

Removal of Cationic Surfactants from Aqueous Solutions by Modified Cotton as a Novel High Capacity and Low Cost Adsorbent

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ABSTRACT

Direct and indirect releases of large quantities of surfactants to the environment may result in serious health and environmental problems. Therefore, surfactants should be removed from water before release to the environment or delivery for public use. Using cotton-based adsorbent may be an effective technique to remove surfactants. In this study, the removal of cationic surfactants by modified cotton was investigated. N-Cetyl-N,N,N-trimethylammonium bromide (CTAB) was selected as a cationic surfactant for the experiments. The results revealed that the modified cotton has a high affinity toward the cationic surfactants. Experiments were conducted to examine the effects of applied adsorbent dosage, initial concentration of adsorbate, pH, temperature, salt concentration on the removal efficiency. By increasing the salt concentration, removal efficiency was decreased slightly. The temperature had an adverse effect on removal efficiency. The adsorption of the CTAB increases with increasing pH of the solution. A series of batch experiments were performed to determine the sorption isotherms of modified cotton. Surfactant equilibrium data fitted very well to the Langmuir model. The Langmuir model showed that the maximum adsorption was 909 mg/g which is higher than the capacity of other adsorbents reported until now. The pseudo first-, second- order and corresponding rate equation kinetic models were investigated. Adsorption complies with a pseudo-second-order rate equation.

Indexing terms/Keywords

Removal; Cationic Surfactant; Modified Cotton; Adsorbent; Water

Academic Discipline And Sub-Disciplines

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1. INTRODUCTION

Water is one of the abundantly available resources in nature and is essential for animal and plant life. Pollution of water bodies are increasing steadily due to industrial application and urbanization. Surface-active agents, or surfactants, are widely used in many industrial and commercial products and processes throughout the world. Surfactants are not only related to soaps and detergents in daily life, they are also in heavy demand for industrial processes requiring colloid stabilities, metal treatments, mineral flotation, pesticides, oil productions, pharmaceutical formulations, emulsion polymerizations, and particle growth [1, 2]. The broad range of surfactant applications may also cause side effects in the environment and in these industrial processes. Surfactants may also persist in wastewater treatment systems at relatively high concentrations as a consequence of their widespread use and frequent resistant bio-degradation [2-5]. Many of these compounds are biologically non-degradable and threat for environmental conservation [6]. Due to their high volume use, detergent chemicals have the potential for broad scale release into aquatic and terrestrial environment. It is quite frequent, especially in rural areas with no sewerage system, municipal and industrial wastewater containing detergent infiltrates into soil and ground waters from septic tanks. Surfactants can reach humans, animals and plants from the ground waters used as drinking water supplies [7].

Surfactants are a class of industrially very important amphiphilic compounds. One of the characteristic properties of amphiphilic substances is that they tend to assemble at interfaces and therefore they are often referred to as surface-active agents. Another characteristic property of these substances is the formation of large aggregates (micelles). Surfactants are categorized into four groups depending on the charge on the head group: nonionic, anionic, cationic and amphoteric surfactants [8].

Different processes, such as biological treatment, foam fractionation, chemical precipitation, oxidation, adsorption and membrane processes were used in order to remove surfactant from aqueous solution [9]. However, the presence of surfactants at high concentrations in biological stations produces foams that cause perturbations on the treatment process [6,8]. Furthermore, wastewaters containing a large amount of surfactants and high chemical oxygen demand cannot be easily treated either by conventional physico-chemical or biological processes [10, 11]. Besides the toxic effects of surfactants their existence in waters even under the toxic level causes many adverse effects on biological life. They cause pathological, physiological and biochemical effects on aquatic animals. In aquatic plants types, they have effects such as break-up of the chlorophyll-protein complex, death of the cell by damaging the membrane, delay in metabolism and growth [7]. A large number of surfactants are not easily biodegradable. On the other hand it is not possible to use easily biodegradable surfactants in all household and industrial applications due to the economic reasons. Thus, pretreatment methods such as ozonation and other advanced chemical oxidation of surfactant in the water need to be developed which allow safe use of refractory types of surfactants [7]. Although effective on improving the biodegradability of refractory surfactants, ozonation or photocatalytic oxidation is a relatively costly method. Biological treatment techniques require long time and increase the cost, therefore they are considered not to be effective [13]. The conventional methods for surfactant removal from water involve processes such as chemical and electrochemical oxidation, membrane technology, chemical precipitation, photo-catalytic degradation, adsorption and various biological methods [13, 15]. Many of these processes are not cost effective and/or not suitable for application on a household scale. Adsorption technology can be of low cost and can be applied in small devices.

Adsorption plays an important role in these processes. One of the common methods to remove surfactants from water is to use adsorption technology. Surfactant adsorption to activated carbon promises high removal efficiencies [16,17]. C.A. Basar et al. used activated carbon for removing cationic surfactant with maximum capacity of 400.9 mg/g [17]. However, the particle size of activated carbon should be small to increase the removal efficiency, which causes problems such as clogging in short duration in the use of conventional adsorption bed reactors.

Another technology to remove cationic surfactants from aqueous solution is using cotton based adsorbents. It is a low-cost and more environmentally accepted adsorbent. In this work, cotton was modified by chlorosulfonic acid. As a result of this modification, anionic functional group of sulfate was attached to the cotton which has a high affinity toward the cationic surfactants. N-Cetyl-N,N,N-trimethylammonium bromide (CTAB) shown in Fig 1, was selected as a cationic surfactant for investigation of adsorbent efficiency. First, a series of batch experiments were performed to identify the adsorption kinetics and sorption isotherms of surfactants. Influences of effective parameters on the removal efficiency were investigated. Removal efficiency was obtained by spectrophotometric determination of chemical oxygen demand (COD) of sample solutions.

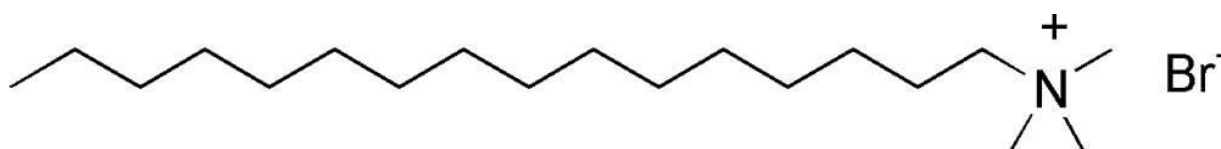


Fig 1: N-Cetyl-N,N,N-trimethylammonium bromide

2. EXPERIMENTAL

2.1. Material

CTAB was obtained from Central Drug House (CDH) at 99% purity and was used as received. The critical micelle concentration CMC of CTAB was reported as 0.92 mM 25 °C (28). Water for solutions was distilled and deionized (Milli-Q Plus, Millipore).

2.2. Instruments

An spectrophotometer (DR5000 HACH) equipped with a thermal reactor was used to determine CTAB concentration. A CHNS analyzer (Costech) was used for characterization of modified cotton.

2.3. Adsorbent Preparation

Firstly, the Cotton was dried in an oven at 80 °C for two hours. In a typical procedure, 150 mL of dimethyl fomamide (DMF) was added into a 1000 ml flasks containing 10 grams cotton and followed by stirring for 30 min and cooled in an ice bath. 150 mL of DMF was slowly added into a 1000 mL flask containing 30 g of CSA under stirring. The mixture was slowly added to cotton and DMF under stirring. After sufficient contact time, the mixture was washed by deionized water and afterwards the modified cottons were neutralized with sodium carbonate followed by deionized (DI) water for several times. After drying under vacuum, the removal efficiency of obtained adsorbent was investigated.

2.4. Adsorbent Characterization

In order to confirm the modification, elemental composition of modified cotton was determined by CHNS analyzer (C:35 H:5.1 O:55 S:4.9 %). According the obtained result, the modified cotton contains 1.53 meq/g negative charge responsible for adsorption of cationic surfactant.

Point of zero charge was obtained according to the following method. A 0.1M solution of NaCl was prepared using distilled water, which was degasified by boiling for 30 min. Solutions with different pH ranging from 4 to 11 were prepared using 0.1M solution of NaCl. 0.05 g of the sample was added to 20mL of each solution, and stirred to reach equilibrium. The final pH was measured, and plotted as a function of the initial pH of the solution. The pzc was determined as the pH of the NaCl solution that did not change after the contact with the adsorbent [10]. As shown in Fig 2, pH=7 is pzc.

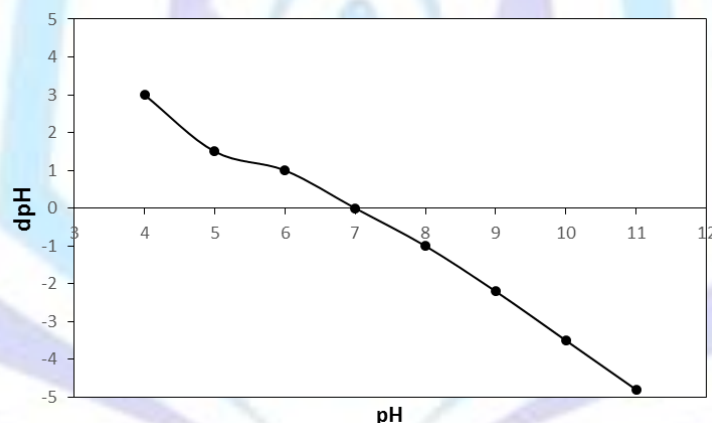


Fig 2: Point of zero charge of modified cotton

2.5. Adsorption Studies

Sorption of CTAB by cotton cellulose was studied in batch method. A fixed amount of adsorbent (0.02 g) was added to 100 ml of the CTAB solution varying concentration from 150 mg/l to 400 mg/l. The solutions were stirred (150 rpm) at room temperature for 1 hour to achieve the equilibration. The adsorbent was filtered. The adsorbate uptake q_e (mg/g), can be calculated as

$$q_e = (C_0 - C_e)V / W$$

where C_0 and C_e are the initial and equilibrium adsorbate concentrations (mg/L), V , the volume of the solution and W the mass of the adsorbent (g) and q_e is the amount adsorbed.

2.6. Kinetic Studies

1000 ml of sample solution containing CTAB (400 ppm) was stirred at 150 rpm at room temperature. The adsorbent was introduced to the reaction tank at zero time and 5 ml of the solution phase was withdrawn at various time intervals. These aliquots were filtered to remove particulates of adsorbent and were analyzed for the remaining concentration of CTAB.

3. RESULTS AND DISCUSSION

3.1. Effect of pH

The adsorption of CTAB onto the cellulose over a pH range of 2–11 was studied and shown in Fig 3. The adsorption of the CTAB increases with increasing pH of the solution. This can be explained by considering the zpc of modified cellulose. As pH of the system decreased below the zpc of the adsorbent, the number of negatively charged adsorbent sites decreased, At higher pH, negatively charged adsorbent sites increased, which enhances the adsorption of positively charged CTAB through electrostatic forces of attraction [18].

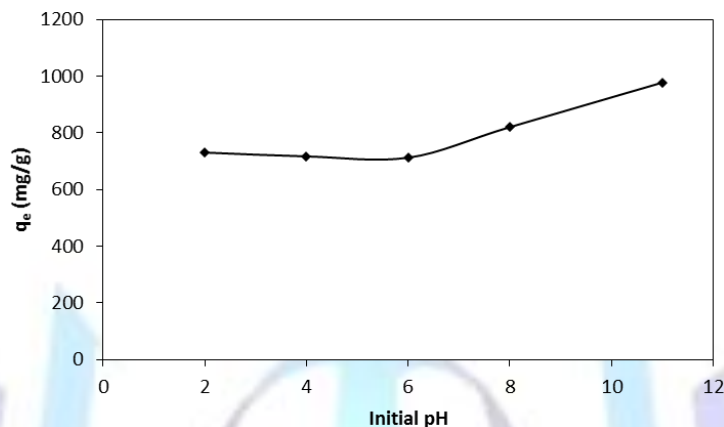


Fig 3: Effect of pH on adsorption of CTAB on modified cotton

3.2. Effect of Salt

The effect of salt on the sorption was tested. The adsorption efficiency of the modified cotton in present of different amounts of Na_2SO_4 ranged from 1-5 % was studied and shown in Fig 4. The sorption of CTAB is mainly dominated by cation-exchange, so the sorption capacity varies with the concentration of salt [19]. The result showed that as the amounts of Na_2SO_4 increased, the CTAB removal efficiency decreased.

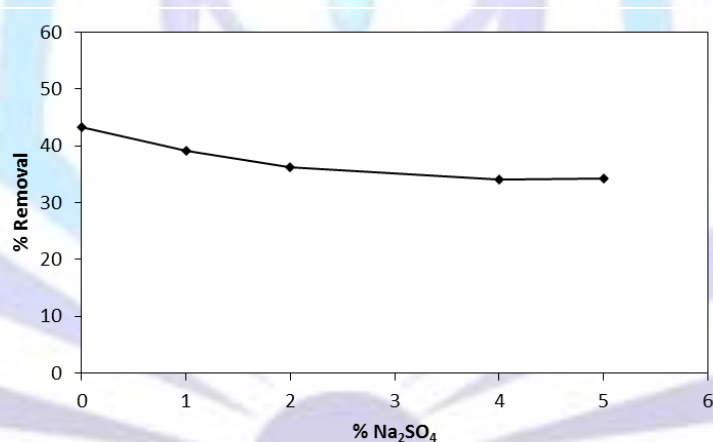


Fig 4: Effect of Na_2SO_4 on adsorption of CTAB on modified cotton

3.3. Effect of Adsorbent Dosage

The effect of adsorbent dosage was studied on CTAB removal from aqueous solutions by varying dosage of modified cotton from 0.005 to 0.04 g in 100 ml of the solution at a fixed initial concentration of 400 mg/l. The result is shown in Fig 5. It showed that an increase in adsorbent dosage could increase the CTAB removal efficiency from the solution, because with increasing adsorbent dosage, more surface area was available for adsorption. According to Fig 5, 0.02 g of modified cotton is the optimum dosage of the adsorbent for the CTAB removal. On the other hand, by reduction of adsorbent dosage, q_e increases which indicates the lower dosage of adsorbent is suitable for usage of maximum capacity of adsorbent.

3.4. Effect of Contact Time

1000 ml of sample solution containing CTAB (400 ppm) was stirred at 150 rpm at room temperature. The adsorbent was introduced to the reaction tank at zero time and 5 ml of the solution phase was withdrawn at various time intervals. As it is shown in Fig 6, increasing the contact time increased the adsorption of CTAB and then after 10 minutes remained almost constant.

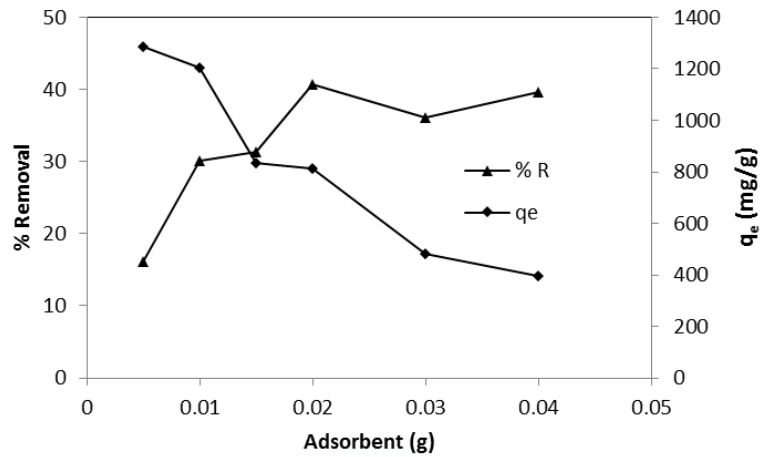


Fig 5: Effect of adsorbent dosage on adsorption of CTAB on modified cotton

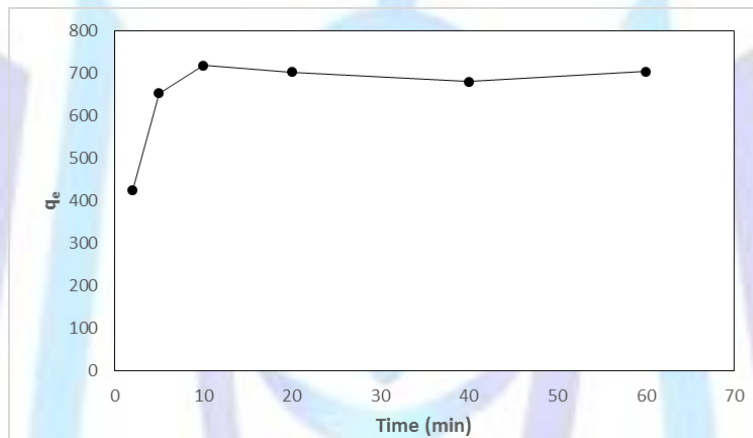


Fig 6: Effect of contact time on adsorption of CTAB on modified cotton

3.5. Adsorption Isotherms

The isotherm in Fig 7 showed an L-shape adsorption according to the classification of Giles et al. [20].

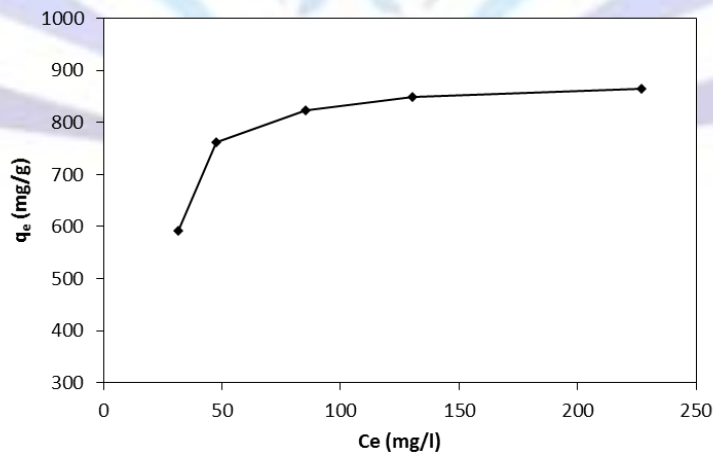


Fig 7: Adsorption isotherm of CTAB on modified cotton

Langmuir isotherm [21] is represented by the following equation:

$$q_e = \frac{Q_0 b C_e}{1 + b C_e}$$

$$C_e / q_e = 1 / Q_0 b + C_e / Q_0$$



where, C_e is the concentration of CTAB (mg/L) at equilibrium, q_e is the amount of adsorbate adsorbed on per unit mass of adsorbent at equilibrium in (mg/g), Q_0 is the maximum adsorption at monolayer coverage in (mg/g), b is the adsorption equilibrium constant related to the energy of adsorption in L/mg, The plots of C_e/q_e vs C_e are linear and presented in Fig 8. The adsorption of CTAB shows that the adsorption follows the Langmuir isotherm model for CTAB adsorption. The values of Q_0 and b have been evaluated from the intercept and slope of these plots Table 2. The adsorption capacities, Q_0 is 909 mg/g.

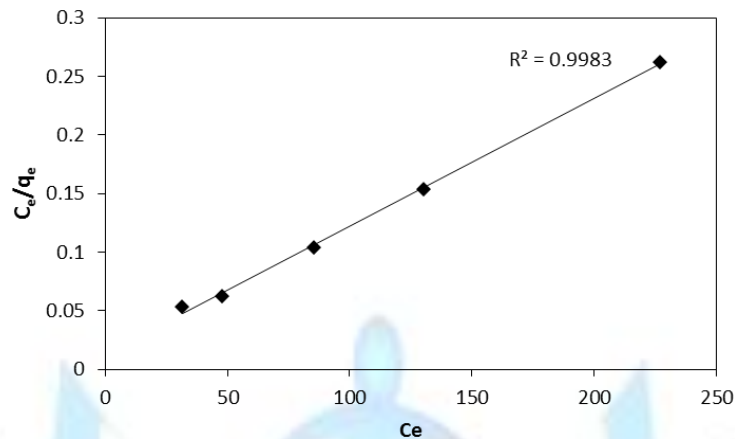


Fig 8: Langmuir plot for the adsorption of CTAB on modified cotton

The logarithmic form of the Freundlich isotherm equation is given as

$$\log q_e = \log K_f + 1/n \log C_e$$

where K_f and n are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. The values of K_f and n can be calculated from the intercept and slope of the Fig 9 and presented in Table 2. The results showed that the adsorption fits better in the Langmuir equation.

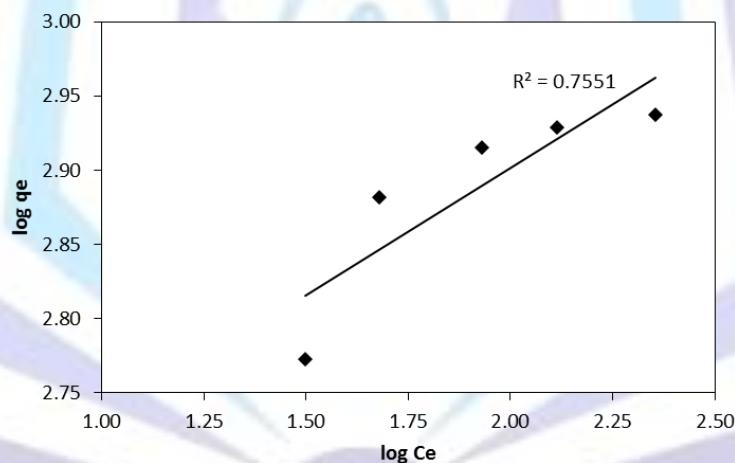


Fig 9: Freundlich plot for the adsorption of CTAB on modified cotton

Table 1 : Langmuir and Freundlich constants for the adsorption of CTAB on Modified Cellulose

Langmuir constants			Freundlich constants		
Q_0 (mg/g)	b (L/mg)	R^2	n	K_f	R^2
909	0.0011	0.9983	5.8	362	0.7551



Table 2 : Comparison of adsorption capacity of cationic surfactant with other adsorbents

Adsorbent	Q ₀ (mg/g)	References
Powder Activated Carbon and Microfiltration	400	C.A. Basar et al. [17]
Activated carbon obtained from corncob	1200	S. M. Yakout et al. [16]
Clinoptilolite zeolite	73	Zhaohui Li [23]
Cellulosic Fibers	90 - 120	S. Alila et al. [14]
Modified cotton	909	Present work

3.6. Kinetics of Adsorption

The rate constants for the adsorption of CTAB was determined using pseudo-first-order, pseudo-second-order equations and intraparticle diffusion. The pseudo-first-order rate equation can be written as

$$\log(q_e - q_t) = \log q_e - k_1 t / 2.303$$

where k_1 is the rate constant for pseudo-first-order adsorption, q_e and q_t are the amounts of adsorption at equilibrium and at time t , respectively and presented in Fig 10. The corresponding pseudo-second-order rate equation is

$$t / q_t = 1 / k_2 q_e^2 + t / q_e$$

where k_2 is the rate constant for pseudo-second-order adsorption. The rate parameters k and q_e can be directly obtained from the intercept and slope of the plot of t / q_t against t and presented in Fig 11. The possibility of intraparticle diffusion was explored by using an intraparticle diffusion model. The corresponding rate equation being

$$q_t = k_{id} t^{1/2} + c$$

where c is constant and k_{id} is the intraparticle diffusion rate constant ($\text{mg/g min}^{1/2}$) and presented in Fig 12.

According to the results, correlation coefficient of second-order kinetics model is greater than those of other rate laws. Also, a comparison is made between the equilibrium adsorption capacity (q_e calc) evaluated from the pseudo- second-order model and achieved from practical (q_e exp). This indicates that the adsorption complies with a pseudo-second-order rate equation. Kinetic parameters for their three kinetics models and correlation coefficients are summarized in Table 3.

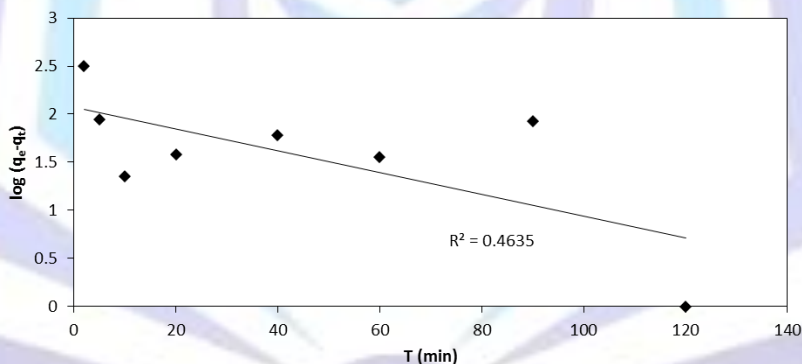


Fig 10: Pseudo-first-order plot for the adsorption of CTAB on modified cotton

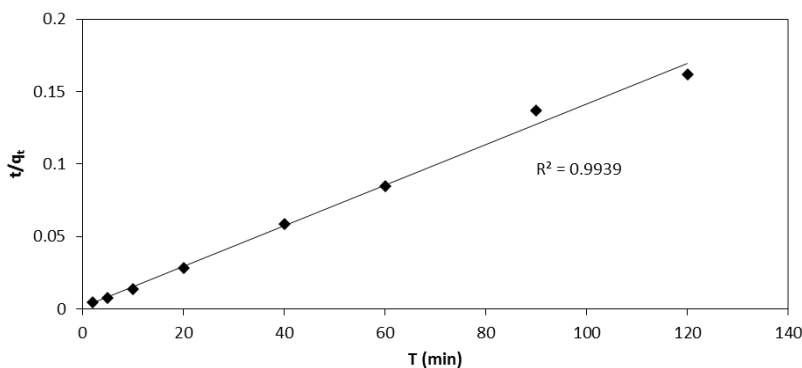


Fig 11: Pseudo-second-order plot for the adsorption of CTAB on modified cotton

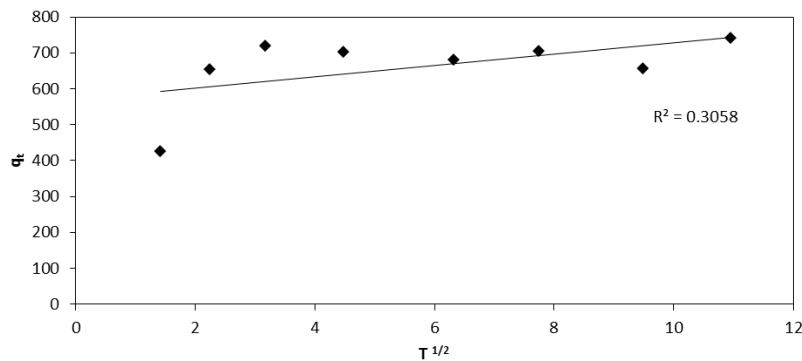


Fig 12: Intraparticle diffusion equation plot for the adsorption of CTAB on modified cotton

Table 3 : Kinetic parameters for the adsorption of CTAB on Modified

Pseudo-first-order				Pseudo-second-order			Intraparticle diffusion rate equation	
q _e exp. (mg/g)	k ₁ × 10 ⁻³ (min ⁻¹)	q _e calc. (mg/g)	R ²	k ₂ × 10 ⁻³ (mg/g min)	q _e calc. (mg/g)	R ²	k ₂ (mg/g min ^{1/2})	R ²
741.57	26.25	118.7	0.4635	12.25	714.3	0.9939	15.78	0.3058

3.7. Thermodynamic Parameters

To examine the effect of temperature, adsorption experiments were conducted at 298, 313 and 333 K, respectively. The thermodynamic parameters such as change in enthalpy (ΔH°), free energy (ΔG°) and entropy (ΔS°) for the adsorption of CTAB on Modified cotton were calculated using the following equations:

$$K_c = C_{ae} / C_e$$

$$\Delta G^\circ = -RT \ln K_c$$

$$\ln K_c = \Delta S^\circ / R - \Delta H^\circ / RT$$

where, K_c is the equilibrium constant, C_{ae} is the concentration of adsorbate in the solid phase and C_e is the concentration of adsorbate in the liquid phase at equilibrium (mg/L). The plot of $\ln K_c$ vs $1/T$ was found to be linear and shown in Fig 13. Using linear regression analysis, ΔH° and ΔS° values were calculated from the slope and the intercept of the van't Hoff plot (Table 5). The negative ΔG° values increased with temperature, confirming the spontaneous nature of the adsorption with temperature. The positive values of ΔH° indicate the endothermic nature of adsorption [22] whereas the positive values of ΔS° show the increased randomness at the solid/solution interface during adsorption.

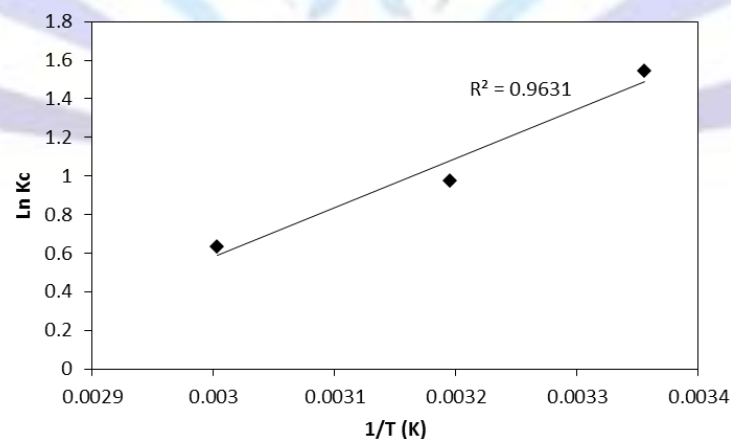


Fig 13: Van't Hoff plot for the adsorption of CTAB on modified cotton

**Table 4 : Thermodynamic Parameters of Adsorbent**

$\Delta G = \Delta H - T.\Delta S$		ΔH (KJ.mol ⁻¹)	ΔS (J.mol ⁻¹)
T (°k)	ΔG (KJ.mol ⁻¹)	-21.3	-58.9
298	-3.74		
313	-2.85		
333	-1.68		

4. CONCLUSION

The adsorption of CTAB from aqueous solution onto modified cotton has been studied in detail. The results present in this paper showed that CTAB was adsorbed by the outer surface of modified cotton particle, so the adsorption rate was very fast. When the adsorption of the outer surface reached saturation, the CTAB entered into modified cotton particle by the pore within the particle and was adsorbed by the inner surface of the particle. Removal of CTAB is found to be more effective at higher pH. The Langmuir adsorption isotherm fits well for the systems. Adsorption of CTAB onto modified cotton decreased with increase in temperature, indicating the process to be exothermic. The adsorption follows a pseudo-second-order kinetic model. The present study shows that modified cotton, an economic and inexpensive material, can be an alternative for many expensive adsorbents used for the removal of CTAB in water treatment.

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