

Full Length Research Paper

Synthesis and application of polyethylene glycol/vinyltriethoxy silane (PEG/VTES) copolymers

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Accepted 27 June, 2011

Many studies have explored dye wastewater treatment methods; however, concerns relating to the dye wastewater composition and cost still exist. In this study, we used polyethylene glycol (PEG) and vinyltriethoxy silane (VTES) in different proportions to produce a series of PEG-VTES copolymers, to investigate the interaction between various dyes and the impact of these copolymers on dye absorption. The copolymer molecular structure was confirmed by Fourier transform infrared spectroscopy (FT-IR) and their impact on dye absorption and dye interaction was investigated. We demonstrate that the series of copolymers produced displayed enhanced dye decolorization with increasing copolymer dose and time. Additionally, the PEG/VTES copolymers and dyes interacted, as the copolymer enabled a shift of the λ_{\max} of UV, reducing the absorbance. We also demonstrate that addition of the copolymers reduced the overall zeta electrical potential value of the dye solution and improved dye decolorization most potently at the lowest PEG-VTES molar ratio (2:1).

Key words: Polyethylene glycol, copolymer, compound, decolorization.

INTRODUCTION

With the development of the dye industry, dye wastewater has emerged as a major source of water pollution. In addition to a large number of organic substances, dye wastewater possesses a deep color, toxicity and may pollute the environment (Qi et al., 2009; Valeria et al., 2008). Wastewater treatment methods include adsorption procedures, chemical coagulation, membrane separation, ultrasonic processes, oxidation processes, electrolytic procedures and biological methods. These methods are effective but are not without their disadvantages. Fenton's reagent and membrane filter techniques have been applied to all dye types, but may cause sludge; the ozone half-life is only 20 min after it is injected into water, electrochemical destruction is safer but has high electrical power costs and activated carbon adsorption can remove various dyes, but is not cost-effective (Tim et al., 2001). Thus, developing new copolymers for wastewater treatment is required and the copolymer

adsorption of dyes can be used to enhance textile color prior to dye pre-treatment.

Polyethylene glycol (PEG; molecular formula $H-(O-CH_2-CH_2)_n-OH$) is a high-molecular weight polyether compound produced by the interaction of ethylene oxide with water, ethylene glycol or ethylene glycol oligomers. PEG is a glycol non-ionic surface active agent in which the oxygen atoms are hydrophilic, while the $-CH_2-CH_2-$ displays lipophilicity, meaning PEG is soluble in water and most organic solvents (Inui et al., 2010; Zhao et al., 2010; Sawant and Torchilin, 2010). PEG has many physical and biological properties, including hydrophilicity, dissolubility, non-toxicity, non-immunogenicity and no reject reactions. It is widely used in the pharmaceutical industry, agriculture, food handling, biological and material science and chemical engineering fields (Kitagawa et al., 2010). In recent years, a PEG functional monomer has been used to prepare hydrogels of differing structures (Hazer, 1992; Yildiz et al., 2010; Lynn and Bryant, 2011; Diez, 2009; Stahl et al., 2010). For wastewater treatment, PEG has served as a carrier for the immobilization of activated sludge.

Vinyltriethoxy silane (VTES) is a silane containing

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Table 1. Code description of vary copolymers.

PEG: VTES (mole ratio)	Code
3 : 1	PV25
2 : 1	PV33
1 : 1	PV50
1 : 2	PV67
1 : 3	PV75

unsaturated double bonds. It produces graft or hydrolytic condensation with free radicals (Zhi et al., 2011). Olefin homo- or copolymers can be cross-linked with vinyl-triethoxy silane (Youngchan et al., 2008; Sachin et al., 2005), including low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), polyvinyl chloride (PVC), chlorinated polyethylene (CPE), ethylene propylene rubber (EPR), ethylene vinyl acetate (EVA) and other ethylene copolymers. Copolymers and VTES are cross-linked through hydrolysis and condensation reactions with alkoxy groups, which greatly increase the impact strength, heat resistance, chemical resistance, creep resistance, wear-resistance and adhesive properties of the copolymers. Additionally, VTES can use Sol-Gel to compose heterocyclic azo dyes (Yen and Chen, 2010), but no relevant study on its application to dye wastewater treatment has been reported.

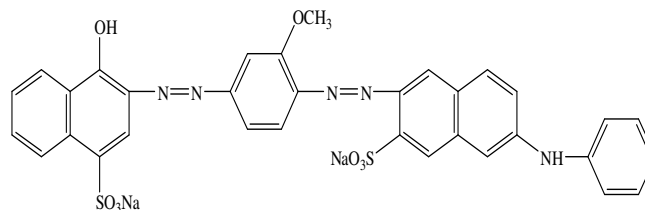
Many studies have explored dye wastewater treatment methods; however, concerns related to the complex dye wastewater composition and cost still exist. In this study, we used the copolymerization of PEG and VTES in varying proportions. We found that the copolymer contains the ability of decolorization; the decolorization can be rated the highest when the PEG: VTES (mole ratio) was 2:1. The copolymer also interacted with dyes and resulted in λ_{max} of the dye solution shifted to the wavelength. In addition, by adding the copolymer, a lower zeta potential was obtainable and increased the accumulation of the dye particles.

MATERIALS AND METHODS

Polyethylene glycol (PEG, M.W. 400), triethoxyvinylsilane (97%, VTES) (Acros Organics), and ceric ammonium nitrate (CAN) (Acros Organics) were obtained from Hayashi Pure Chemical Ind., Ltd. Polyacrylamide (solid content 90%, commercially sold as high-molecule coagulant, PAAm) was purchased from Seimao Chemical Material Co., Ltd. and C.I. Direct Blue 146 was purchased from C.I. Direct Blue 146.

Assay determination and methods

We used a FT-IR (Bio-Rad Digilab FTS-3000) and UV/vis spectrophotometer (UV-vis) (JASCO V-530). The testing conditions were 475 to 660 nm. For the decolorization rate test method, 0.05 g/l of dye solution was prepared and 100 ml of the solution was added to the PEG/VTES copolymer. The solution was then stirred for 20 min at 1000 rpm and left to stand for 4, 6, 8, 10, 12 or 24 min.



The absorbance was assessed using the UV/vis spectrophotometer decolorization rate (R) calculated as follows:

Everlight Chemical Industrial Corp.; the structural formula is as follows:

$$\text{Decolorization rate (R)} = [1 - (A/A_0)] \times 100\%$$

Where A_0 = absorbance of the maximum wave prior to decolorization; A = absorbance of the maximum wave after decolorization (Ming et al., 2000).

PEG/VTES copolymer preparation

For the PEG/VTES copolymer preparation, PEG 400 was added to a 250 ml reaction flask containing four necks, a stirring rod and a thermometer. VTES was added dropwise into the solution through an additional funnel. The solution was then stirred at ambient temperature for 30 min and 0.5 g ammonium ceric nitrate was added. The temperature of the solution was then increased to 60°C for 6 h. The product numbers are shown in Table 1 (Arslan and Hazer, 1999).

RESULTS AND DISCUSSION

FT-IR analysis of the copolymers

Figure 1 represents the infra-red spectra of PV67, VTES and PEG. As shown in Figure 1c, the PEG characteristic absorption peaks were 1296 and 1249 cm^{-1} , representing the -C-O-C- absorption peak and 1103 and 945 cm^{-1} , representing the -C-O- absorption peak (Zhimei et al., 2011; Hong et al., 2010; Philip et al., 2010). From Figure 1b, the VTES characteristic absorption peaks were 1101 and 775 cm^{-1} , representing the -Si-O-R- absorption peak, 956 cm^{-1} representing the -Si-OEt absorption peak and 1292 cm^{-1} representing the -Si-C-absorption peak (Yen and Chen, 2010; Rakesh et al., 2004). Figure 1a displays the PEG and VTES characteristic absorption peaks. As PEG and VTES produced ether bonds, a wider absorption band at 1105 cm^{-1} was evident, the -Si-C-absorption peak at 1292 cm^{-1} shifted to 1298 cm^{-1} and the -C-O-C peak at 1249 cm^{-1} shifted to 1255 cm^{-1} . At 1644 cm^{-1} , the C=C absorption peak of the PV67 was weaker than that of VTES's, because copolymer still contains a small amount of PEG impurity.

Figure 2 shows the infra-red spectra of products PV25, PV33, PV50, PV67 and PV75. Increasing doses of VTES led to more obvious hydrolytic condensation. The characteristic -Si-O-R- absorption peak at 1091 to 1105 cm^{-1} represents a wide absorption band with increasing doses of VTES. The -Si-O-R- absorption peak at 765 cm^{-1}

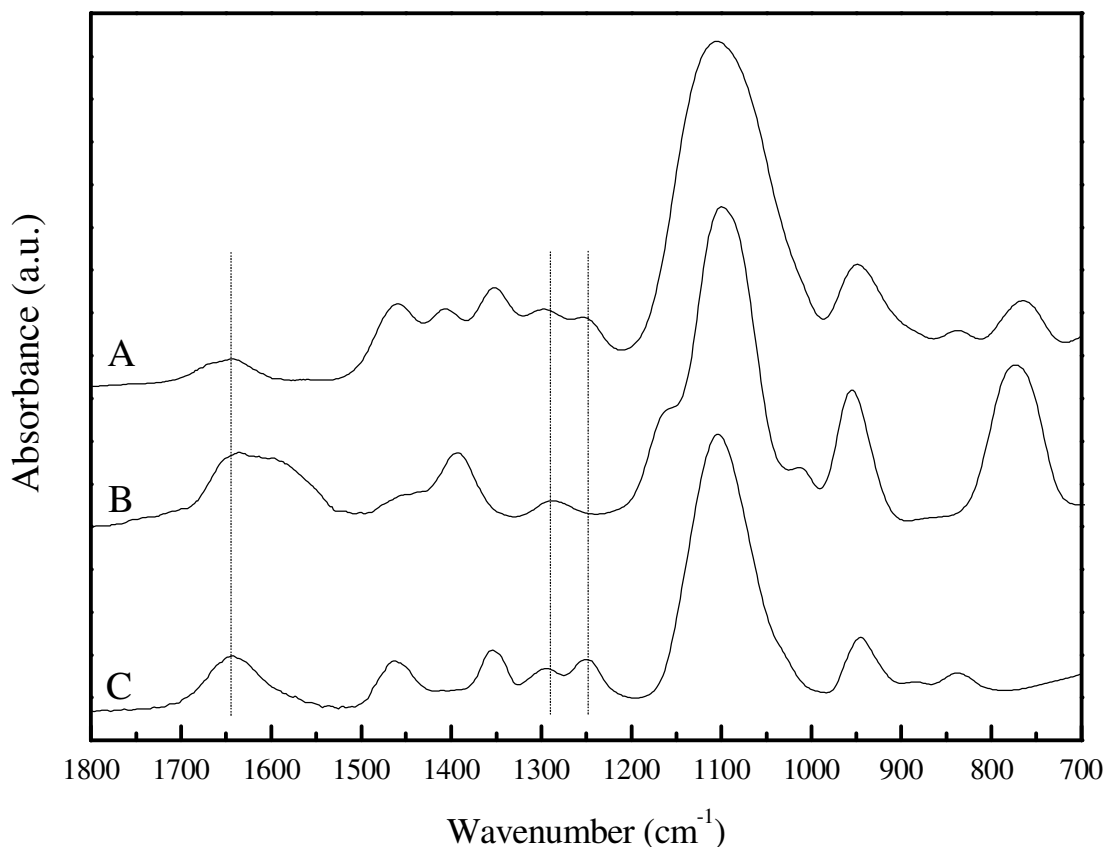


Figure 1. IR spectra of the PV67, VTES and PEG. A, PV67; B, VTES; C, PEG.

also tended to be more significant.

Application of PEG-VTES copolymers to dye solution decolorization

The impact of the PEG and VTES molar ratio and absorption time on the decolorization rate are shown in Table 2. The decolorization rate (R%) in the dye solution with the addition of the copolymers increased with time. Table 2 demonstrates that PV33 displayed the optimal decolorization rate, which was slightly increased compared with PV25. Thus, the decolorization effects increased with increasing doses of VTES during the copolymer reaction, when the VTES dosage was less than 33%. Following a comparison of PV50, PV67 and PV75, the decolorization rate observed was PV50 > PV67 > PV75. It was evident that the decolorization displayed the reverse effect when the VTES dosage exceeded 33%. PV33 displayed the optimal decolorization effect, in the order of PV33 > PV25 > PV50 > PV67 > PV75. The affinity proportion was optimal when the synthetic copolymer of PEG: VTES molar ratio was 2:1. Under high-speed rotation, the product and dye solution are mixed and as they collide in solution, hydrogen bonds with an -OH in the dye molecular

structure and $-\text{SO}_3^-$ decomposed from the dye molecules are produced, leading to absorption and deposition (Yongchun and Enpu, 2003). When VTES is present in small proportions, the hydrophilic product dissolves in water, meaning the adsorbed dye cannot deposit and the discoloration effect worsens. If the VTES dosage is excessive, the product becomes too lyophobic, so it does not fully mix with the dye solution, reducing the absorption effect. As shown in Table 2, as the time for the product dye absorption increased, the decolorization ratio increased. If the absorption time reaches 24 h, the decolorization rate of PV25, PV33, PV50 and PV67 exceeded 90%. Polyacrylamide (PAAm) is the wastewater treatment agent currently used in industry. For comparison, the copolymer product decolorization ratio exceeded that of PAAm. After several hours, the decolorization rate of the product increased, while PAAm displayed no significant effect. PAAm can be combined with dyes; however, the solution viscosity increases when PAAm is dissolved in water. As a result, the solid solution displays a slow separation speed and the flocculate displays a poor separation effect that does not deposit quickly. Figure 3 shows the decolorization effect in the dye solution with the addition of PV33 or PAAm. When PV33 was added for 8 h, it was clearer than when PAAm was added for same hours; there was still a deep color,

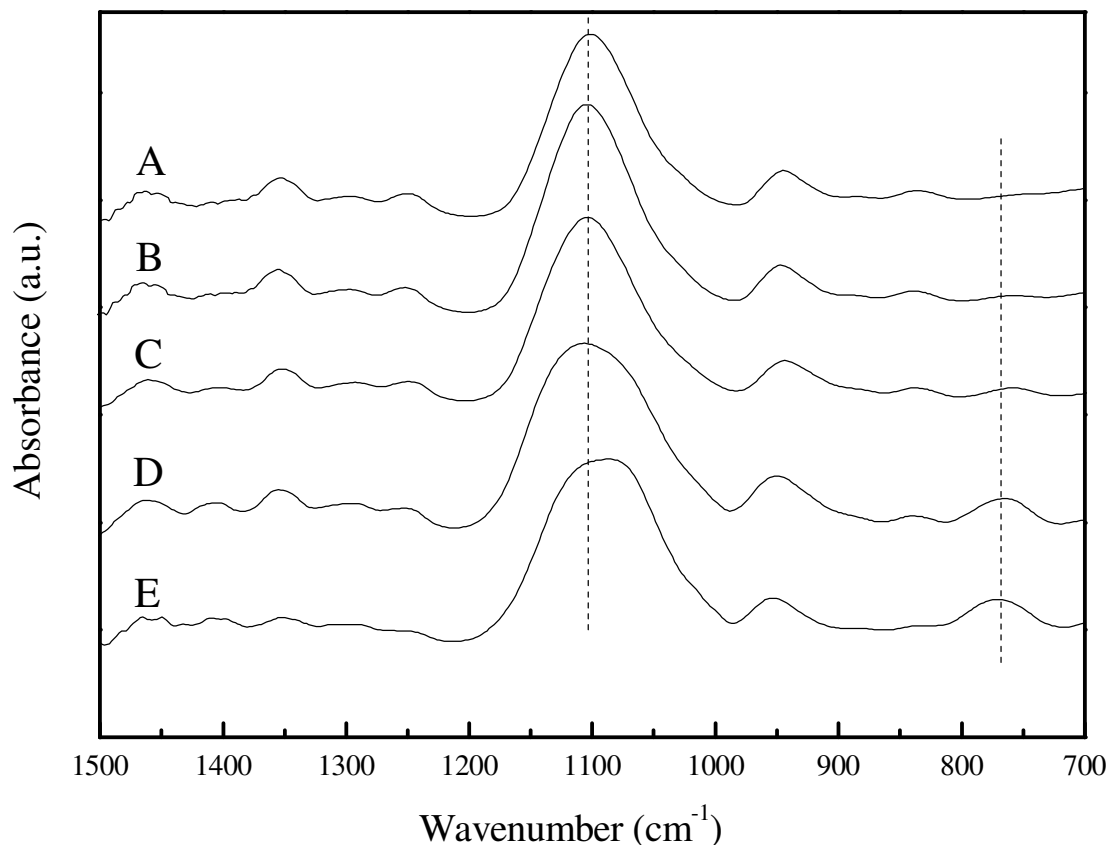


Figure 2. IR spectra of the copolymers. A, PV25; B, PV33; C, PV50, D, PV67; E, PV75.

Table 2. The effect of the decolor processing time on the decolor rate (%).

Copolymer ^a	Decolor process time (h)					
	4	6	8	10	12	24
PV25	74.14	80.59	82.18	82.27	82.91	92.10
PV33	77.09	81.55	82.60	83.61	85.19	93.04
PV50	71.89	76.09	80.58	80.29	83.17	92.22
PV67	69.27	74.76	75.15	77.79	79.06	91.34
PV75	35.12	54.02	58.98	60.44	63.46	72.12
PAAm	22.61	23.27	23.54	24.04	24.53	26.39

^a The concentration was 1.0 g/100 ml.

and some flocculate had failed to deposit. Additionally, the decolorization effect of PV33 increased with time over 24 h, while the decolorization effect of polyacrylamide was not alter, consistent with the data in Table 2.

Impact of the PEG-VTES copolymer concentration on the decolorization ratio of the dye solution

Table 3 illustrates the effects of the varying concen-

trations of the PEG-VTES copolymers on the decolorization rate (R%) of the dye solution. Table 3 shows that the levels of PV25, PV33 and PV75 increased with increasing doses of the copolymers, while the decolorization rate also increased. Taking PV33 as an example, the decolorization ratio was 69.53% when the PV33 dosage was 0.5 g/100 ml, which increased to 83.30% when the PV33 dose increased to 3.0 g/100 ml. As the product dosage increased, the increasing collision rate of the product and dye molecules occurs, increasing

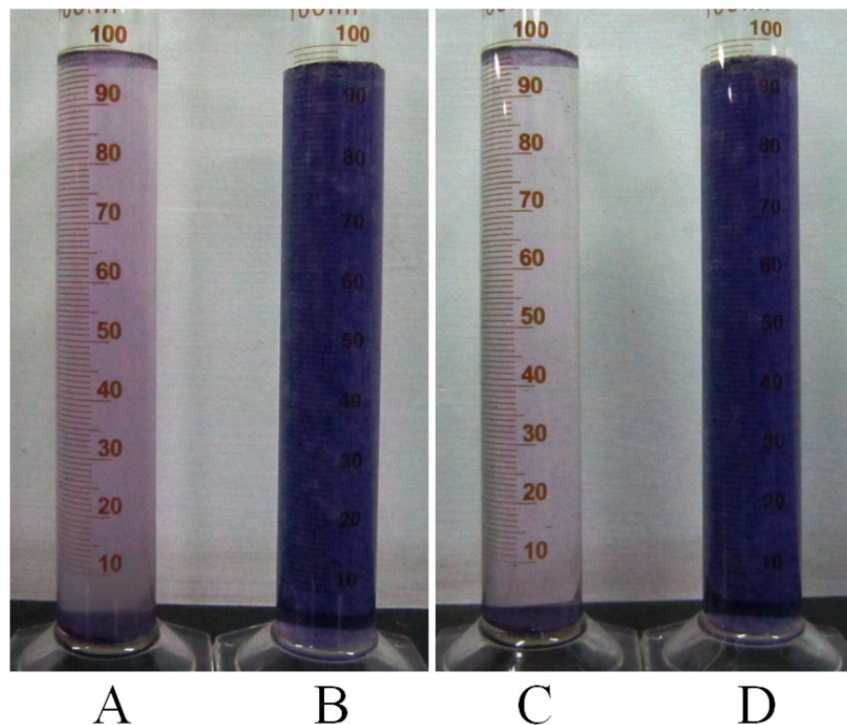


Figure 3. The effect of the PV33 and PAAm on the decolor solutions under various processing time [8 h: PV33 (A); PAAm(B); 24 h; PV33 (C); PAAm(D)].

Table 3. The effect of the copolymers concentrations on the decolor rate^a (%).

Copolymer	Concentration of copolymer (g/100 ml) ^b			
	0.5	1.0	2.0	3.0
PV25	60.46	74.14	76.04	80.22
PV33	69.53	77.09	77.42	83.30
PV75	2.63	35.12	40.58	44.52

^a Time of the decoloration was 4 h; ^bdye solution volume was 100 ml.

hydrogen bond production, leading to adsorption and deposition, which increased the decolorization effect.

Interaction between PEG-VTES copolymer and dyes

Figure 4 shows the UV absorption spectrum of PV33 in the dye solution, where A = the solution without product. The PV33 concentrations of Figure 4B to I were 6.0×10^{-4} , 9.0×10^{-4} , 1.5×10^{-3} , 2.0×10^{-3} , 3.0×10^{-3} , 4.0×10^{-3} , 5.0×10^{-3} and 6.0×10^{-3} g/l, respectively. The λ_{\max} of the dye solution without the product was 566 nm, which did not change in the presence of 6.0×10^{-4} g/l PV33. However, the λ_{\max} of the dye solution shifted to the shorter wavelength of 565 nm when the PV33 concentration increased to 9.0×10^{-4} g/l. Further increases in the PV33 concentration led to further shifts in the λ_{\max} towards shorter wavelengths. When the PV33 concentration increased to 6.0×10^{-3} g/l,

the λ_{\max} of the dye solution shifted to a shorter wavelength (536 nm) compared with the dye solution without the product, because the interaction between the PV33 hydrophobic group and the dye affinity produced new compounds (Sis and Birinci, 2009; Ofir et al., 2007; Wanwisa et al., 2008). The compound formation led to a blue shift in the UV absorption spectrum. The UV absorbance reduced with increasing concentrations of PV33, due to PV33 dye adsorption reducing the dye concentration.

Zeta electrical potential under the interaction between PEG-VTES copolymers and dyes

Figure 5 shows the zeta electrical potential in the interaction between the PEG-VTES copolymers and dyes. Figure 5A to E represent PV25, PV33, PV50, PV67

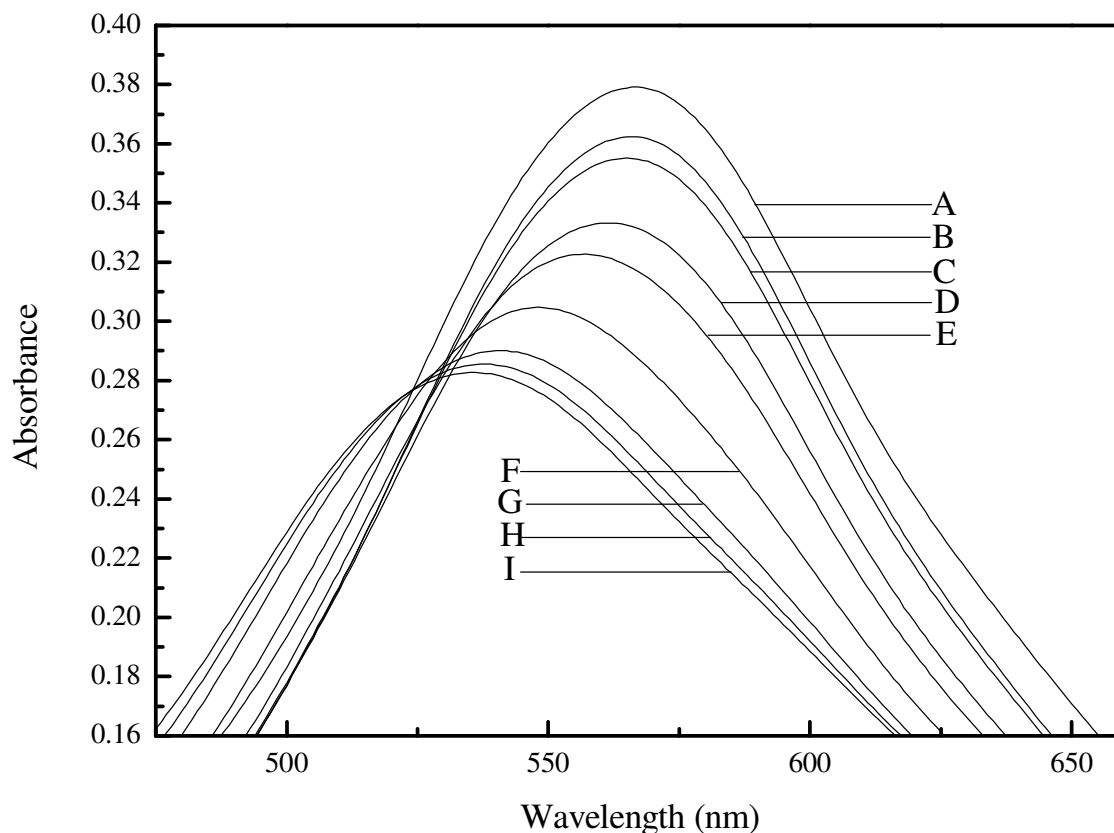


Figure 4. UV-Vis absorption spectra of the PV33. A, No added copolymer, concentration of the PV33 (g/l); B, 6.0×10^{-4} ; C, 9.0×10^{-4} ; D, 1.5×10^{-3} ; E, 2.0×10^{-3} ; F, 3.0×10^{-3} ; G, 4.0×10^{-3} ; H, 5.0×10^{-3} ; I, 6.0×10^{-3} .

and PV75, respectively. Figure 5 shows that the zeta potential value was lowest for PV33, while PV75 displayed the highest value. For the dye solution, the dye particles and distributed media displayed frictional electrification. Once the dye particles were electrified, the dye molecules displayed electrostatic repulsion, meaning that contact and accumulation between the dye particles did not occur. The addition of the PEG-VTЭС copolymers reduced the surface load of dye particles, reducing this repulsive force. The particles were accumulated and deposited during collisions (Lai and Chen, 2008; Sergey et al., 2010; Safavi et al., 2008). When the dye solution was added with PV33, the lowest zeta electrical potential may have resulted from efficient dye accumulation and an optimal decolorization effect. When PV75 was added to the dye solution, the highest zeta electrical potential means little effect on the reduction of the dye surface load occurred. Thus, the particle accumulation effect was not as efficient as PV25, PV33, PV50 or PV67 following PV75 addition. These results are consistent with the decolorization effects observed. Table 3 illustrates the effects of the varying concentrations of the PEG-VTЭС copolymers on the decolorization rate (R%) of the dye solution. Table 3 shows that the levels of PV25, PV33 and PV75 increased with increasing doses of the copolymers, while the decolorization rate also increased. Taking PV33

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Interaction between PEG-VTЭС copolymer and dyes

Figure 4 shows the UV absorption spectrum of PV33 in the dye solution, where A = the solution without product. The PV33 concentrations of Figure 4B to I were 6.0×10^{-4} , 9.0×10^{-4} , 1.5×10^{-3} , 2.0×10^{-3} , 3.0×10^{-3} , 4.0×10^{-3} , 5.0×10^{-3} and 6.0×10^{-3} g/l, respectively. The λ_{\max} of the dye solution without the product was 566 nm, which did not change in the presence of 6.0×10^{-4} g/l PV33. However, the λ_{\max} of the dye solution shifted to the shorter wavelength of 565 nm when the PV33 concentration increased to 9.0×10^{-4} g/l. Further increases in the PV33 concentration led to further shifts in the λ_{\max} towards shorter wavelengths. When the PV33 concentration increased to 6.0×10^{-3} g/l, the λ_{\max} of the dye solution shifted to a shorter wavelength (536 nm) compared with the dye solution without the product, because the interaction between the

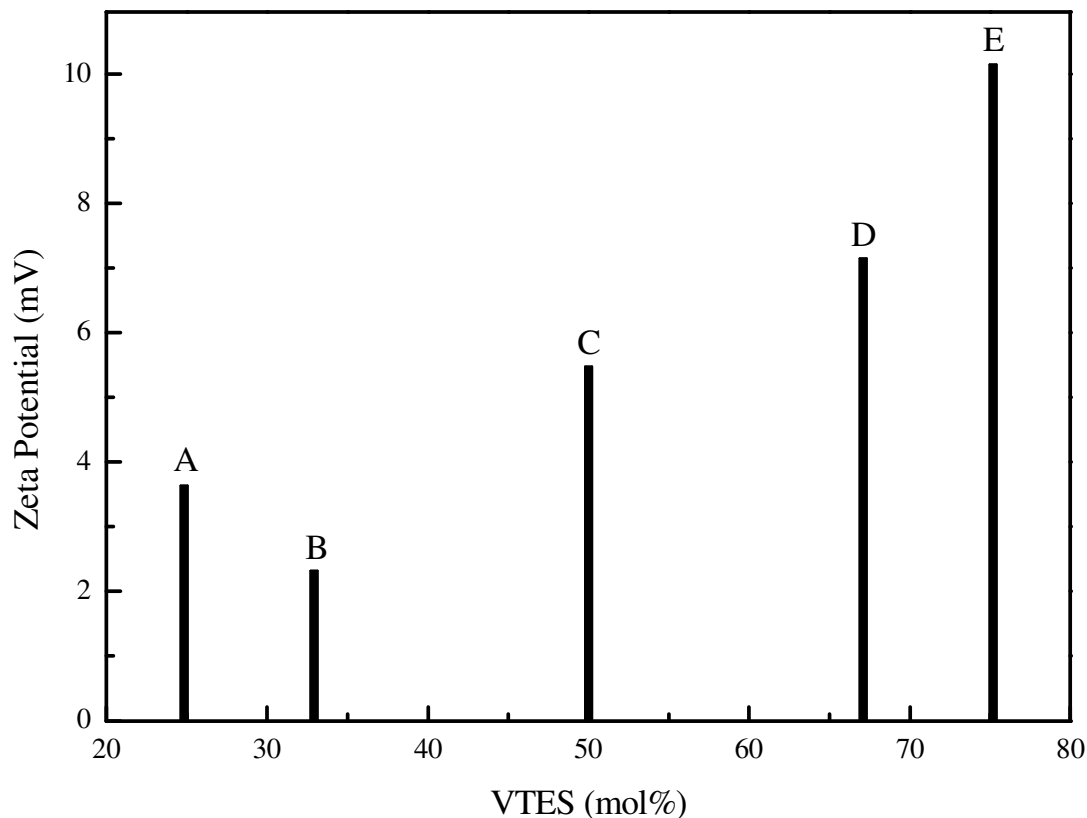


Figure 5. Zeta potential of the decolor solution. A, PV25; B, PV33; C, PV50; D, PV67; E, PV75.

PV33 hydrophobic group and the dye affinity produced new compounds (Sis and Birinci, 2009; Ofir et al., 2007; Wanwisa et al., 2008). The compound formation led to a blue shift in the UV absorption spectrum. The UV absorbance reduced with increasing concentrations of PV33, due to PV33 dye adsorption reducing the dye concentration.

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Conclusions

This study applied a titration of PEG and VTES to investigate copolymerization and the impact of a series of copolymers on both dye absorption and the interaction between dyes. The following conclusions could be drawn from this study; the product decolorization effect increased as the VTES dose increased below 33% during the reaction and the product decolorization effect reduced when the VTES dose exceeded 33%. The order of the product decolorization effects was PV33 > PV25 > PV50 > PV67 > PV75. The product decolorization rate increased with increased time and product dosage and for comparison, displayed a superior decolorization effect than PAAm. The λ_{max} of the dye solution in the absence of the product was 566 nm. When the concentration of

PV33 reached 6.0×10^{-3} g/l, the λ_{\max} of the dye solution shifted to the shorter wavelength (536 nm) versus that of the dye solution without product and the absorbance lowered with increasing concentrations. The PEG/VTES copolymers and dyes displayed an interaction and when PV33 was added to the dye solution, the lowest zeta electrical potential, indicating the most efficient accumulation of the dye particles and optimal decolorization effect occurred.

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