-3 and WP-4, is slight. It

could be deduced that the saturated dye sorption of the fine wool powders occurred at 25°C. Dye molecules penetrated the interior of the fine wool powders, and occupied almost all of the dye sites at 25°C; therefore, there were no additional interactions between wool and dye molecules when increasing temperature to 50°C.

Isotherm adsorption of wool powders

During dye sorption by wool powders, both absorption and adsorption can occur. The penetration of dye into wool powders has been examined using a confocal microscopy in conjunction with a fluorescent stain, Uvitex CF 530%⁸. In this study, the surface sorption model of wool powders was investigated using Langmuir and Freundlich isotherm models, both of which are commonly used for describing adsorption isotherm of various adsorbents.^{2,5,22}

The Langmuir isotherm is based on the assumption that the adsorbed material forms a monolayer on the uniform surface of an adsorbent at a constant temperature, and the adsorption of molecules at one site is not affected by the sorbed molecules at the adjacent sites.²³ The widely used Langmuir equation is given below:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \quad (3)$$

where q_e is the amount of dye adsorbed on the adsorbent at equilibrium (mg/g)

C_e is the equilibrium dye concentration in solution (mg/L)

q_{max} is the maximum monolayer capacity of the adsorbent (mg/g)

K_L is the Langmuir adsorption constant (L/mg).

The plot of C_e/q_e versus C_e is a straight line with the slope of $1/q_{max}$ and the intercept of $1/q_{max}K_L$.

The Freundlich isotherm is an empirical equation, which describes the adsorbate molecules are adsorbed on the stronger binding sites of the adsorbent first and then the binding strength decreases as the sorption proceeds.²³ It is not limited to a monomer layer.²² The well known Freundlich isotherm is represented by the following equation:

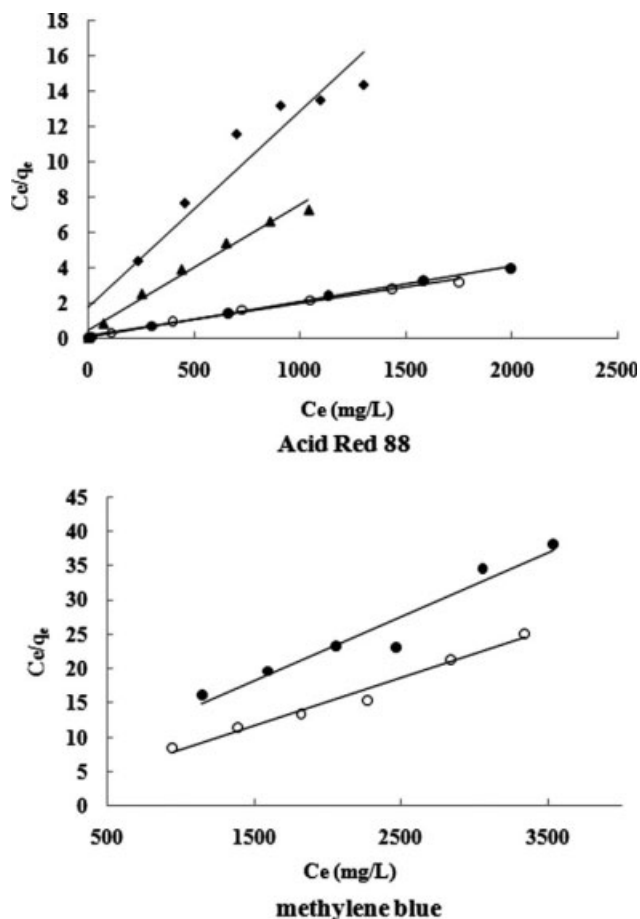


Figure 9 Langmuir plots for dye adsorption of WP-1 (◆), WP-2 (▲), WP-3 (●) and WP-4 (○) at 25°C.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where q_e is the amount of dye adsorbed on the adsorbent at equilibrium (mg/g)

C_e is the equilibrium dye concentration in solution (mg/L)

K_F is the adsorption capacity of the adsorbent (L/g)

n is the adsorption intensity.

The plot of $\log q_e$ against $\log C_e$ gives a straight line with the slope of $1/n$ and the intercept of $\log K_F$.

TABLE II
Langmuir Isotherm Parameters for Dye Adsorption of Wool Powders at 25°C

Wool powder	C. I. acid red 88			Methylene blue		
	q_{max} (mg/g)	K_L (L/mg)	R^2	q_{max} (mg/g)	K_L (L/mg)	R^2
WP-1	106.4	0.003	0.9064	–	–	–
WP-2	149.3	0.009	0.9839	–	–	–
WP-3	500	0.042	0.9988	107.53	0.0022	0.9376
WP-4	555.6	0.013	0.9916	142.86	0.0057	0.9798

TABLE III
Freundlich Isotherm Parameters for Dye Adsorption of Wool Powders at 25°C

Wool powder	Acid red 88				Methylene blue			
	1/n	log K_F	K_F (L/g)	R^2	1/n	log K_F	K_F (L/g)	R^2
WP-1	0.2857	1.0226	10.53	0.8167	–	–	–	–
WP-2	0.1779	1.5903	38.93	0.9528	–	–	–	–
WP-3	0.0622	2.493	311.17	0.961	0.2422	1.1355	13.66	0.5541
WP-4	0.0982	2.3924	246.83	0.9557	0.1473	1.6299	42.65	0.5476

In this study, experimental data, the amount of sorbed dye (q_e) and the equilibrium dye concentration (C_e), obtained from sorption of C. I. Acid Red 88 and methylene blue on wool powders at various initial dye concentrations at 25°C, were fitted to Langmuir and Freundlich isotherm equations. The plots of Langmuir and Freundlich are shown in Figures 8 and 9, respectively. The values of the constants along with the correlation coefficients (R^2) are summarized in Tables II and III, respectively.

It can be seen from Figures 9 and 10, as well as Tables II and III, that the dye adsorption of wool powders fit Langmuir isotherm very well because of the linear plot with the range of correlation coefficient (R^2) between 0.9064 and 0.9988. This fact indicates that the dye sites homogeneously distribute on the surface of wool powders, and the monolayer of dye molecules covers the surface of wool powders.

The Langmuir isotherm model can be used to estimate the maximum sorption capacity of an adsorbent where it could not be reached through experiments.²⁴ The parameter q_{max} in Table II reveals that the maximum uptake of C. I. Acid Red 88 by WP-1, WP-2, WP-3, and WP-4 at 25°C was 106.4 mg/g, 149.3 mg/g, 500 mg/g, and 555.6 mg/g, respectively, and that of methylene blue was 107.5 mg/g and 142.9 mg/g by WP-3 and WP-4, respectively. The dye sorption capacities of fine wool powders are comparable with, or even better than, that of most other sorbents (as listed in Table IV).

Some Langmuir constants can also provide useful information to estimate the efficiency of dye sorption by wool powders. For example, the Langmuir adsorption constant K_L represents the affinity between the sorbent and the sorbate; the higher the value of K_L , the higher is the affinity. The values of K_L in Table II indicate that the affinities of wool powders, WP-3 and WP-4, for C. I. Acid Red 88 are higher than those for methylene blue. Therefore, using wool powder to remove acid dyes would be more efficient than to sorb basic dyes.

The thermodynamic parameters, free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°), were calculated from the following equations,²⁵ respectively.

$$\Delta G^\circ = -RT \ln(K) \quad (5)$$

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (6)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (7)$$

Where R is the ideal gas constant (8.314 J mol⁻¹ K⁻¹)

T is the absolute temperature (K)

K is the equilibrium constant, which is obtained from K_L in Langmuir equation. K_1 and K_2 are the equilibrium constants at temperatures T_1 (25°C) and T_2 (50°C), respectively.

The values of ΔG° , ΔH° , and ΔS° are summarized in Table V. The positive values of ΔG° indicate that

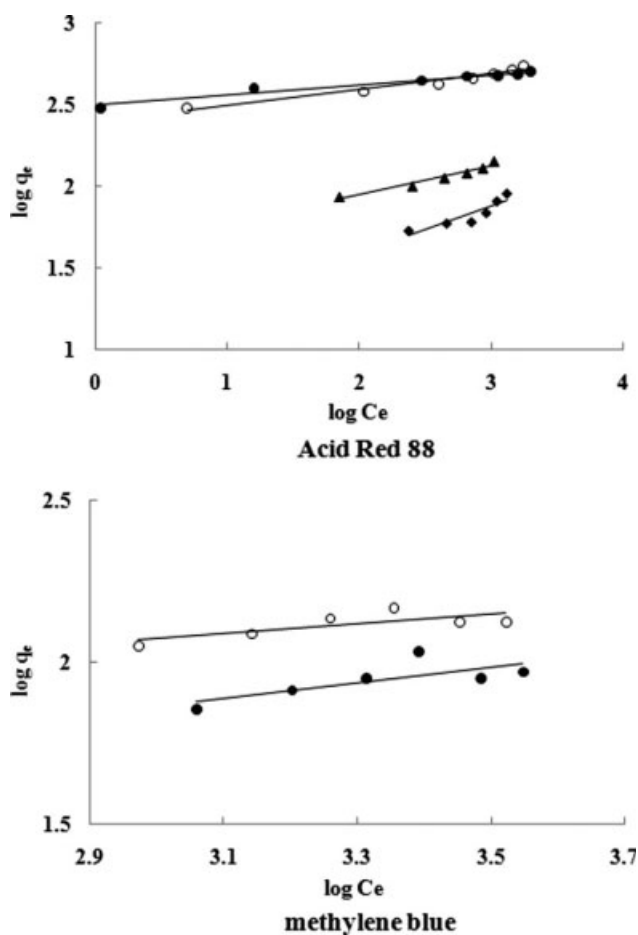


Figure 10 Freundlich plots for dye adsorption of WP-1 (◆), WP-2 (▲), WP-3 (●), and WP-4 (○) at 25°C.

TABLE IV
Sorption of Methylene Blue and Acid Red 88 by Other Sorbents FROM Literatures

Sorbate	Sorbent	Temperature (°C)	Contact time (hour)	pH	q_{\max} (mg/g)
Methylene blue	Activated charcoal ²⁵	25	0.5		0.024
	Lemon peel ²⁶	32	24		33.2
	Fe (III) / Cr (III) hydroxide ²⁷	Room temperature			22.8
	Banana peel ²⁸	30	24		20.8
	Orange peel ²⁸	30	24		18.6
	<i>Corynebacterium glutamicum</i> ¹⁸	25	12	6	117.4
				9	207.3
	Succinated <i>Corynebacterium glutamicum</i> ¹⁸	25	12	6	147.5
				9	337.5
	Activated carbon (SPC-100) ¹⁸	25	12	6	295.6
				9	457.4
	Activated carbon (SPS-200) ¹⁸	25	12	6	493.6
			9	500.6	
	Clay ²¹	20	1		6.3
	Fly ash ²⁹	30	2	8	5.72
acid red 88	A fresh water macro alga <i>Azolla filiculoides</i> ³⁰	Room temperature	12	7.0	123.5
	<i>Azolla rongpongs</i> ²⁴	25	12	2.5	71.43
	<i>Azolla microphylla</i> ²³	30	12	3.0	54.89

the adsorption of C. I. Acid Red 88 by wool powders was spontaneous, and the decrease in ΔG° with the increase in temperature suggests that the adsorption process is favorable at high temperature. The positive values of ΔH° and ΔS° show the adsorption is endothermic and the affinity of wool powders for C. I. Acid Red 88.

CONCLUSIONS

The influence of pH on the dye sorption behavior of wool powders is dependent on the type and the hydrophobic/hydrophilic character of the dyes. As the pH of dye solution was increased from pH 2 to pH 10, the sorption capacity of wool powders for acid dyes decreased, but increased for a basic dye. The maximum uptake of acid dyes occurred at pH 2.5, and at pH 7.5 for methylene blue. In the case of acid dyes, uptake of the hydrophilic acid dyes (C. I. Acid Red 13 and C. I. Acid Red 18) declined remarkably, whereas that of the relative hydrophobic dye (C.I. Acid Red 88) decreased slightly with increasing pH. It is concluded that the hydrophilic acid dyes bind to wool mainly through the electrostatic forces,

whereas the hydrophobic dyes through hydrophobic interactions.

Maximum dye sorption occurred at 25°C for the finer wool powders. Increasing dyeing temperature did not impact the dye sorption of fine wool powders, but increased the dye uptake of wool powders with a large particle size.

Comparison with activated charcoal and other sorbents indicates that fine wool powders have excellent dye sorption capacity even at room temperature, and may be used as a potential sorbent.

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TABLE V
Thermodynamic Properties of Wool Powders for C. I. Acid Red 88

Wool powder	Temperature (°C)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol K)
WP-1	25	14.62	104.58	0.302
	50	7.07		0.302
WP-2	25	11.67	147.58	0.456
	50	0.27		0.456
WP-3	25	7.85	39.19	0.105
	50	5.23		0.105
WP-4	25	10.79	52.98	0.142
	50	7.22		0.142

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