

## Removal of Acid Blue 113 Textile Dye from Synthetic Aqueous Solution by Adsorption and Flocculation Process Using Cationic Copolymer Poly(n-hexadecyl-4-vinylpyridinium Bromide)

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In this work, the retention of the acid blue 113 (AB113) textile dye from synthetic dye solution by using cationic poly(n-hexadecyl-4-vinylpyridinium bromide) [P4VP-C<sub>16</sub>Br] was reported. The removal of anionic dye was ascribed to two different processes. First, the batch adsorption experiments performed to investigate the effect of experimental parameters on the AB113 adsorption equilibrium. Then, the adsorption characteristics of copolymer and acid blue 113 in dilute aqueous solution were studied by UV-Vis spectrophotometry. Indeed, the adsorption equilibrium was reached within 3 h of poly(4-vinylpyridine) quaternized at 50% and the adsorption kinetics was best described by a pseudo-second-order model. Furthermore, the equilibrium modelling of AB113 removal process was described by Langmuir isotherms. On the other hand, the second method was based on the flocculation process where the [P4VP-C<sub>16</sub>Br] as a flocculant in its soluble form in acidic medium was used. Different parameters affecting the retention were studied as variable including pH of AB113; [P4VP-C<sub>16</sub>Br] dose, AB113 concentration, and contact time between the copolymer and the used dye. At the optimal dose of [P4VP-C<sub>16</sub>Br] flocculant, the removal ratio of acid blue 113 could reach more than 98% in the pH range of 2-8. Furthermore, the flocculation process using [P4VP-C<sub>16</sub>Br] was a very fast process.

**Keywords:** Removal, Acid blue 113, Adsorption, Flocculation, Isotherm, Kinetic

### INTRODUCTION

Water contaminated with dye through the discharge of toxic effluents is a serious global problem and received much attention in recent years [1-2]. Water pollution has happened due to the fast development of chemical industries such as textiles, plastics, leather, dyeing and cosmetics worldwide [2-5]. Notably, the textile industry is one of the primary industries using dyes [6].

One of the most severe environmental problems arises from the difficulties in the dye's removal due to its complicated molecular structure and low biodegradability [7-

9]. Most of these dyes, which make up 60 to 70% of all commercially produced dyes [10,11], are hazardous polyaromatic compounds with azo (-N=N-) linkages and require time-consuming processing. Acid Blue 113 (AB 113) is one of the most well-known azo dyes [12]. It is a diazo group containing acid dye widely used for polyamide, wool, and silk dyeing [13]. The presence of aromatic rings and azo bonds in the structure of this dye group reduces their biodegradability in conventional biological treatment systems. Hence, it is necessary to effectively develop techniques to remove azo dyes from wastewater [14].

Recently, many methods and technologies have been proposed and used for the treatment of wastewaters contaminated with dyes, such as membrane filtration [15],

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biological treatment [16], oxidation, photocatalytic degradation [17-19], adsorption [20,21] and coagulation-flocculation [22].

Polymeric materials such as polyelectrolytes constitute a viable alternative to remove textile dyes from polluted waters [23]. Hydrophilic and hydrophobic polymers have found wide applications in chemical separation. The ionic groups in the polyelectrolytes produce an electrostatic field that attracts diverse organic compound.

Polymers with hydrophilic and hydrophobic properties have broad applications in treating industrial waste. These molecules are characterized by the presence of alternately charged and hydrophobic groups. The balance between charge repulsions and hydrophobic interactions is sensitive to the pH of the environment, and therefore, changes in pH produce controlled conformational changes.

Poly(4-vinyl pyridine) is a polymer with an essential character allowing it to exhibit variable properties depending on the medium's acidity. Indeed, these polymers are sensitive to acids, where they become water-soluble and adopt a polyelectrolyte behaviour. Modifying these polymers by grafting new substituents introduces new chemical properties into these macromolecules [24,25].

In this work, we were interested in polymers of the same type where the main chain is poly(4-vinyl pyridine) grafted by brominated alkyl chains. This polymer exhibits a formal positive charge over the entire pH range. Therefore, it can interact effectively through electrostatic and hydrophobic interactions. The hydrophilic-hydrophobic character can be modulated by using alkyl halides for the quaternization reaction of the pyridine group of different sizes and percentages of quaternization.

This amphiphilic character would allow this polymer

matrix to pass from a charged extended chain to a compact structure. The latter is demonstrated in their field of application and allows them to interact effectively with the organic anions present on the molecule of dye.

The aim of this study is the removal of acid blue 113 in aqueous solutions by P4VP quaternized with 1-bromohexadecane at 50% using adsorption and flocculation process. The optimization of the adsorption and flocculation conditions was made possible by investigating the effects of several parameters such as the pH of AB113 solution, contact time, adsorbent dose and initial dye concentration.

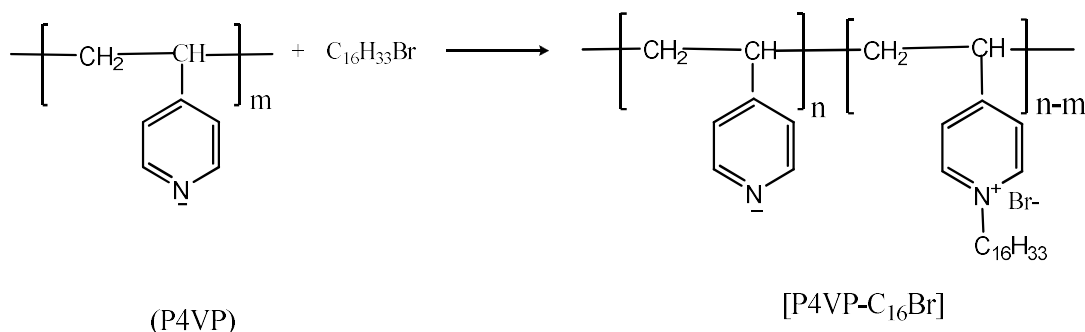
## EXPERIMENTAL

### Materials

Poly(4-vinylpyridine) (P4VP) powder was supplied by Aldrich Company. Its average molecular weight was close to 160,000 g mol<sup>-1</sup>. Acid blue 113 powder; alkyl bromide (C<sub>16</sub>H<sub>33</sub>Br) and all the solvents (analytical grade) were also supplied by Aldrich Company and used without further purification.

### Preparation of Poly(N-hexadecyl-4-vinylpyridinium bromide)

In our previous study [26,27], [P4VP-C<sub>16</sub>Br] copolymer preparation and characterization were discussed (see Fig. 1). The quaternization was done by refluxing hexadecylbromide and poly(4-vinyl pyridine) P4VP in ethanol. The reactions were conducted in a thermostated water bath (0.1 °C) under nitrogen. In order to achieve a 50% quaternization rate, the mixture was agitated for 7 days based on kinetic research that had already been completed [26,27]. The final product was dissolved in chloroform and then precipitated in a sizable



**Fig. 1.** Obtained poly(N-hexadecyl-4-vinylpyridinium bromide) by quaternization reaction of P4VP and C<sub>16</sub>H<sub>33</sub>Br.

volume of hexane under vacuum at room temperature to reach a consistent weight after the excess solvent had been evaporated.

The quaternization rate in the final product [P4VP-C<sub>16</sub>Br] was obtained by conductimetric titration method [28,29] using a standard conductimeter CD75 Taccusel. [P4VP-C<sub>16</sub>Br] quaternization rate 50% was confirmed by <sup>1</sup>H-NMR spectroscopy and ATG.

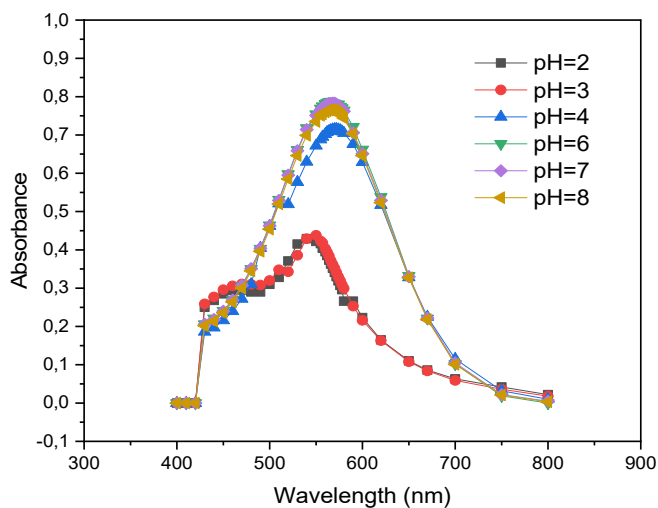
### Acid Blue 113 Solution

Acid Blue 113 dye [C.I. 26360, chemical formula: C<sub>32</sub>H<sub>21</sub>N<sub>3</sub>Na<sub>2</sub>O<sub>6</sub>S<sub>2</sub>, molecular weight: 681.65 g mol<sup>-1</sup>] was dissolved in water to imitate dye effluent.

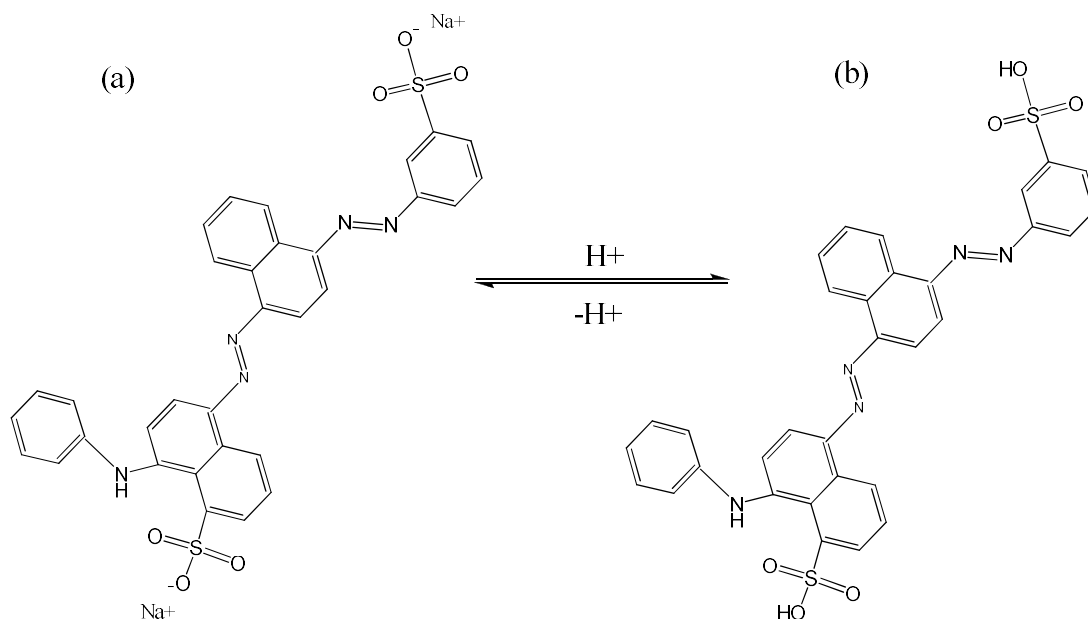
The stock solution for acid blue 113 (AB113) was made by dissolving 1000 mg of dye in 1L of double-distilled water. The diluted AB113 solution was used to create the various concentrations needed for subsequent uses. Solution pH levels were adjusted by utilizing either 1 M sodium hydroxide (NaOH) or 1 M hydrochloric acid (HCl).

It is worth noting that AB113 is a pH-sensitive dye, *i.e.*, it changes its color, its maximum wave number absorption  $\lambda_{\max}$ , and its molar attenuation coefficient  $\epsilon$  (1 mg<sup>-1</sup> cm<sup>-1</sup>) as the pH changes. From Fig. 2, we observe that the absorption intensity increases significantly when the acidity of the dye decreases. The successive deprotonation of sulfonate groups

of AB113 and the decrease in the basicity of the medium may explain this behavior (shown Fig. 3). Because of this specific compartment, it was necessary to establish the calibration curve for AB113 at different pH, which led to these findings:  $\epsilon$ :  $\epsilon = 0.00983$  l mg<sup>-1</sup> cm<sup>-1</sup> determined at  $\lambda_{\max} = 550$  nm for pH 2 and  $\epsilon = 0.01355$ ; 0.01419; 0.01553 l mg<sup>-1</sup> cm<sup>-1</sup> determined at  $\lambda_{\max} = 566$  nm for pH = 4; 6 and 8, respectively.



**Fig. 2.** UV-visible absorption spectra of acid blue 113 at different pH and at fixed concentration  $C_{AB113} = 50$  mg l<sup>-1</sup>.



**Fig. 3.** Chemical structure of AB113. (a) deprotonated (b) protonated.

## Experiments for Removal of Acid Blue 113

The removal of dye molecules from the synthetic aqueous solutions was carried out following two different methods. The first one is the batch adsorption and second method is the flocculation experiments.

### Adsorption Experiments

The [P4VP-C<sub>16</sub>Br] copolymer was added in predetermined batches to 40 ml of the AB113 solution in 100 ml beakers for each desorption experiment. At room temperature, the mixture of adsorbent and adsorbate was continuously stirred at 400 rpm (298 K). Using a UNIVERSAL Hettich type centrifuge 23 R, the sample was extracted from the solution by centrifugation after a predetermined contact time.

### Flocculation Experiments

The copolymer [P4VP-C<sub>16</sub>Br] is used as a flocculant to remove the dye AB113. First, a liquid stock solution of copolymer with a concentration of 4 g l<sup>-1</sup> was prepared by adding 0.1 g of the copolymer in a volumetric flask of 25 ml that contained 3 ml of absolute ethanol in order to solubilize our powder. Then, hydrochloric acid solution (H<sub>3</sub>O<sup>+</sup> + Cl<sup>-</sup>) was added to the 25 ml line at a 2.5 × 10<sup>-4</sup> M concentration. The prepared solution was steered for 24 h at a room temperature of 25 °C. All the required concentrations were obtained by diluting the [P4VP-C<sub>16</sub>Br] stock solution. Afterward, different volumes of [P4VP-C<sub>16</sub>Br] flocculant solution were added to 20 ml of AB113 dye solution, and that optimum flocculant concentration was then calculated. The mixture was stirred at 160 rpm and 298 K for 30 min, after which the suspension was left to settle for one minute. A UV-Vis spectrophotometer Optizen 1412V-FB was used to determine the absorbance of the supernatant. After the determination of the supernatant concentration, we used the Eqs. (1) and (2) to calculate the dye removal efficiency and the adsorption capacity q<sub>e</sub>:

$$q_e = (C_0 - C_e)V/m \quad (1)$$

$$\text{Dye removal (\%)} = 100(C_0 - C_e)/C_0 \quad (2)$$

In above equations, C<sub>0</sub> and C<sub>e</sub> are the initial and equilibrium concentrations (mg l<sup>-1</sup>) of dye AB113 solution, V is the

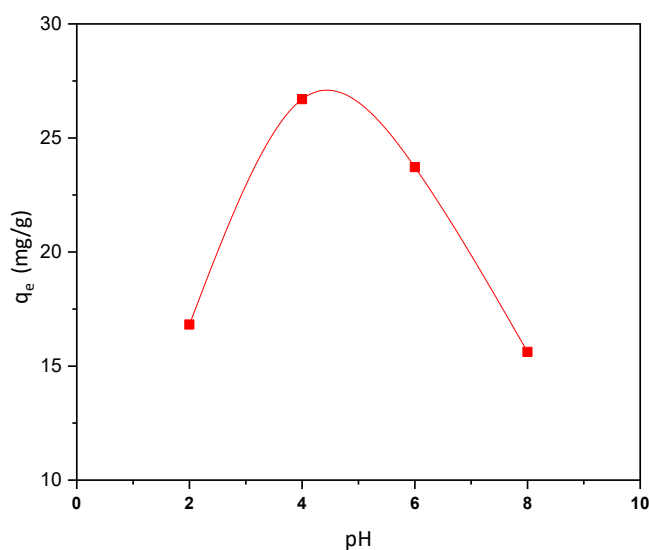
volume (ml) of dye solution, and m is the [P4VP-C<sub>16</sub>Br] mass (g) used in the experiments.

## RESULTS AND DISCUSSIONS

### Adsorption Experiments

**Effect of pH.** The pH significantly influences the adsorption process of [P4VP-C<sub>16</sub>Br] copolymer. The chemical properties of both adsorbent and adsorbate are changed by pH. Figure 4 shows the plot of adsorption capacity q<sub>e</sub> versus the pH of AB113. The pH value is varied within the range of 2-8. It is known that the positive charge of [P4VP-C<sub>16</sub>Br] copolymer and the negative charge of AB113 have a crucial role in the retention process for both acidic and basic mediums.

It is clear from Fig. 4 that the adsorption of AB113 increased with an increase in the pH from 2 to 4; after that, it decreased with an increase in the pH from 4 to 8. At a very acidic medium, AB113 is not charged due to the total protonation reaction of their sulfonate groups -SO<sup>3-</sup>Na<sup>+</sup> conducting to their transformation too -SO<sub>3</sub>H. This protonation prevents the electrostatic interactions that can exist between adsorbent and adsorbate. From pH 4 to 8, a decrease in the q<sub>e</sub> value was remarked, especially at pH 8.

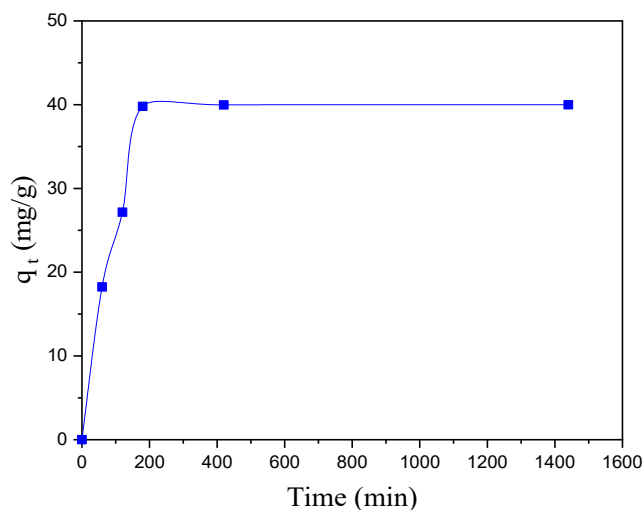


**Fig. 4.** pH effect on AB113 adsorption capacity by [P4VP-C<sub>16</sub>Br]. (V<sub>solution</sub> = 40 ml, m adsorbent = 20 mg, adsorption time = 1 h, initial dye concentration = 50 mg l<sup>-1</sup>, T = 298 K).

This decrease is justified by the existence of hydroxide groups OH<sup>-</sup>, interacting with the positively charged nitrogen of the quaternized pyridinium units. This interaction screens the positive charges of our copolymer and reduces the number of active sites of [P4VP-C<sub>16</sub>Br]. The best retention capacity was obtained at pH = 4. At this pH value, we considered that we have a balance between the positive charge of [P4VP-C<sub>16</sub>Br] and the negative charge of AB113. We also suggest that an addition protonation reaction of the non-quaternized [P4VP-C<sub>16</sub>Br] units can be done, leading to the formation of new pyridinium units (-NH<sup>+</sup>). In this study, the pH was kept constant at 4 in all the other experiments.

**Effect of contact time and kinetic study.** A critical factor in the adsorption process is the contact time. It is crucial to achieve the most dye clearance in the shortest time [30]. The effect of contact time on the adsorption of AB113 is shown in Fig. 5. Adsorption experiments were conducted for 24 h to find the optimal contact time. Figure 5 shows that the adsorption consists of two distinct phases. The first part of the curve reveals that AB113 retention is a long process. The adsorbed quantity of AB113 onto the [P4VP-C<sub>16</sub>Br] increased slowly until it reached the equilibrium time ( $t_{eq}$ ). This is due to the increased hydrophobicity caused by the alkyls preventing the easy opening of the alkyl chains and subsequently, the accessibility of the dye molecules to be adsorbed on the copolymer surface by electrostatic attraction. In this part, we also obtained that the dye removal (%) was at its maximum value at 3 h of contact between AB113 aqueous solution and [P4VP-C<sub>16</sub>Br]. The second part was fast and was characterized by the presence of a plateau in which  $q_t$  became constant, indicating a saturation of the adsorption of the AB113 on the surface of the copolymer.

Equations (3) and (4), which fit the pseudo-first-order model [31] and the pseudo-second-order model [32], were used to fit the experimental data. Figure 6a and Fig. 6b provide the graphical representations of the two models.



**Fig. 5.** Kinetics of AB113 adsorption on [P4VP-C<sub>16</sub>Br] at pH = 4 of the dye solution, ( $V_{\text{solution}} = 40$  ml,  $m_{\text{adsorbent}} = 50$  mg, initial dye concentration =  $50 \text{ mg l}^{-1}$ ,  $T = 298 \text{ K}$ ).

$$\text{Pseudo-first order: } \ln(q_e - q_t) = \ln q_e - K_1 t \quad (3)$$

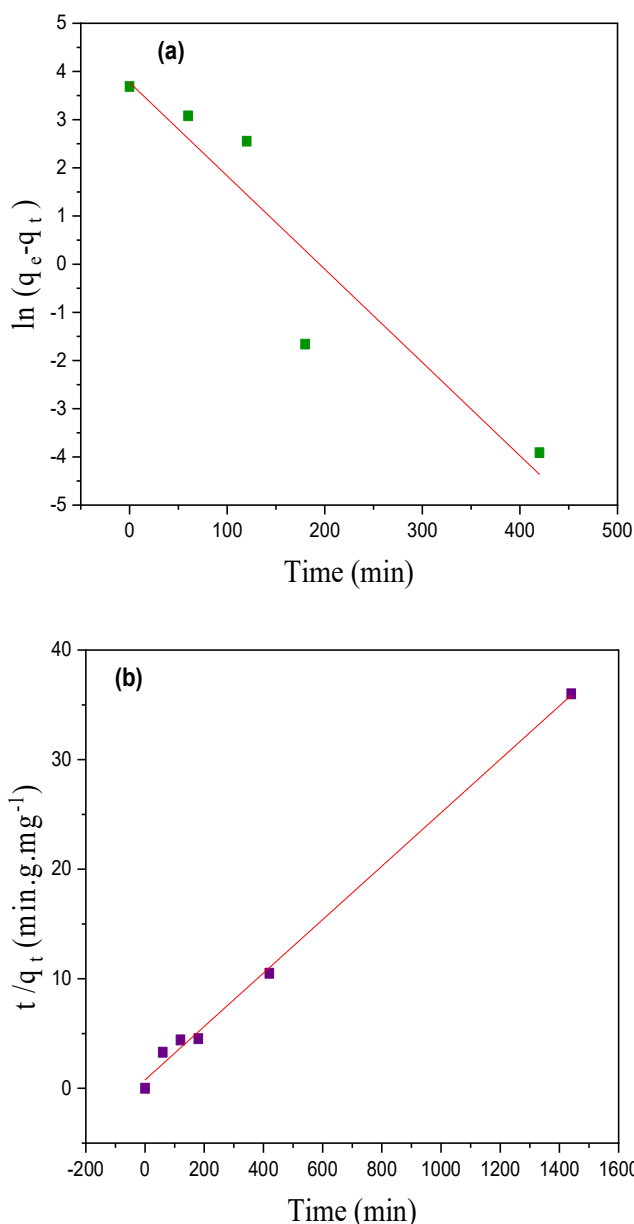
$$\text{Pseudo-second order: } \frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

In above formulations,  $q_e$  ( $\text{mg g}^{-1}$ ) is the equilibrium adsorption capacity,  $q_t$  ( $\text{mg g}^{-1}$ ) is the amount of dye adsorbed at time  $t$ ,  $k_1$  ( $\text{min}^{-1}$ ) and  $k_2$  ( $\text{g mg}^{-1} \text{ min}^{-1}$ ) are the pseudo-first and pseudo-second order rate constants, respectively. The adsorption kinetic plots are shown in Fig. 6a and Fig. 6b. The kinetic parameters and the correlation coefficient of the models are given in Table 1.

The pseudo-second-order model may explain the adsorption of AB113 on adsorbent based on the correlation coefficient, showing that the adsorption process is carried out in more than one stage. As a result, the quantity of active sites in the adsorbent material affects the adsorption rate. The adsorptions of various dyes onto various polymers are found

**Table 1.** Characteristic Parameters Obtained by the Pseudo-first Order and Pseudo-second Order Models

	$q_e$ (exp) ( $\text{mg g}^{-1}$ )	Pseudo-first order model			Pseudo-second order model		
		$q_e$ ( $\text{mg g}^{-1}$ )	$K_1$ ( $\text{min}^{-1}$ )	$R^2$	$q_e$ ( $\text{mg g}^{-1}$ )	$K_2$ ( $\text{g mg}^{-1} \text{ min}^{-1}$ )	$R^2$
[P4VP-C <sub>16</sub> Br]	39.99	43.36	0.019	0.838	41.01	0.0007	0.996



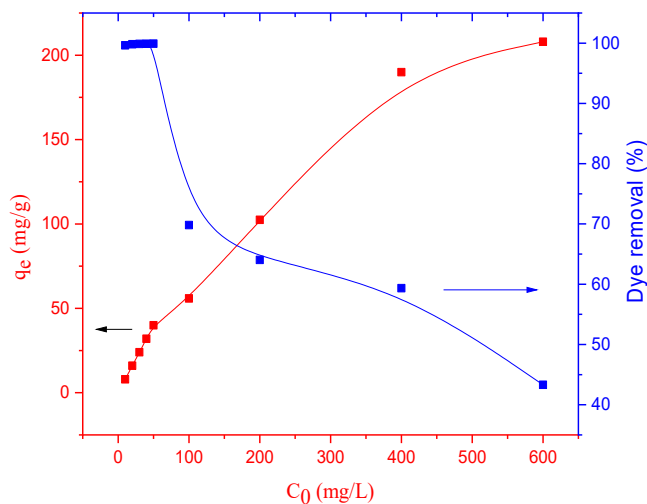
**Fig. 6.** (a) pseudo-first -order and (b) pseudo-second-order adsorption kinetics of AB 113 on [P4VP-C<sub>16</sub>Br] at pH = 4 of the dye solution ( $V_{\text{solution}} = 40$  ml,  $m_{\text{adsorbent}} = 50$  mg, initial dye concentration =  $50 \text{ mg l}^{-1}$ ,  $T = 298 \text{ K}$ ).

to follow the pseudo-second-order kinetic model, and this finding is shown to be compatible with those previously obtained in other investigations [33]. The experimental adsorption capacities  $q_e$  (exp) obtained after 3 h of contact between adsorbent and adsorbate are similar to the

equilibrium adsorption capacities ( $q_e$ ) provided in Table 1.

**Effect of AB113 initial concentration and isotherms study.** The impact of the initial dye concentration was examined within the concentration range of  $10 \text{ mg l}^{-1}$  to  $600 \text{ mg l}^{-1}$ . Figure 7 demonstrates how raising the initial dye concentration causes an increase in the quantity of AB113 absorbed into the [P4VP-C<sub>16</sub>Br] copolymer. The achieved adsorption capacity is equal to  $207.96 \text{ mg g}^{-1}$  at the initial AB113 concentration of  $600 \text{ mg l}^{-1}$ . The values determined by V. Priya *et al.* (2019) and Süheyla Pura & GültenAtun (2009), who investigated the adsorption of AB113 onto Nanocarbon Spheres and Fly Ash, are less significant than this value [34-35].

From Fig. 7, we observed that the percentage of dye removal exceeded 99.5% in the range of dye concentration from  $10 \text{ mg l}^{-1}$  to  $50 \text{ mg l}^{-1}$ . For higher concentrations, dye removal (%) decreased when the initial concentrations increased, suggesting the consumption of the majority of active sites of [P4VP-C<sub>16</sub>Br]. The plot of equilibrium concentration *versus* adsorption capacity is shown in Fig. 8. By comparison with the IUPAC classification [36], the obtained isotherm is type-L (Langmuir). According to the isotherm described above, chemical adsorption often shows a relatively high affinity between the adsorbent and adsorbate. When there was a significant increase in the



**Fig. 7.** AB113 removal capacity ( $q_e$ ) and dye removal (%) as a function of the initial dye concentration.  $V_{\text{AB113}} = 40$  ml, pH = 4,  $t_{\text{eq}} = 3$  h,  $T = 298 \text{ K}$ ,  $m_{[\text{P4VP-C}_{16}\text{Br}]}$  = 50 mg.

$q_e$  vs.  $C_e$ , the first step (1) in the identical Fig. 8 confirmed the high affinity of the adsorbent toward the adsorbate. Because there were more dye molecules than active sites on the adsorbents in the second range,  $q_e$  values fluctuated slowly.

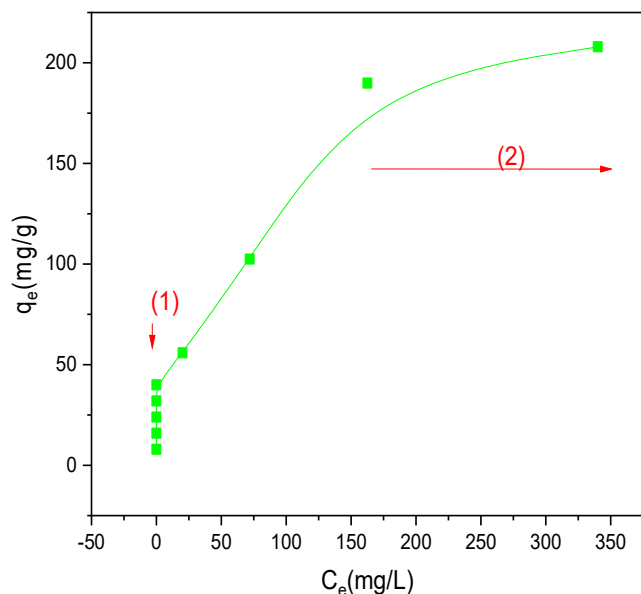
Adsorption data fitted the Langmuir and Freundlich isotherms, which are presented in Figs. 9a and 9b, respectively.

Langmuir and Freundlich isotherms are presented by Eqs. (5) and (6).

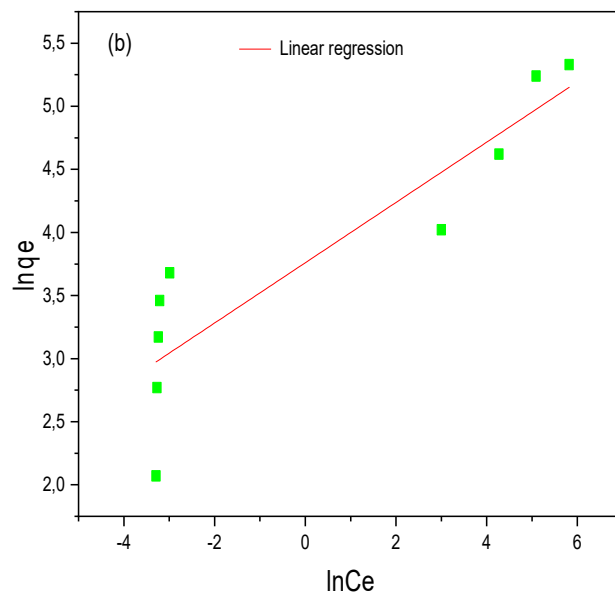
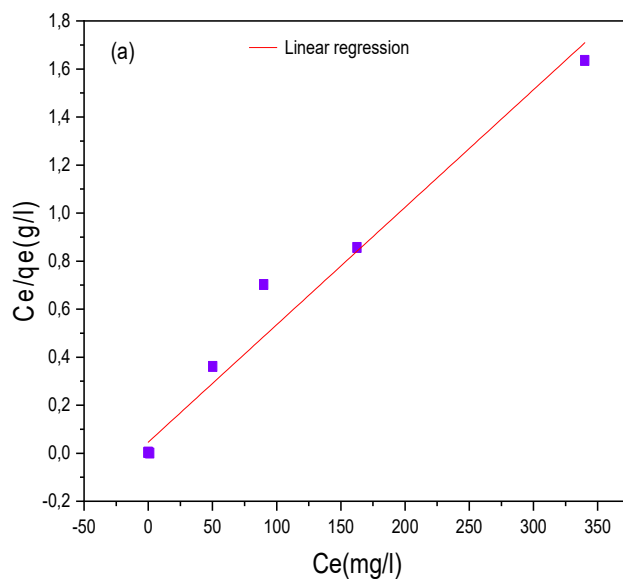
$$\frac{C_e}{q_e} = \left( \frac{1}{K_L q_{\max}} \right) + \left( \frac{C_e}{q_{\max}} \right) \quad (5)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (6)$$

Here,  $C_e$  is the equilibrium concentration of dye ( $\text{mg l}^{-1}$ ),  $q_e$  is the amount of dye adsorbed on the [P4VP- $C_{16}\text{Br}$ ] ( $\text{mg g}^{-1}$ ),  $K_L$  is the Langmuir adsorption constant ( $\text{l mg}^{-1}$ ),  $q_{\max}$  is the maximum monolayer adsorption capacity of the adsorbent ( $\text{mg g}^{-1}$ ),  $K_F$  is the Freundlich adsorption constant, which is related to the adsorption capacity, and  $n$  is the heterogeneity factor.



**Fig. 8.** Isotherm plots ( $q_e$  versus  $C_e$ ) of AB113 adsorption onto the [P4VP- $C_{16}\text{Br}$ ].  $V_{\text{AB113}} = 40$  ml,  $\text{pH} = 4$ ,  $t_{\text{eq}} = 3$  h,  $T = 298$  K,  $m_{[\text{P4VP-C}_{16}\text{Br}]}$  = 50 mg.



**Fig. 9.** Linear fit of the experimental data by using (a) Langmuir and (b) Freundlich isotherm models.

The isotherm parameters and correlation coefficients ( $R^2$ ) obtained from these models are summarized in Table 2.

The correlation coefficient data demonstrate that the Langmuir model more accurately describes the AB113 adsorption onto the [P4VP- $C_{16}\text{Br}$ ]. The Langmuir model estimated a maximal adsorption capacity of  $207.4 \text{ mg g}^{-1}$ . The Langmuir model's applicability proves that monolayer adsorption occurs at the adsorbent surface.

**Table 2.** Parameters of the Isotherm Models for the Adsorption of AB113 onto the [P4VP-C<sub>16</sub>Br]

Langmuir				Freundlich		
q <sub>max</sub> (exp)	q <sub>max</sub> (cal)	K <sub>L</sub>	R <sup>2</sup>	N	K <sub>f</sub>	R <sup>2</sup>
207.96	204.4	0.106	0.970	3.921	38.466	0.782

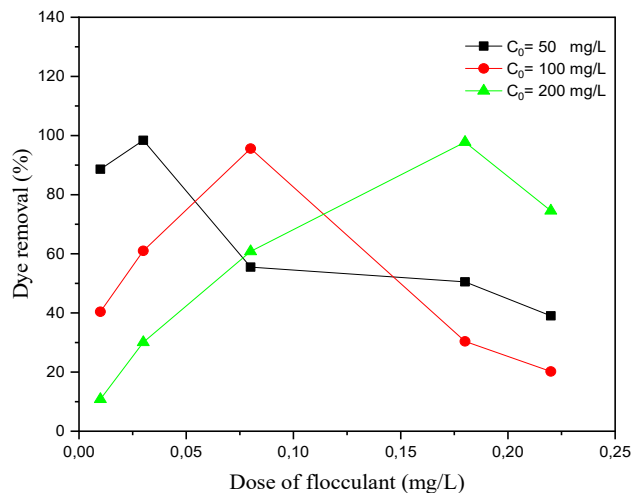
### Flocculation of Anionic Dye

**Coagulation-flocculation studies.** In order to maximize the removal of dye utilizing [P4VP-C<sub>16</sub>Br], it is essential to take into account the elements that can affect the mechanism of this process. This study examined the effects of several of these variables, including dye concentration, flocculant dose, solution pH, and settling time (t).

#### Effect of initial dye concentration and flocculant dose.

Figure 10 illustrates how the dye concentration and the flocculant dose affect the clearance of the anionic dye AB113. In order to find the ideal dose of [P4VP-C<sub>16</sub>Br] flocculant for dye, the dye concentration has been altered. According to the findings in Fig. 10, the dye removal percentage was grown with increasing flocculant dose to an ideal level for each of the three concentrations of AB113, then reduced with increasing doses of [P4VP-C<sub>16</sub>Br]. Additionally, a more significant dose of [P4VP-C<sub>16</sub>Br] was necessary to obtain the desired amount of colour removal when the dye concentration was increased from 50 mg l<sup>-1</sup> to 200 mg l<sup>-1</sup>.

For dye concentrations of 50, 100, and 200 mg l<sup>-1</sup>, the optimum doses for [P4VP-C<sub>16</sub>Br] were 0.03, 0.08, and 0.18 mg ml<sup>-1</sup>. These tendencies are typical of flocculant systems managed by a mechanism for neutralizing charges [37,38]. The efficacy of the dye flocculation was exceptionally high when there was an adequate supply of cationic charge to completely neutralize the anionic charge. Following flocculant overdose, excess cationic charge causes a dispersion re-stabilization phenomenon, which lowers flocculation efficiency [37-39]. Electrostatic repulsion between the copolymer chains in the flocs created by the flocculants [P4VP-C<sub>16</sub>Br] caused by their excess cationic charge led to the dispersion of the polymer chains [40].



**Fig. 10.** Effect of dye concentration and flocculant dose on the removal on the acid blue 113 dye. pH = 5, T = 298 K, time = 30 min.

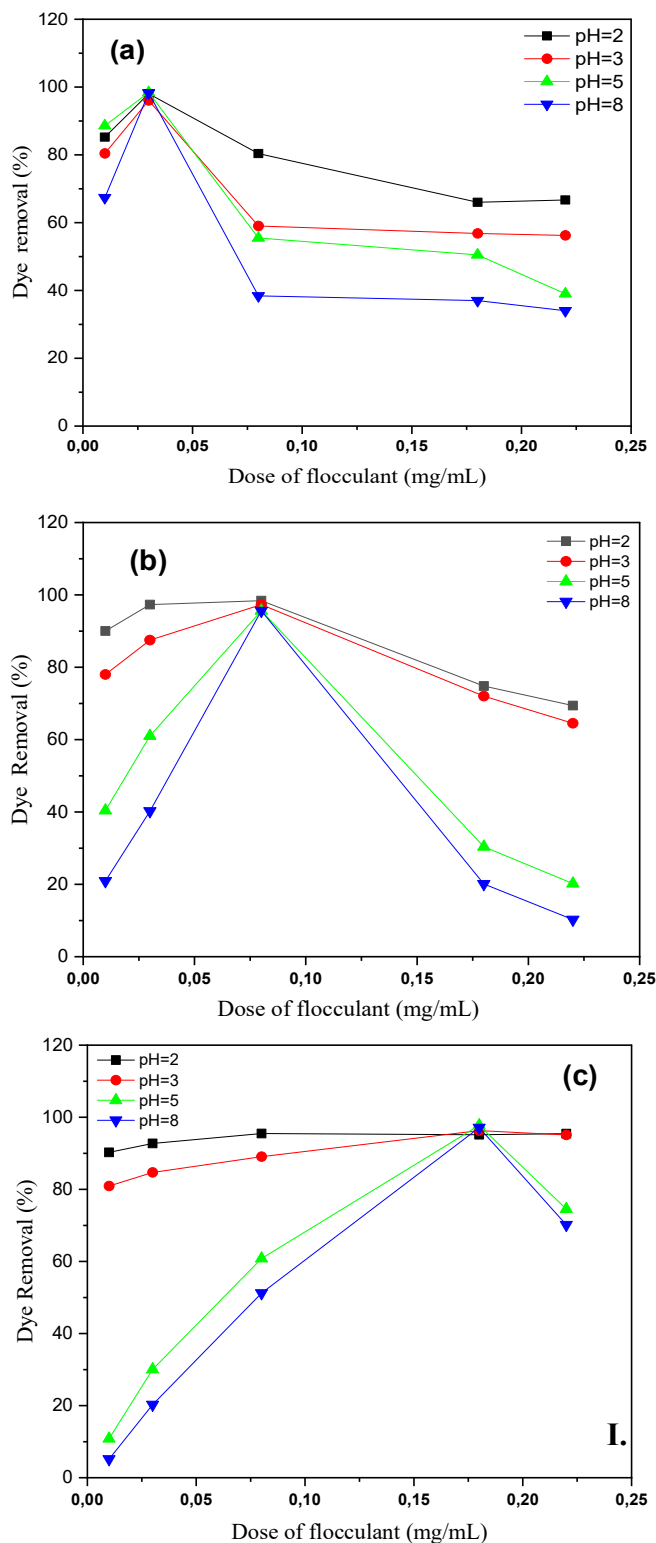
**pH solution effect.** The pH was critical index to investigate the flocculation performance [41]. Figure 11 shows the effect of pH on the removal of dye acid blue 113 at three concentrations (C<sub>0</sub>) 50, 100 and 200 mg l<sup>-1</sup>.

The clearance ratio of AB113 weakened as the dye solution's pH climbed, which is shown in Figs. 11a, b and c. This is because the pyridine group is more prevalent in the protonated ammonium (-NH<sup>+</sup>) form, and more dye removal is anticipated as a result of electrostatic interaction between the protonated ammonium ion and the anionic group (-SO<sup>3-</sup>) of the dye [42-44]. Additionally, the removal ratio of acid blue 113 at the recommended dose of [P4VP-C<sub>16</sub>Br] flocculant could reach more than 98% at pH 2-8, indicating that [P4VP-C<sub>16</sub>Br] can retain a strong flocculation effect throughout a broad pH range. The flocculation of acid blue 113 demonstrated a high dependence on the quaternized poly(4-vinyl pyridine), confirming the charge neutralization mechanism as the likely mode of flocculation.

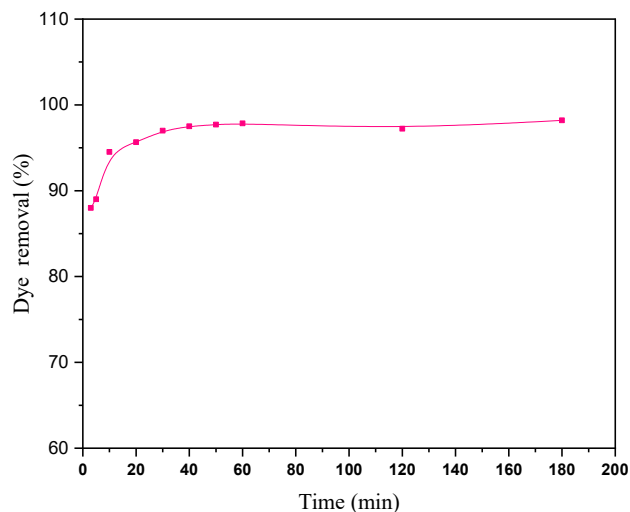
**Flocculation kinetics.** The contact time between dye and [P4VP-C<sub>16</sub>Br] flocculant is another critical parameter for understanding the flocculation kinetics.

The effect of contact time between [P4VP-C<sub>16</sub>Br] and dye AB113 was investigated to evaluate the percentage of removal dye. An optimum dose of flocculant [P4VP-C<sub>16</sub>Br] was added to 50 ml of dye solution with an initial





**Fig. 11.** pH solution effect on the removal of acid blue 113 dye: (a)  $C_0 = 50 \text{ mg l}^{-1}$ , (b)  $C_0 = 100 \text{ mg l}^{-1}$ , (c)  $C_0 = 200 \text{ mg l}^{-1}$ ,  $T = 298 \text{ K}$ , time = 30 min.



**Fig. 12.** Contact time effect on the removal of dye AB113.  $C_0 = 50 \text{ mg l}^{-1}$ , dose of optimum flocculant =  $0.03 \text{ mg ml}^{-1}$ ,  $\text{pH} = 5$ ,  $T = 298 \text{ }^\circ\text{C}$ .

concentration  $C_0 = 50 \text{ mg ml}^{-1}$ . After agitation at different contact times of 3-180 min and setting time for one minute, the residual dye concentration of the filtrate was measured. The progress of the percentage of dye removal monitored at different time intervals is shown in Fig. 12. This figure shows the effect of flocculation time on the dye's removal efficiency. It indicates that the AB113 dye removal rate was increased from 88% to 94.52% by increasing the flocculation time from 3 to 10 min. From these results, it can be concluded that the flocculation process using prepared copolymer [P4VP- $\text{C}_{16}\text{Br}$ ] was swift. The rapid flocculation indicates that the process is controlled by charge neutralization [45-46]. After 10 min, a slight increase was observed in the percentage of dye AB113 removal. A flocculation plateau beyond 50 min followed this small increment in flocculation. The presence of the plateau means that the percentage of removal dye had attained its maximum value under the considered experimental conditions.

## CONCLUSION

The retention of the acid blue113 textile dye from synthetic solution by using cationic poly(n-hexadecyl-4-vinylpyridinium bromide) [P4VP- $\text{C}_{16}\text{Br}$ ] was studied. The pH significantly influenced the adsorption process of the [P4VP- $\text{C}_{16}\text{Br}$ ] copolymer. The adsorption equilibrium was

reached within 3 h of poly(4-vinylpyridine) quaternized at 50%, and the equilibrium modelling of AB113 removal process was described by Langmuir isotherms. Also, the adsorbed quantity of AB113 onto the [P4VP-C<sub>16</sub>Br] increased slowly until it reached the equilibrium time ( $t_{eq}$ ). This is due to the increased hydrophobicity caused by the alkyls preventing the easy opening of the alkyl chains and subsequently, the accessibility of the dye molecules to be adsorbed on the copolymer surface by electrostatic attraction. The removal ratio of acid blue 113 at the recommended dose of the [P4VP-C<sub>16</sub>Br] flocculant could reach more than 98% at pH 2-8, indicating that the [P4VP-C<sub>16</sub>Br] can retain a strong flocculation effect throughout a broad pH range. The flocculation of acid blue 113 showed a high dependence on the quaternized poly(4-vinyl pyridine), confirming the charge neutralization mechanism as the likely mode of flocculation.

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