Removal of paraquat herbicide from water by textile coated with anionic cyclodextrin polymer

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Abstract

The coating of anionic cyclodextrin polymer on polyethylene terephthalate (PET) textile was achieved by crosslinking between β -cyclodextrin (β -CD) and citric acid (CTR) to adsorb paraquat herbicide from aqueous solution. This coating performance (30 min, 170 °C) was 22.18% of weight gain which was corresponded to 0.51 mmol/g of ion exchange capacity (IEC). Then, the samples were characterized by scanning electron microscopy (SEM), attenuated total reflection–Fourier transform infrared spectroscopy (ATR–FTIR) and thermogravimetric analysis (TGA). The appropriated pH was 6.5 and the equilibrium time was 420 min. At 30 °C, the adsorption capacity towards paraquat (PQ) was enhanced (4.5, 18.9 and 23.7 mg/g) when the initial concentration of paraquat was increased (10, 50 and 250 mg/L). The adsorption kinetics was fitted to the pseudo-second-order model and the adsorption isotherm was suitable to Langmuir model. For the thermodynamic studies, the negative ΔG° revealed a spontaneous process, the negative ΔH° showed an exothermic process and the positive ΔS° displayed an enhanced disorder. Finally, the reusability of functionalized textile in methanol was reached 78.6% after six regeneration cycles and the stability of sample in various solvents was also studied.

Graphical abstract Anionic cyclodextrin polymer coated on PET textile issued from the crosslinking between β -cyclodextrin and citric acid was used as an efficient adsorbent for paraquat removal from aqueous solution.

Keywords Paraquat · Adsorption · Cyclodextrin polymer · Functional textile · Water pollution

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1 Introduction

The use of pesticides in agriculture become more important because it is a rapid, efficient and easy way to reduce production costs and increase agricultural productivity. Moreover, the disadvantage of pesticides have resulted in contamination of ecosystem, accumulation of pesticides is harmful to biotic and abiotic components. Most of these chemical substances are toxic which are difficult to eliminate from the environment, especially contamination of water is a ubiquitous problem which requiring water treatment. Paraquat (PQ) is a non-selective herbicide classified in bipyridinium groups. PQ is a famously used pesticide in the world [1, 2] according to a low price, a high efficiency at low concentration and a minor accumulative effect on soil. Paraquat is employed in plantations (rice, sugar cane, coffee, beans and other crops) [3] as well as in defoliation (grass and weed) [4]. This agrochemical is very hydrosoluble (620 g/L of solubility in water at 25 °C) because of the presence of cationic charge on the molecule, which eradicates plants by interrupting photosynthesis [1]. Nevertheless, paraquat is very dangerous for health such as dermal exposure [5], respiratory failure [6], pulmonary fibrosis [7, 8], neurotoxicity [9], damage of digestive apparatus [1] and Parkinson's disease [10, 11]. The paraquat amount of 35 mg/kg displays lethal dose for human being owing to European standards [12]. The paraquat concentration of 0.1 and 1–3 µg/L exhibits respectively the maximum permissible concentration for drinking water and for surface waters [13].

Recently, various wastewater treatment processes have been reported in the literature so as to eliminate paraquat contaminated in water such as physical methods (adsorption [14], filtration [15, 16] and ion-exchange [17, 18]), chemical methods (extraction [19], photocatalytic degradation [20, 21], oxidation [22, 23] and electrochemical process [24]) and biological method (fungi decomposition [25]). Among the methods mentioned above, the adsorption process demonstrates a simplicity of operation, a low-cost process and a high efficiency. Up to now, several adsorbents have been prepared to remove paraquat from aqueous solution: activated carbon [12] [26], biochar [27], membrane based on chitosan and alginate [16], activated bleaching earth [28], goethite [29, 30], clays [31], rice husk [32], phillipsite–faujasite tuff [33], bentonite [34], graphene oxide nanocomposite [35], multi-walled carbon nanotubes [36], silica [37, 38], faujasite zeolite [39], iron oxide coated quartz particles [40], pillararene based porous polymer [41] and magnetic hybrid nanosorbent [42].

Cyclodextrins (CD) are cyclic oligosaccharides produced from starch by enzyme cyclodextrin glucanotransferase (CGTase), which are composed of 6, 7 and 8 units

of D-glucose linked by α -(1,4) glycosidic bonds (named α -cyclodextrin, β -cyclodextrin and γ -cyclodextrin successively). The specific and well-defined structure like bowl-shaped displays a hydrophobic cavity and a hydrophilic exterior. This hydrophobic cavity provides encapsulation with suitable size and polarity of organic substances by the formation of inclusion complexes according to reversible host–guest interaction, especially inclusion with aromatic compounds. Cyclodextrin polymers are obtained from polymerization of native cyclodextrin to gain different structures which could give better encapsulation properties than pristine cyclodextrin. Moreover, the addition of charge on cyclodextrin or cyclodextrin polymers allows a good ionic interaction with the opposite charge of the guest molecule [43, 44]. Cyclodextrin and their derivatives have fascinated important attention as selective and greater efficiency for environmental applications [45, 46] so as to eliminate organic substances or heavy metal [47] such as organic substances [48, 49], volatile organic compounds [50, 51], dyes [52, 53] and pesticides [54, 55]. Anionic cyclodextrin polymer issued from crosslinking between β -cyclodextrin as a monomer and citric acid as a crosslinker was coated on the textile surface in order to remove organic substances [56] and heavy metals [57, 58] which were contaminated in water. Nowadays, this cation-exchange textile has never reported and used for PQ removal from aqueous solution.

In relevance of this work, we aimed to carry out adsorption efficiency of paraquat from water by textile coated with anionic cyclodextrin polymer using citric acid as a bridging agent with an environment-friendly process (Fig. 1). The effect of the initial concentration of paraquat, pH of the solution and adsorption temperature on the removal of paraquat were investigated. The appropriated models were chosen for adsorption kinetics and adsorption isotherm. Thermochemical studies were also operated at different temperatures. This adsorption technique could be an alternative way for wastewater treatment.

2 Materials and methods

2.1 Materials

PET textile was kindly given by Luckytex (Thailand) Public Company Limited. β -CD (Acros organics), CTR monohydrate (RCI labscan), sodium bicarbonate (RCI labscan) sodium hypophosphite (CARLO ERBA Reagents) and paraquat dichloride hydrate (Sigma Aldrich) were gained from commercial sources. Other chemicals used in this work were analytical grade. Milli-Q ultrapure water was used for all experiments.

2.2 Functionalization and characterization of PET textile

PET textile was cut off ($10 \times 10 \text{ cm}^2$), it was firstly washed with soxhlet apparatus (250 mL) using ethanol (1 h) and ultrapure water (2 h) before drying at 100°C in hot air oven (UF10, Memmert). Cleaned textile was dipped into 100 mL of solution containing 10%w/v of β -CD, 10%w/v of CTR and 3%w/v sodium hypophosphite, then it was rolled on aluminum foil by homemade roller for both sides several times before curing at 170°C during 30 min in hot air oven (UF10, Memmert). Finally, treated sample was washed again with soxhlet apparatus (250 mL) using ultrapure water (2 h) so as to eliminate unreacted products before drying at 100°C in hot air oven (UF10, Memmert). Weight gain referring to coating yield was calculated according to this equation:

$$\% \text{ Weight gain} = \frac{m_f - m_i}{m_i} \times 100 \quad (1)$$

where m_i and m_f relate respectively to textile weight before and after curing. Experiments were carried out in triplicate.

Functionalized textile was quantified ion exchange capacity (IEC) by pH-metric titration using calcium acetate method [59]. Textile (0.5 g) cut in small pieces was dipped into 50 mL of calcium acetate solution (2% w/v) for 4 h under agitation at 150 rpm. Textile was removed and clear solution (production of acetic acid) was titrated by NaOH

solution (0.05 M) employing phenolphthalein as an indicator. IEC value was expressed in mmol of COOH groups per gram of textile and it was obtained from the following equation:

$$\text{IEC (mmol/g)} = \frac{C_{\text{NaOH}} \times V_{\text{NaOH}}}{m} \times 100 \quad (2)$$

where C_{NaOH} and V_{NaOH} correspond respectively to the concentration and equivalent volume of NaOH. The symbol m stands for sample weight. Experiments were performed in triplicate.

After that, functionalized textile was activated by soaking in 0.15 M of NaHCO_3 for 30 min, washed with water until obtaining a neutral pH of the rinsed solution and dried at 100°C . This activation step was realized so as to convert carboxylic groups into carboxylate form without polymer hydrolysis before using this activated textile in all adsorption experiments. Experiments were performed in triplicate.

TGA (Thermogravimetric analysis) experiments were performed in an alumina pan with Thermal Analyzer—STA 449 F3 (NETZSCH) from ambient to 500°C with a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen gas.

ATR-FTIR (Attenuated total reflection–Fourier transform infrared spectroscopy) experiments were performed with Nicolet Nexus iS5 spectrometer (Thermo Scientific) which collected from 16 scans in $650\text{--}4000 \text{ cm}^{-1}$ range with a resolution of 32 cm^{-1} .

Samples were preliminarily coated with gold before SEM (Scanning Electron Microscopy) investigation on a

Fig. 1 Functionalization of textile with anionic cyclodextrin polymer for paraquat adsorption

JEOL 6010 electron microscope, operating with an acceleration voltage of 15 kV.

2.3 Adsorption experiment

Functionalized textile (0.1 g) was added into 50 mL of PQ solution (50 mg/L of initial concentration) with different pH from 2 to 10 under stirring at 150 rpm during 420 min at 30 °C. Solution pH was adjusted with 1 M NaOH and 1 M HCl. The measurement of PQ was investigated by GENESYS 10S UV–Vis spectrophotometer (Thermo Scientific) at 257 nm using the extinction coefficient (ϵ) of PQ in water which was 0.066 L mg⁻¹ (with $R^2 = 0.9994$). The adsorption capacity at time t (mg/g) was computed by the following equation:

$$Q_t = \frac{(C_0 - C_t)V}{m} \quad (3)$$

where C_0 and C_t relate successively to the initial and real-time concentration of PQ, V is solution volume and m is the weight of functionalized textile. Experiments were carried out in triplicate.

2.4 Adsorption kinetics

Functionalized textile (0.1 g) was put into 50 mL of PQ solution with 10, 50 and 250 mg/L of initial concentration with optimal pH at different times (15, 30, 60, 180, 300, 420, 1440 min) under agitation (150 rpm and 30 °C). The quantification of PQ was previously mentioned in Sect. 2.3. Raw data was then fitted with two kinetics models:

$$\text{Pseudo-first-order model} \quad \ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (4)$$

$$\text{Pseudo-second-order model} \quad \frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \quad (5)$$

where Q_e and Q_t are the amounts of PQ adsorbed (in mg/g) at equilibrium and at time t respectively, k_1 (1/min) and k_2 (g/(mg min)) are adsorption rate constant and t is contact time (min).

2.5 Adsorption isotherm

Functionalized textile (0.1 g) was put into 50 mL of PQ solution with 10, 50 and 250 mg/L of initial concentration with optimal pH at equilibrium time under agitation (150 rpm and 30 °C). The quantification of PQ was previously mentioned in Sect. 2.3. Raw data was then fitted with two isotherm models:

$$\text{Langmuir isotherm} \quad \frac{C_e}{Q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_e} \quad (6)$$

$$\text{Freundlich isotherm} \quad \ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (7)$$

where C_e is the equilibrium concentration of PQ, Q_e is the amount of PQ adsorbed (in mg/g) at equilibrium, Q_m is the theoretical maximum adsorption capacity, K_L is Langmuir isotherm constant, K_F is Freundlich constant and $1/n$ is heterogeneity factor.

The same experiments as mentioned above were also performed at 40 °C and 50 °C in order to estimate thermodynamic parameters which indicated energy change in adsorption process according to the following equations:

$$\ln \frac{Q_e}{C_e} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad \text{for determination of } \Delta H^0 \text{ and } \Delta S^0 \quad (8)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad \text{for determination of } \Delta G^0 \quad (9)$$

where C_e is equilibrium concentration of PQ, Q_e is amount of PQ adsorbed (in mg/g) at equilibrium, ΔH^0 is the standard enthalpy change in kJ/mol, ΔS^0 is the standard entropy change in J/K mol, ΔG^0 is the standard free energy change in kJ/mol, T is temperature in Kelvin and R is gas constant (8.3124 J/K mol).

2.6 Regeneration experiments

Functionalized textile (0.1 g) was placed into 50 mL of PQ solution (50 mg/L of initial concentration with optimal pH) at equilibrium time under agitation (150 rpm and 30 °C). The quantification of PQ was previously mentioned in Sect. 2.3. Then, the adsorbent was separated and regenerated by washing in different solvents such as methanol, water and 50%v/v of acetic acid for PQ desorption. After 420 min of soaking, the adsorbent was cleaned with ultrapure water and reconditioned for sorption in posterior cycles.

2.7 Adsorbent stability

The stability of functionalized textile was performed in different solvents used in the regeneration process such as methanol, water and 50%v/v of acetic acid. Modified textile (0.1 g) was placed into 50 mL of each solvent under agitation (150 rpm and 30 °C). At the desired time, this textile was removed, dried at 110 °C for 30 min and

finally weighed. The percentage of weight loss was calculated using the following equation:

$$\% \text{ Weight loss} = \frac{m_f - m_d}{m_f} \times 100 \quad (10)$$

where m_f and m_d relate respectively to functionalized textile weight and degraded textile weight. Experiments were carried out in triplicate. Then, this textile was put back in the fresh solvent with the previous process before recalculating the weight loss.

3 Results and discussion

3.1 Functionalization and characterization of adsorbent

The coating of anionic cyclodextrin polymer on PET textile surface was achieved by crosslinking between β -CD and CTR through esterification reaction in order to promote negative character on PET textile surface thanks to the presence of non-crosslinked carboxylic groups from CTR, which this thermofixation process was previously reported [58, 59]. Coating performance was measured by weight gain of polymer (22.18 wt%, S.D. = 0.89) and ionic exchange capacity (0.51 mmol/g, S.D. = 0.03). So, the loading amount of cyclodextrin polymer on the textile surface could be quantified by coating performance because the unreacted crosslinked polymer was previously removed after washing with soxhlet apparatus in order to ensure the presence of polymer on the textile surface.

As observed in Fig. 2a, the coating of anionic cyclodextrin polymer was assessed by FTIR spectroscopy with ATR mode which displayed functionalized textile comparing with untreated textile, pristine β -CD and CTR. PET textile spectra revealed the specific bands at 1709 cm^{-1} corresponding to C=O stretching of ester, at 2965 cm^{-1} assigning to C-H stretching of CH_2 , at 1623, 1573, 1503 and 1468 cm^{-1} attributing to stretching of benzene skeleton, at 1410 cm^{-1} ascribing to C-C stretching of phenyl ring, at 1336 cm^{-1} allocating to wagging vibration of CH_2 and at 1236 and 1089 cm^{-1} mentioning to C-O asymmetric and symmetric of ester respectively. β -CD spectra showed the characteristic peaks at 3265 cm^{-1} corresponding to OH stretching, at 2910 cm^{-1} assigning to CH_2 stretching, at 1151 cm^{-1} mentioning to C-C stretching and at 1021 cm^{-1} notifying to C-O-C stretching of the glycosidic bond. CTR spectra exhibited the peak of carboxylic groups at $1683\text{--}1732 \text{ cm}^{-1}$ corresponding to C=O stretching and at 1012 cm^{-1} ascribing to C-O stretching. After surface modification, some absorption bands altered in the spectra of treated textile by polymer

coating because of the presence of particular peaks of each component such as at $3500\text{--}3200 \text{ cm}^{-1}$ ascribing to O-H stretching of residual hydroxyls of β -CD and at 1710 cm^{-1} corresponding to C=O stretching of textile, CTR or anionic polymer.

Thermal stability and degradation profile of raw materials and modified textile were evaluated by TGA as illustrated in Fig. 2b. The first stage below 100°C , the loss of mass was 13% and 3% for β -CD and modified textile respectively which indicated dehydration of materials. The second stage, thermal degradation began at 135, 260, 300 and 303°C for CTR, modified textile, β -CD and untreated textile successively. Apparently, modified textile had two degradation steps as a virgin textile. Functionalized textile displayed a lower thermal stability at the temperature below 360°C but a higher thermal stability at the temperature upper than 360°C , compared with untreated textile. The final stage of degradation of each component was constantly seen due to a tardy decomposition of a residue which was thermally stable.

The yellow color of functionalized textile was remarked because of crosslinking with citric acid at high temperature which was different from PET virgin textile as seen in Fig. 3. The morphology of fibrous structure was observed with two magnifications. No difference could be distinguished for untreated textile (Fig. 3a) and functionalized (Fig. 3b) at $100\times$ magnification. However, the coating of polymer on the textile surface was clearly seen at $2000\times$ magnification as rough surface thanks to deposition of anionic polymer, comparing with virgin textile which exhibited smooth surface.

3.2 pH optimization of paraquat adsorption onto the modified textile

Preliminary studies also displayed that the adsorption of PQ on non-modified textile was negligible in all experimental conditions because the maximum adsorption capacity of virgin textile reached only 0.04 (S.D. = 0.02), 0.23 (S.D. = 0.05) and 0.56 (S.D. = 0.09) respectively for these initial concentrations of PQ (10, 50 and 250 mg/L). pH of the solution is an important factor for adsorption performance depending on the characteristics of both adsorbate (PQ) and adsorbent (modified textile). In this study, the PQ molecule which is a quaternary compound and pH-independent. So, the essential factor is focused on the adsorbent. The initial pH of the PQ solution was evaluated in the pH range of 2–10 (Fig. 4b). Adsorption capacity was very poor at pH of 2, adsorption process could only occur by network capture (imprisonment of PQ molecules in three-dimensional crosslinked polymer network) and inclusion complex (entrapment of PQ molecules in the β -CD cavity by host–guest interaction), as seen in

Fig. 2 ATR-FTIR spectra (**a**) and TGA thermograms (**b**) of virgin textile, β -CD, CTR and modified textile

Fig. 4a. Indeed, modified textile showed mediocre acidity in aqueous solution at very low pH due to the crosslinking agent which was citric acid. Although, activated textile had already been in carboxylate form after alkaline treatment but actual functional groups could become carboxylic form at very low pH. At this state, carboxylic groups of citric acid on the textile surface were not fully dissociated to carboxylate groups because pH solution was lower than the pK_a of this triprotic acid (3.13, 4.76 and 6.40). Adsorption ability was very bad at low pH which was previously reported for a citric-crosslinked CD with sawdust [60]. So, adsorption of PQ was inferior.

Then, adsorption capacity increased up to 13.9 mg/g at pH of 3 and enhanced slightly with pH raise while the maximum adsorption capacity reached (18.9 mg/g) at pH of 6.5. In this case, adsorption procedure could happen by network capture, inclusion complex and electrostatic interaction between the cationic character of PQ and anionic character of citric acid crosslinked on finished textile (Fig. 4a). Effectively, carboxylic functions were partially or totally ionized to carboxylate functions while pH of the solution was higher than pK_a of citric acid which improved adsorption capacity between 16.5 and 18.9 mg/g. Thus, adsorption capacity at this condition was enhanced thanks to electrostatic interaction which gave a supplementary force and could play an important role in the adsorption process. Thus, optimal pH was equal to 6.5 for following adsorption experiments as a mild condition.

Fig. 3 Pictures and SEM images of virgin textile (**a**) and functionalized textile (**b**) with two magnifications ($\times 100$ resolution with 100 μm of full scale and $\times 2000$ resolution with 10 μm of full scale)

3.3 Adsorption kinetics

The adsorption capacity of modified textile against contact time were carried out at various initial concentrations of PQ (10, 50 and 250 mg/L) at 30 °C (Fig. 5a). It was found that adsorption of PQ enhanced rapidly for the first 60 min, followed by a slow adsorption rate for the next 360 min until achieving a saturation of adsorption thanks to the replete occupation of available sites. At equilibrium time, adsorption capacity increased with the higher initial concentration of PQ and contact time of 420 min was selected for adsorption isotherm studies to endorse attainment of saturation state in different initial concentrations of PQ.

The pseudo-first-order model and pseudo-second-order model were employed to further study adsorption process relating to chemical reaction, mass transfer and the adsorption order. According to fitting curves with two models (Table 1), it noted that all values of correlation coefficient (R^2) were much higher for pseudo-second-order model ($R^2 = 0.9994, 0.9995$ and 0.9980) than pseudo-first-order model ($R^2 = 0.7588, 0.6455$ and 0.8322) for these initial concentrations of PQ (10, 50 and 250 mg/L respectively). These R^2 values of pseudo-second-order model were approximately closed to 1 so as to obtain a straight line (Fig. 5b), which adsorption kinetics was described by pseudo-second-order model. Moreover, adsorption capacity at equilibrium calculated by pseudo-second-order model ($Q_{e,cal} = 4.6, 19.3$ and 24.1 mg/g) was nearly to experimental values ($Q_{e,exp} = 4.5, 18.9$ and 23.7 mg/g) for these initial concentrations of PQ (10, 50 and 250 mg/L respectively).

3.4 Adsorption isotherm

Adsorption isotherm displays how pesticide interacts with modified textile at equilibrium state. The adsorption capacity of modified textile against concentration at equilibrium was performed at various initial concentrations of PQ (from 10 to 250 mg/L) at 30 °C (Fig. 5c). Adsorption capacity at equilibrium was very fast at a low initial concentration of PQ, but it became stable because of the unavailability of active sites on the adsorbent.

Langmuir and Freundlich isotherm models were applied to fit raw data (Fig. 5d, e respectively). Isotherm parameters were calculated and listed in Table 2. Due to fitting curves with two models, correlation coefficient (R^2) value was much higher for Langmuir isotherm model ($R^2 = 0.9990$) than Freundlich isotherm model ($R^2 = 0.8539$). This R^2 value from Langmuir isotherm model was imminent to 1 in order to obtain a linear relationship. So, Langmuir isotherm appeared a good demonstration of adsorption behavior which indicated that monolayer adsorption for PQ dominated on the homogenous surface of the functionalized textile. Additional information from Langmuir isotherm model, the separation factor (R_L) revealed the tendency of the adsorption process. The R_L values were 0.349, 0.097 and 0.021 for various initial concentrations of PQ (10, 50 and 250 mg/L successively), which displayed a great affinity between PQ molecule and treated textile because this tendency is advantageous if $0 < R_L < 1$. The functionalized textile could be used as an adsorbent for paraquat removal from aqueous solution and the maximum adsorption capacity of modified textile was 24.2 mg/g. However, it showed the mediocre adsorption efficiency comparing with other adsorbents listed in Table 3.

Fig. 4 **a** Proposed adsorption mechanism of PQ adsorption on textile coated with anionic β -CD polymer by inclusion complex, network capture and ionic interaction **b** effect of pH on adsorption

capacity of PQ (2 g/L of adsorbent dosage, 50 mg/L of PQ initial concentration, 420 min of contact time and temperature at 303 K)

Fig. 5 **a** Effect of contact time on adsorption capacity of PQ **b** pseudo-second-order kinetics of PQ adsorption **c** equilibrium isotherm **d** Langmuir isotherm **e** Freundlich isotherm of PQ adsorp-

tion for 10–250 mg/L of initial concentration of PQ (2 g/L of adsorbent dosage, temperature at 303 K and pH at 6.5)

Table 1 Kinetics parameters of adsorption of PQ on modified textile for 10, 50 and 250 mg/L of initial concentration (2 g/L of adsorbent dosage, temperature at 303 K, and pH at 6.5)

C_0 (mg/L)	$Q_{e,exp}$	Pseudo-first-order model			Pseudo-second-order model		
		R^2	$Q_{e,cal}$	k_1	R^2	$Q_{e,cal}$	k_2
10	4.5	0.7588	1.2	0.0035	0.9994	4.6	0.0095
50	18.9	0.6455	8.2	0.0030	0.9995	19.3	0.0015
250	23.7	0.8322	11.7	0.0023	0.9980	24.1	0.0008

3.5 Thermodynamic parameters

The influence of temperature on adsorption circumstance at different temperatures (30, 40 and 50 °C) was studied as shown in Fig. 6. The fitted curve of Q_e/C_e against $1/T$ was executed to determine different thermodynamic parameters by Vant' Hoff equation which exhibited a straight line with a good correlation coefficient ($R^2=0.9953$). The standard enthalpy change (ΔH°) was -1.0 kJ/mol, this negative sign indicated exothermic process and the reduction of adsorption capacity with temperature raised were earlier reported for paraquat adsorption [38, 61]. Furthermore, the weak ΔH° ($\Delta H^\circ < 40$ kJ/mol) was also described physisorption mechanism as the host–guest interaction between β -CD and PQ. Herein, it was probably that inclusion

complex mechanism was dominant than two others proposed mechanism because the size of PQ ($13.4 \text{ \AA} \times 3.6 \text{ \AA}$ [62]) was suitable for CD cavity ($7.8 \text{ \AA}$ of the internal cavity). By the way, the adsorption of the cationic organic compound on crosslink CD polymer was also informed about the important role of the CD cavity for methylene blue entrapment [47]. The standard entropy change (ΔS°) was 0.438 J/mol·K, this positive number exhibited an increase of randomness at the solid–liquid interface for PQ adsorption process. The standard Gibbs free energy change (ΔG°) was -1.106 , -1.111 and -1.115 kJ/mol for the temperature at 30, 40 and 50 °C respectively. All negative values expressed a spontaneous behavior of PQ adsorption. Moreover, the ΔG° value decreased with temperature

Table 2 Isotherm parameters of adsorption of PQ on modified textile for 10, 50 and 250 mg/L of initial concentration (2 g/L of adsorbent dosage, temperature at 303 K, 420 min of contact time and pH at 6.5)

Langmuir isotherm							Freundlich isotherm		
$Q_{e,exp}$	R^2	Q_m	K_L	R_L when			R^2	K_f	$1/n$
				$C_0 = 10$ mg/L	$C_0 = 50$ mg/L	$C_0 = 250$ mg/L			
23.7	0.9990	24.2	0.186	0.349	0.097	0.021	0.8539	6.5	0.29

Table 3 Comparison with other adsorbents described by the Langmuir isotherm for paraquat removal

Adsorbent	Adsorption dosage	Paraquat concentration	Adsorption kinetics	Maximum adsorption capacity
Polyester textile coated with cyclodextrin polymer (this work)	0.1 g in 0.05 L	10–250 mg/L	Pseudo-second-order	24.2 mg/g
Activated carbon derived from used tires [12]	1 g in 0.2 L	100–1000 mg/L	Pseudo-second-order	61.0 mg/g
Swine-manure-derived biochar [27]	0.3 g in 1 L	0.5–6 mg/L	Pseudo-second-order	14.8 mg/g
Clays and organoclays [31]	0.1 g in 0.02 L	0.1–1 mmol/L	–	0.19 mmol/g
Rice husk silica [32]	0.05 g in 0.02 L	80–1000 mg/L	–	185.2 mg/g
Multi-walled carbon nanotubes [36]	0.16 g in 0.1 L	20–200 mg/L	Pseudo-second-order	79.4 mg/g
Pillararene porous polymers [41]	5 mg in 5 mL	0.6–2 mmol/L	Pseudo-second-order	209 mg/g
Magnetic hybrid nanosorbents [42]	2.5 mg in 5 mL	30–900 µg/mL	–	242.2 mg/g

Fig. 6 Thermodynamic parameters of PQ adsorption at 303, 313 and 323 K (2 g/L of Adsorbent dosage, 50 mg/L of initial concentration, 420 min of contact time and pH at 6.5)

enhanced which PQ adsorption was suitable at a lower temperature.

3.6 Regeneration

For economic reasons, reusability and stability of adsorbent are important criteria for the adsorption process. The appropriated solvent could play a significant role in the desorption process which is composed of the regeneration

cycle. Water, 50%v/v of acetic acid solution and methanol were selected for PQ desorption from functionalized textile. As demonstrated in Fig. 7, PQ could be easily recycled in methanol and the regeneration efficiency reached 78.6–81.7% which revealed a good stability for desorption performance. Regeneration with methanol was formerly notified a good PQ removal efficiency by pillararene based porous polymers [41]. Nevertheless, the reusability efficiency of 50%v/v of acetic acid solution was only 39.9% after six cycles and this efficiency of water was very poor after only one cycle.

3.7 Adsorbent stability

The adsorbent stability was carried out in various solvents (water, 50%v/v of acetic acid solution and methanol) so as to ensure its physical endurance after solvent contact in adsorption and desorption process. After 7 h of contact time indicated equilibrium time for adsorption and desorption process, the weight loss of functionalized textile was 9.3%, 8.1% and 5.1% respectively for water, 50%v/v of acetic acid solution and methanol (as observed in Fig. 8). However, no degradation change was observed for virgin textile. As expected, the anionic cyclodextrin polymer coated on the textile surface was hydrosoluble which degraded easily in water because the presence of ester bonds from polymer could be hydrolyzed rapidly and the hydroxyl groups from cyclodextrin molecule could create certainly

Fig. 7 Regeneration of modified textile for PQ removal by using water, 50%v/v of acetic acid and methanol respectively. (2 g/L of Adsorbent dosage, 50 mg/L of initial concentration, temperature at 303 K, 420 min of contact time and pH at 6.5)

Fig. 8 Adsorbent stability in various solvents (water, 50%v/v of acetic acid solution and methanol)

hydrogen bonds with water molecules. This result could explain the reduction of regeneration efficiency in water for the second cycle due to the extreme loss of polymer coating on the textile surface. This kind of polymer was employed to build the multilayer assembly which showed the fast degradation rate for the multilayer assembly without thermal crosslinking [44]. Other organic solvents displayed less impact than water. By the way, no weight loss was rarely observed after the first contact with the solvent.

4 Conclusion

The surface modification of PET textile was firstly accomplished by crosslinking between β -CD and CTR through the environmentally friendly process so as to promote anionic charge on the textile surface, resulting modified textile was also characterized and employed as an adsorbent for PQ removal from aqueous solution. The adsorption of PQ on functionalized textile was better at neutral pH and lower temperature. Adsorption kinetics was achieved at 420 min which was suitable for pseudo-second-order-model and adsorption isotherm was appropriated to Langmuir model. Thermodynamic study displayed a spontaneous process, an exothermic procedure and an increased disorder. Ultimately, recyclability of functionalized textile was accomplished in methanol for 78.6% of regeneration efficiency. This kind of textile could be a promising material for cationic pesticide contaminated in water.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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