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β-CD-TDI POLYMER APPLICATION FOR THE REMOVAL OF CARCINOGENIC AROMATIC AMINES FROM THE BATIK INDUSTRY WASTEWATER

(Aplikasi Polimer β-CD-TDI untuk Penyingkiran Amina Aromatik Karsinogenik daripada Air Sisa Industri Batik)

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Abstract

This work demonstrated the use of β-cyclodextrin-toluene-2,4-diisocyanate (β-CD-TDI) polymer as an adsorbent for the removal of 4-aminobiphenyl and benzidine. The successfully synthesised β-CD-TDI polymer was characterised using FT-IR, SEM, and XRD. In the XRD analysis, the decrease in peak intensity indicates a decrease in the degree of crystallinity of the polymer resulting from the inclusion of TDI molecules. The FTIR result shows a peak located at 872 cm^{-1} indicating the presence of α-(1,4) glycopyranose originating from β-CD as well as 1600 cm^{-1} and 1592 cm^{-1} representing the ring from TDI respectively. The surface morphology for β-CD-TDI polymer had shrunk and became rough indicating the cross-linking process between β-CD and TDI taking place during polymerization. The optimal pH for the removal of 4-aminobiphenyl and benzidine was pH 5. The quantitative measurements were performed using a UV-Vis spectrophotometer at 272 nm and 281 nm for 4-aminobiphenyl and benzidine, respectively. The removal percentages under optimised conditions were 99.61 % and 95.65 % for 4-aminobiphenyl and benzidine, respectively. The coefficient of determination (R^2) values were 0.9995 and 0.9996 for 4-aminobiphenyl and benzidine, respectively. Pseudo second-order and Dubinin-Raduchkevich models were found to fit the adsorption of 4-aminobiphenyl and benzidine onto the β-CD-TDI polymer. The current developed method of removal was tested using wastewater collected from 3 different batik manufacturers in Kota Bharu, Kelantan, Malaysia. The β-CD-TDI polymer possesses exceptional adsorption properties, making it a highly efficient alternative adsorbent for the removal of aromatic amines.

Keywords: removal, adsorption, 4-aminobiphenyl, benzidine, βCD-TDI polymer

Abstrak

Kajian ini menunjukkan penggunaan polimer β-siklodekstrin-toluen-2,4-diisosiyanat (β-CD-TDI) sebagai penjerap untuk penyingkiran 4-aminobifenil dan benzidin. Polimer β-CD-TDI yang berjaya disintesis telah dicirikan menggunakan FT-IR, SEM, dan XRD. Dalam analisis XRD, penurunan keamatan puncak menunjukkan penurunan darjah kristaliniti polimer akibat daripada perangkuman molekul TDI. Hasil daripada FTIR menunjukkan bacaan pada 872 cm^{-1} mewakili α-(1,4) glukopiranosa yang berasal dari β-CD serta pada 1600 cm^{-1} dan 1592 cm^{-1} mewakili gelang TDI. Morfologi permukaan polimer β-CD-TDI menunjukkan pengecutan dan kekasaran yang membuktikan bahawa proses penghubung silang antara β-CD dan TDI telah berlaku semasa pempolimeran. Bacaan pH optimum untuk penyingkiran 4-aminobifenil dan benzidin adalah pada pH 5. Pengukuran kuantitatif dilakukan menggunakan spektrofotometer UV-Vis pada 272 nm dan 281 nm untuk 4-aminobifenil dan benzidin. Peratusan penyingkiran di bawah keadaan optimum adalah 99.61 % dan 95.65 % untuk 4-aminobifenil dan benzidin. Nilai pekali penentuan (R^2) adalah 0.9995 dan 0.9996 untuk 4-aminobifenil dan benzidin. Model pseudo kedua dan Dubinin-Raduchkevich didapati sesuai untuk penjerapan 4-aminobifenil dan benzidin ke atas polimer β-CD-TDI. Kaedah penyingkiran yang dibangunkan telah diuji menggunakan air sisa yang dikutip dari 3 kilang batik yang berbeza di Kota Bharu, Kelantan, Malaysia. Polimer β-CD-TDI mempunyai sifat penjerapan yang luar biasa, menjadikannya penjerap alternatif yang sangat cekap untuk penyingkiran amina aromatik.

Introduction

Synthetic dyes are essential in several key industries, including leather, paper, and textiles, due to their colour-enhancing properties. Approximately 700,000 tonnes of different dyes, chosen from around 100,000 commercially available options, are produced annually [1]. The textile industry is one of the major contributors to the presence of dye effluents in the environment. The existence of batik industries in Malaysia began in the 1960s and has been developing over the years. Throughout the years, batik textiles have had a big influence on modern fashion in Malaysia and the batik industry is well known on the East Coast of Peninsular Malaysia. Today, the industry has positively contributed to the economic growth of this country. Unfortunately, there is a big problem that keeps arising and affecting the quality of surrounding life. The batik industry is known as an industry that employs a lot of dyes and colouring agents. The discarded untreated wastewater from this industry into the water bodies affects the terrestrial, animal, and aquatic life. Based on the previously reported study, about 54% of dyes are released from the textile industry which represents about more than half of dyes present in the environment [1].

The situation becomes worse when this untreated wastewater becomes part of the water bodies. It will lead to difficulty in water treatment since the contaminants such as aromatic amines are chemically stable and hard to biodegrade [2]. Thus, affecting the quality of life of the surrounding environment. For instance, the release of untreated wastewater from the batik industry to the soil or river will pass the contaminants into the food chain which are consumed by humans and animals. Dyes can directly impact human health, causing conditions such as haemorrhage, skin ulcers, nausea, severe skin irritation, and dermatitis. Additionally, prolonged exposure to powdered textile dyes has been linked to lung and skin irritations, headaches, and nausea. Widely used dyes like disperse blue, disperse violet, disperse orange, and disperse red contain mutagenic agents and are toxic to humans, animals, plants, and microorganisms. Direct and indirect exposures to an aromatic amine can cause tumours, cancers, and allergies in humans [3].

Currently, there are a lot of physiochemical processes introduced related to treating the wastewater from the textile industry which has been polluted with poisonous and non-biodegradable organic pollutants such as flocculation, biological, oxidation, and electrochemical. However, there were some drawbacks due to the cost and large production of toxic by-products. Therefore, the adsorption process is an attractive way to remove the contaminants in textile wastewater such as 4-aminobiphenyl and benzidine due to the ease of application and low cost [4]. Furthermore, the adsorption process is an effective way for the separation technique due to the ease of recovery, mild conditions, and adsorbent regenerations [5].

Cyclodextrins (CDs) are part of a group of macrocyclic oligosaccharides characterised by a hydrophobic inner cavity and a hydrophilic exterior. It can encapsulate

many types of organic guest molecules in its cavity to form stable complexes without producing any chemical bonds [6]. Typically, CDs consist of 6, 7, or 8 D-glucose units linked by α-1,4-glucosidic bonds, classified as α-, β-, and γ-CD, respectively. A significant property of β-CD is its capacity to create solid inclusion compounds (host-guest complexes) with a wide variety of solid, liquid, and gaseous substances through molecular complexation and various interactions such as van der Waals forces, hydrophobic interactions, electrostatic affinity, dipole-dipole interactions, and hydrogen bonding.

β-cyclodextrin-toluene-2,4-diisocyanate **(**β-CD-TDI) polymer is a suitable adsorbent due to its capability to encapsulate a large scope of molecules. It can encapsulate many types of organic guest molecules in its cavity to form stable complexes without producing any chemical bonds. For that reason, CD is very suitable for the removal of organic environmental pollutants [7]. β-CD is a compound naturally soluble in water however the addition of toluene-2,4-diisocyanate (TDI) as a cross-linker can produce an insoluble β-CD-TDI polymer through polymerization. This study will report on the use of β-CD-TDI polymer as an adsorbent for the removal of benzidine and 4-aminobiphenyl in batik wastewater followed by UV-Visible spectrophotometer (UV-Vis) analysis. Therefore, a new removal technique of 4-aminobiphenyl and benzidine from batik wastewater was explored using β-CD-TDI polymer. This technique involves some parameters to be optimised such as initial concentration, mass of sorbent, temperature, contact time, pH, and ionic strength for an effective adsorption process.**ata kunci:** peyingkiran, penyerapan, 4-aminobifenil, benzidin, βCD-TDI polimer

Material and Methods

Reagent and material

β-cyclodextrin (βCD, 99%) was commercially available and purchased from Merck (United States). Anhydrous N,N-dimethylformamide (DMF) was purchased from Merck (Darmstadt, Germany). Toluene-2,4-diisocyanate (TDI) were purchased from Sigma Aldrich (St. Louis, MO, USA), Acetone (HPLC grade, 99.7%) made in Parkwood, Australia, Acetonitrile (ACN, HPLC grade, 99.9%), Sodium chloride and ultrapure water (18.2 MΩ cm) was generated by an in-home Sartorius Milli-Q system (Aubagne, France). Methanol (MeOH, HPLC grade, 99.7%) was purchased from Seoul. The standard stock solution of 4-aminobiphenyl and benzidine (100 mg/L) was prepared in 25 mL of MeOH and stored in the sample vial at 4°C to avoid any form of degradation. The working solutions were freshly prepared by diluting the stock solution with ultrapure water.

Synthesis of β-CD-TDI Polymer

The β-CD-TDI polymer was synthesised based on the method proposed by Raoov et al. [8]. An amount 2 g, 1.76 mmol of β-CD powder was primarily dissolved in 40 mL of anhydrous DMF at room temperature then toluene-2,4-diisocyanate (TDI) (2.54 ml,17.6 mmol) was added dropwise. The solution was continuously stirred for 24 hours at 70 °C in an inert environment. Excess acetone was used to precipitate the polymer formed after 24 hours of stirring. The white product formed was stirred and allowed to settle in acetone for 30 minutes to remove the residual DMF. Then, the product was filtered and washed with acetone and ultrapure water for few times to remove any unreacted cross-linker. The wet product (β-CD-TDI polymer) was allowed to dry overnight in a vacuum container.

Characterization of β-CD-TDI Polymer

The synthesised material was characterised using Fourier Transform Infrared spectroscopy (FTIR), Scanning Electronic Microscope (SEM) and X-ray Diffraction (XRD). FTIR spectrum was obtained on Perkin‑Elmer RX1 FT-IR (Perkin Elmer, Waltham, MA, USA) ranging from 400 cm^{-1} to 4000 cm^{-1}. For SEM analysis, Leica S440 (Leica, Wetzlar, Germany) was used to investigate the morphology of the β-CD and β-CD-TDI polymer with magnification of 10 Kx, 5 μm. The crystallographic structure was studied using a Siemens D5000 X-ray Diffractometer (XRD) (voltage, 40 kV; current, 100 mA (Siemens, Frimley, UK)) at a scanning rate of 0.02 sec-1 (λ=1.5418 Å).

Performance evaluation of β-CD-TDI polymer

Generally, 25 mg of β-CD-TDI polymer was placed into 10 ml of 0.5 mg/L of solution containing 4-aminobiphenyl and benzidine. Then, the solution was

tightly sealed and shaken at room temperature (298 K) for 120 minutes. The β-CD-TDI polymer was filtered and the solution was directly analyzed by UV-Vis with 1 cm quartz cell at the wavelength of 272 nm and 281 nm, respectively. The percentage of removal, (%R) and number of analytes adsorbed per unit mass of the adsorbent (q_e) in this research were determined using the following equation:

$$\%R = \frac{C_o - C_e}{C_O} \times 100 \quad (1)$$

$$q_e = \frac{(C_o - C_e)}{W} V \quad (2)$$

Based on equations 1 and 2, C_o and C_e are the initial and equilibrium concentration of solution (mg/L) respectively, while V is the volume of the sample solution (L) and W represents the mass of an adsorbent used (g).

Optimization of adsorption analysis: Effect of concentration

The effect of the initial concentration of the sample was investigated in this study. The range of initial concentration used is from 0.1 to 25 mg/L with the sorbent dosage fixed at 20 mg in 10 mL of aqueous solution and 60 minutes of contact time.

Effect of sorbent dosage

Different amount of sorbent dosage was analyzed throughout this parameter (5- 50 mg) to enhance the removal efficiency. This analysis was performed at a fixed initial concentration of 0.5 mg/L in 10 mL at room temperature and the contact time applied was 60 minutes.

Effect of temperature

The influence of temperature on the aqueous solution was investigated at 3 different temperatures 298 K, 318 K and 338 K respectively. The fixed sorbent dosage was 25 mg in 10 mL of 0.5 mg/L of aqueous solution and a contact time of 60 minutes.

Effect of contact time

The effect of contact time was investigated at different intervals (30-180 min) at room temperature. The sorbent dosage was fixed at 25 mg with 0.5 mg/L of initial concentration in 10 mL of aqueous solution.

Effect of pH

The effect of pH was studied on the scale of pH 4 to pH 9 at room temperature. 1 M HCl and 0.1 M NaOH were used to balance the pH. The sorbent dosage used was set at 25 mg, 0.5 mg/L of initial concentration and the contact time was fixed for 120 minutes.

Effect of ionic strength

The influence of ionic strength was analyzed in this study to increase the removal efficiency of 4-aminobiphenyl and benzidine. Sodium chloride (NaCl) was chosen since it is the common salt used for this purpose. The ranges of salt concentration used in this analysis were 5, 10, 15, 20 and 25 %. The salt has been introduced to the 10 ml of 0.5 mg/L of aqueous solution with 25 mg of sorbent at room temperature and 120 minutes of contact time.

Method validation

The precision study was performed as part of method validation for this study. In order to evaluate the precision, the removal studies were conducted under optimised conditions. The intra-day study was carried out within a day with five replicates while the inter-day was performed within two days with five replicates.

Reusability study of β-CD-TDI Polymer

To recover the adsorbed 4-aminobiphenyl and benzidine and to reuse the β-CD-TDI polymer, 25 mg of β-CD-TDI was shaken in 10 ml of 0.5 mg/L of aqueous solution for 120 minutes at 298 K. Then, the mixture was filtered using filter paper and the final and initial concentrations of the aromatic amines were determined by using a UV-Vis spectrophotometer. The used polymer was recycled by washing with acetonitrile (ACN) under constant stirring (200 rpm) and dried in an oven at 70 °C for 1 to 2 hours. Then, the β-CD-TDI polymer was added to another aqueous solution to start a new adsorption batch. The experiment was repeated for the same removal studies using the same polymer for up to 5 cycles.

Application of β-CD-TDI polymer as an adsorbent for the removal of 4-aminobiphenyl and benzidine from batik wastewater

The wastewater from the batik industry was collected from three different private manufacturers in Kota Bharu, Kelantan, Malaysia. About 500 mL of samples were collected in amber sample bottles. All the samples were centrifuged at 600 rpm for 30 minutes to separate all waxes and other dissolved particles from the samples and filtered using the membrane filter (0.45 µm) prior to storage. The samples were stored in the refrigerator at 4 °C until analysis. The polymer was applied to 3 batik wastewater samples to determine the percentage of removal. 25 mg of β-CD-TDI polymer was added to the real samples and directly shaken for 120 minutes at room temperature. The concentrations of 4-aminobiphenyl and benzidine before and after the removal were determined by using a UV-Vis spectrophotometer at 272 nm and 281 nm, respectively.

Results and Discussion

Structural characterization of β-CD-TDI polymer: Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of β-CD, β-CD-TDI polymer and TDI were recorded as shown in Figure 1. Based on Figure. 1(a), the band located at 872 cm^{-1} indicated the presence of α-(1,4) glycopyranose originated from β-CD which simultaneously can be seen in spectra of β-CD-TDI polymer. The presence of the aromatic group in TDI can be seen in Figure 1(b) and Figure 1(c) at 1600 cm^{-1} and 1592 cm^{-1} respectively [8]. Furthermore, the absence of peak 2271 cm^{-1} (isocyanate group) in Figure 1(b) shows the completion of polymerization [5]. Besides, the presence of carbamate linkage, NHCO in Fig. 1(b) too indicated that the polymerization has been completed. Based on Table 1, it can be concluded that the polymerization between the β-CD and cross-linker TDI was completed and the β-CD-TDI polymer was successfully formed.

X-ray diffraction (XRD)

The crystalline pattern of β-CD and β-CD-TDI polymer in Figure 3 was analysed using XRD. There is no significant visible peak for β-CD-TDI polymer Figure 3b compared to the native β-CD peak Figure 3a. This is due to the changes in crystalloids after the polymerization of TDI cross-linker. The decreasing peak of β-CD-TDI polymer at 2θ=13° compared to the β-CD peak shows that the degree of crystallinity was decreased due to the presence of bulky TDI molecules which caused the loss of regularity throughout the polymeric chain [8]. Based on this study, it was confirmed that the β-CD-TDI polymer is amorphous.

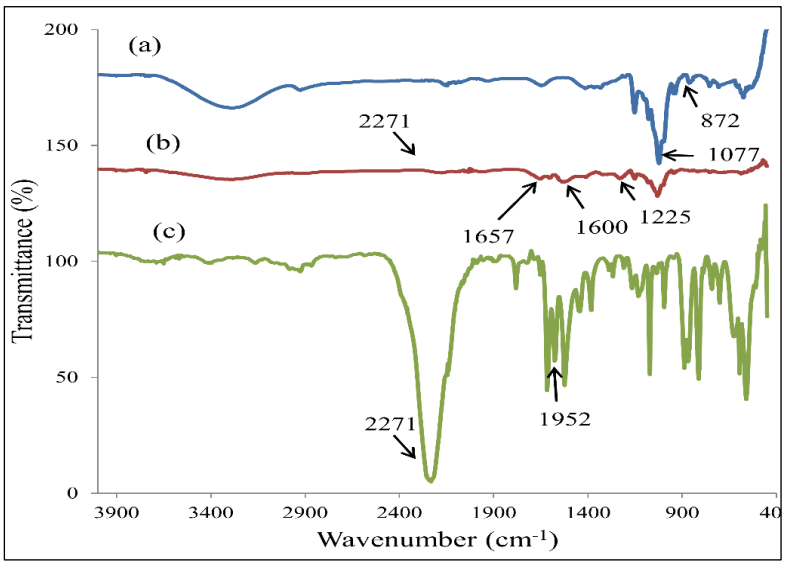

Figure 1. FTIR spectra (a) β-CD (b) β-CD-TDI polymer and (c) TDI

Table 1. FTIR result analysis of synthesized material

Sample	Wavelength (cm^{-1})	Assignments
β-CD	872	α-1,4- glucopyranose
	1023, 1077	C-OH stretching vibration
β-CD-TDI polymer	1225	C=O vibration of aromatic polyurethane
	1600	Aromatic group in TDI
	1534,1657	NHCO, carbamate linkage
	2271	Absence of isocyanate group
TDI	2271	Isocyanate group
	1592	Aromatic group in TDI

Scanning electronic microscope (SEM)

The SEM analysis was carried out to investigate the morphologies of the material used in this study, β-CD-TDI polymer and β-CD. The result of the SEM analysis is shown in Figure 2. The structure of β-CD (Figure 2a) was reported as rock-like while the surface morphology for β-CD-TDI polymer (Figure 2b) had shrunk and was rough. This indicated that the cross-linking process between β-CD and TDI has taken place during polymerization [6]. Hence, the increase of pore size in Figure 2b indicated that β-CD has been polymerized by TDI linker and formed β-CD-TDI polymer.

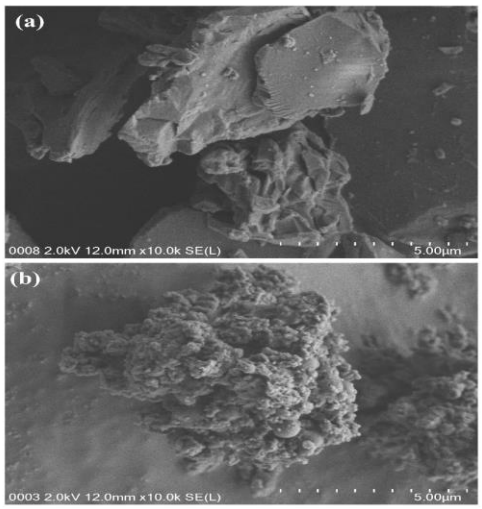

Figure 2. SEM image of (a) β-CD and (b) β-CD-TDI polymer (Magnification: 10Kx, 5µm)

Removal of 4-aminobiphenyl and benzidine by using β-CD-TDI polymer from aqueous solution

The synthesised adsorbent of β-CD-TDI polymer was used to develop a new method for the removal of two selected aromatic amines known as 4-aminobiphenyl and benzidine. In order to increase the removal efficiency, some parameters were studied throughout this adsorption process such as the effect of initial concentration, mass of sorbent, temperature, contact time, pH and ionic strength. Thus, the adsorption properties of kinetic, equilibrium and thermodynamics were studied and compared with the other few adsorption properties from previous studies. The standard calibration curve was plotted using the concentration ranging from 0.1 to 1 mg/L for both 4-aminobiphenyl and benzidine. The linearity of the standard calibration curve was calculated using the value of absorbance obtained from UV-Vis and the concentration (mg/L) involved. The data obtained was used to calculate the regression equation and coefficient

of determination, R^2 for each analyte. Appendices 1(a) and 1(b) show the standard calibration curve obtained from the study together with the regression equation and R^2 for 4-aminobiphenyl (y = 0.1882 x - 0.0014; R^2= 0.9973) and benzidine (y = 0.1330 x - 0.0020; R^2= 0.9973), respectively.

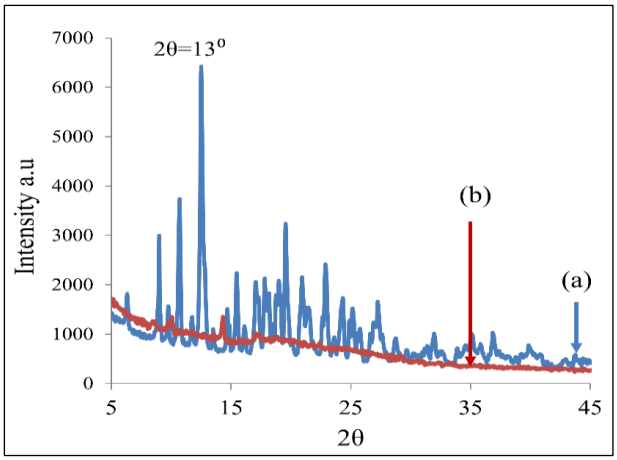

Figure 3. XRD pattern of (a) β-CD and (b) β-CD-TDI polymer

Effect of initial concentration

The initial concentration and has been selected as the first parameter for the removal technique of 4-aminobiphenyl and benzidine using β-CD-TDI polymer. The adsorption study for the initial concentration of 4-aminobiphenyl and benzidine was carried out from 0.1 to 25 mg/L utilizing 20 mg of β-CD-TDI polymer and one hour of contact time at room temperature (298 K). The result obtained is presented in Figure 4a. The percentage of removal was increased from 0.1 to 0.5 mg/L and gradually declined after 0.5 mg/L. The high percentage of removal at 0.5 mg/L was due to the abundance of active sites on the adsorbent, however; at higher initial concentrations the amount of analytes was higher causing the removal efficiency to decrease [9]. The percentage of removal of both 4-aminobiphenyl and benzidine was reduced as the initial concentration was increased due to the saturation phase reached by the β-CD-TDI polymer. After that phase, the analytes tend to use the energy to overcome the boundary layer effect which then decreases the percentage of removal [10]. Therefore, 0.5 mg/L was selected as an optimum initial concentration for this study.

Effect of mass of sorbent

To examine the effect of adsorbent dosage on the removal technique of 4-aminobiphenyl and benzidine, the adsorption study was completed by varying the mass of sorbent used from 1 to 50 mg. The result presented in Figure 4b shows the percentage of removal of 4-aminobiphenyl and benzidine with different sorbent dosages. There was an increasing pattern in the percentage of removal as the sorbent dosage used was increased from 1 to 25 mg due to the addition of active sites [11]. However, the removal efficiency decreased after 25 mg of β-CD-TDI polymer caused by the conglomeration of adsorbent [12]. Thus, 25 mg of sorbent dosage was selected as an optimum dose for the removal technique of 4-aminobiphenyl and benzidine.

Effect of solution temperature

Based on Figure 4c, the trends for the removal efficiency of 4-aminobiphenyl and benzidine decreased as the temperature increased (298 K, 318 K and 338 K). The ideal temperature for 0.5 mg/L of initial concentration was at room temperature (298 K) based on the highest value of removal efficiency 73.45 % (4-aminobiphenyl) and 72.39 % (benzidine). According to the result obtained, it was suggested that the adsorption process was exothermic [13]. An increase in the temperature of the solution could damage the active binding site of the analytes thus reducing the interaction of the analytes with an adsorbent [5].

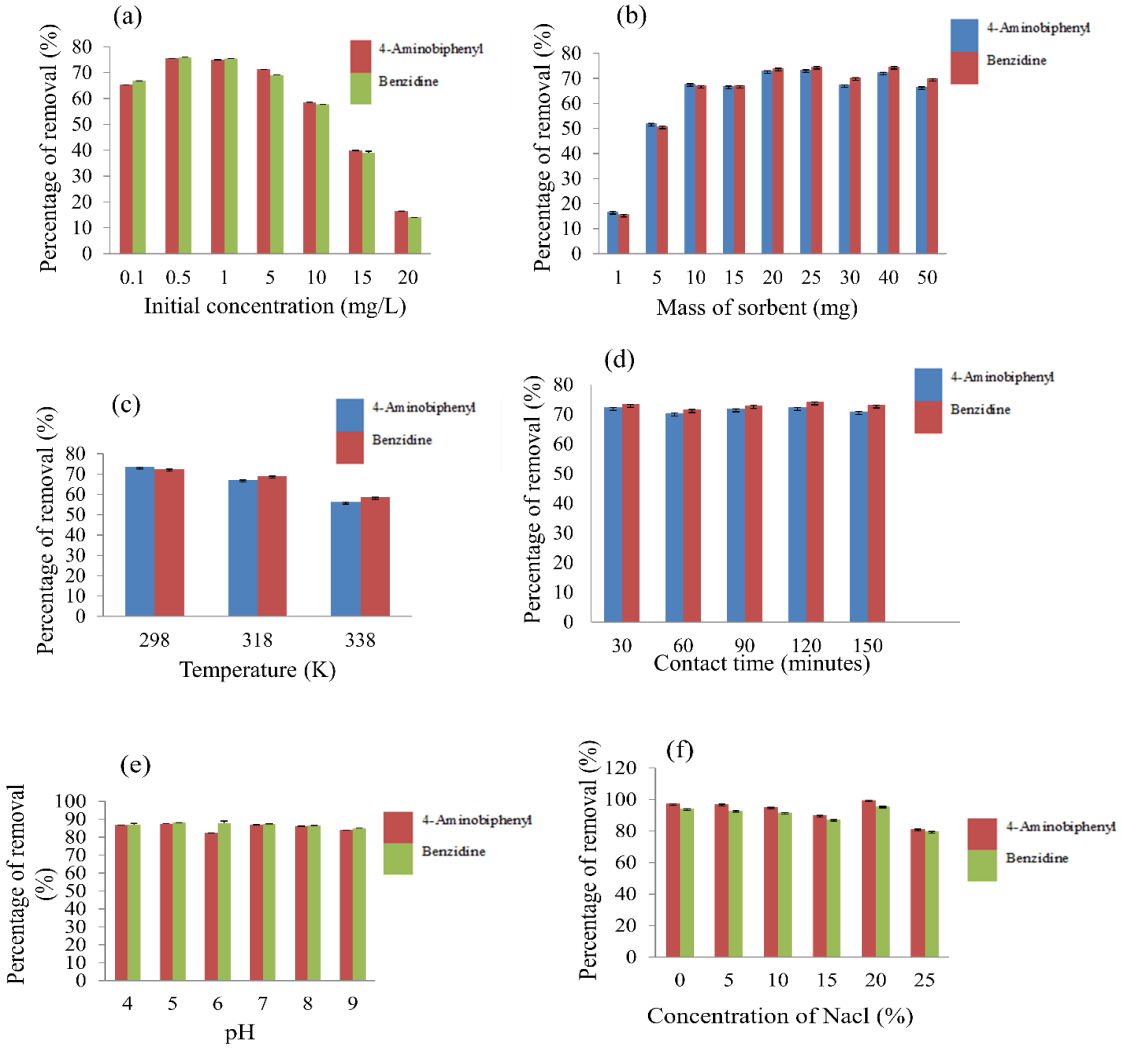

Figure 4. (a) Effect of initial concentration on the removal of 4-Aminobiphenyl and Benzidine by β-CD-TDI polymer; (b) Effect of mass of sorbent dosage on the removal of 4-Aminobiphenyl and Benzidine by β-CD-TDI polymer; (c) Effect of temperature on the removal of 4-Aminobiphenyl and Benzidine by β-CD-TDI polymer; (d) Effect of contact time on the removal of 4-Aminobiphenyl and Benzidine by β-CD-TDI polymer; (e) Effect of pH on the removal of 4-Aminobiphenyl and Benzidine by β-CD-TDI polymer; and (f) Effect of ionic strength on the removal of 4-Aminobiphenyl and Benzidine by β-CD-TDI polymer

Effect of contact time

The effect of contact time towards the removal technique of 4-aminobiphenyl and benzidine by β-CD-TDI polymer was explored in the range of 30 - 150 minutes at room temperature (298 K) and the result is presented in Figure 4d. There is no significant difference in the removal efficiency observed for 4-aminobiphenyl and benzidine in the first 120 minutes due to the presence of active sites on the surface of the β-CD-TDI polymer. There was a slight decreasing pattern for the percentage of removal after 120 minutes due to the saturation phase on the surface of the β-CD-TDI polymer. Thus, unoccupied active sites that were available were hardly occupied by analytes [14]. This

phenomenon was caused by the repulsion between the surface of β-CD-TDI and analytes. The removal efficiency decreased because the analytes needed to use extra energy to penetrate the surface of the adsorbent to bind with any available active sites [15].

Effect of pH

The effect of pH was studied by analyzing the performance of β-CD-TDI polymer during the removal technique of 4-aminobiphenyl and benzidine with different scales of pH. The range of pH studied is from pH 4 to pH 9. The result of this parameter is shown in Figure 4e. According to the data obtained, the maximum percentage of removal could be seen in pH 5 for both 4-aminobiphenyl and benzidine at 87.52 % and 88.05 % respectively. The effect of pH on the adsorption process of removal was influenced by the protonation of the functional group for both adsorbent and analytes [16]. At pH 5, the analyte reached the neutral form which allows it to take part in the hydrophobic interaction with β-CD-TDI polymer. While at low pH (pH 4) and high pH (pH 6-9), the analytes tend to be in protonated and deprotonated form which is not preferable to form an inclusion complex thus slightly affecting the removal efficiency [17]. At pH 6-9, the removal efficiency did not change significantly. During this stage, the role of pH is not significant for the removal technique however the high reactivity between 4-aminobiphenyl and benzidine towards β-CD-TDI polymer has been identified as the factor which caused the removal efficiency to maintain or change insignificantly. This is due to the ability of aromatic cross-linker TDI to form strong π-π stacking interaction with aromatic amines [5].

Effect of ionic strength

The ionic strength was investigated using, NaCl in the range of 0-25 % (w/w). Based on Figure 4f, there were no significant changes in the graph pattern as the percentage of the NaCl added was increased up to 15% however, there was a significant increase at 20 % of salt addition. This study proved that the addition of NaCl was able to facilitate the adsorption process [18]. The increased salt concentration reduced the solubility of analytes in the aqueous solution which increased the removal efficiency. Based on the data obtained, 20 % salt addition was selected as the best point for the removal of 4-aminobiphenyl and benzidine using β-CD-TDI polymer.

Adsorption studies: Adsorption kinetic

In the first part of the adsorption studies, two kinetics parameters were investigated on the adsorption of 4-aminobiphenyl and benzidine onto β-CD-TDI polymer. As shown in Appendix 2, the two models studied are pseudo first-order [19-20] and pseudo second-order [21]. The normalized standard deviation value, Δq (%) and relative error (%) were calculated to determine the suitability of the model. The equation for Δq (%) and relative error (%) is shown below:

$$\Delta q(\%) = \sqrt{\frac{[(q_{exp} - q_{cal})/q_{exp}]^2}{N-1}} \times 100 \quad (3)$$

$$Relative\ error(\%) = \left|\frac{q_{exp} - q_{cal}}{q_{exp}}\right| \times 100 \quad (4)$$

Where N indicates the number of data points, while q_{exp} and q_{cal} (mg/g) is defined as experimental and calculated adsorption capacities, respectively. The lower the value of the relative error (%) and Δq, the better and more suitable the model fit to the research [22,23]. Table 2 shows the calculated correlation of determination (R^2), normalized standard deviation, Δq (%) and relative error (%) for the adsorption of the 4-aminobiphenyl and benzidine based on 2 different types of models. Based on Appendix 2(b), the model that was well-fitted to the adsorption of 4-aminobiphenyl and benzidine was a pseudo second-order kinetic model due to the excellent value of the coefficient of determination, $R^2 > 0.999$, a lower value of Δq of 0.68% (4-aminobiphenyl) and 0.25% (benzidine) as well as relative error value of 1.37% and 0.50%, respectively. Furthermore, the calculated q_e value was closely like experimental data obtained at 0.171 mg/g (4-aminobiphenyl) and 0.256 mg/g (benzidine).

Table 2. Details of Kinetic parameter for the adsorption of 4-Aminobiphenyl and Benzidine onto β-CD-TDI polymer

Kinetic Model	Parameters	Analyte	
		4-Aminobiphenyl	**Benzidine**
	q_e, exp (mg/g)	0.1740	0.2579
Pseudo first order	q_e, cal (mg/g)	0.1718	0.0076
	K_1 (min^{-1})	0.0037	0.0032
	R^2	0.0834	0.1304
	Δq (%)	0.6322	48.5266
	Relative Error (%)	1.2644	97.0531
Pseudo second order	q_e, cal (mg/g)	0.1716	0.2566
	K_2 (min^{-1})	-24.18	5.1052
	H	-0.712	0.3361
	R^2	0.9995	0.9996
	Δq (%)	0.6897	0.2520
	Relative Error (%)	1.3793	0.5041

Based on the parameter value, it is suggested that the adsorption process in this study was controlled by chemisorptions [24], which involved the valence through the sharing or exchange of electrons [25]. Based on the suggestion stated, the adsorption mechanism was dependent on adsorbent and adsorbate [26, 27]. In comparison to the pseudo first-order kinetic model (2(a)), there was a poor correlation in the coefficient of determination value, R^2 which is 0.0834 (4-aminobiphenyl) and 0.1304 (Benzidine). The huge difference between q_{cal} to the q_{exp} increased the value of Δq which was 0.632% (4-aminobiphenyl) and 48.526% (benzidine). This showed that pseudo first-order was not well fitted to this study. Generally, the experimental data on the adsorption of 4-aminobiphenyl and benzidine on β-CD-TDI polymer fitted with the model of pseudo second-order.

Adsorption isotherm

The coefficient of determination, R^2 was used to estimate the relationship between the adsorbate and adsorbent through the formation of linear form. Table 3 demonstrated the experimental equilibrium data for the adsorption of 4-aminobiphenyl and benzidine on β-CD-TDI polymer at constant temperature, 298 K. The adsorption isotherm for these two aromatic amines on β-CD-TDI polymer was well fitted with the Dubinin kinetic model where the $R^2 > 0.8926$ for both analytes as shown in Appendices 3(c) and 3(f).

Table 3. Details of isotherm constant for the adsorption of 4-Aminobiphenyl and Benzidine onto β-CD-TDI polymer

Isotherm Model	Parameters	Analyte	
		4-Aminobiphenyl	**Benzidine**
Langmuir	q_m (mg/g)	1.4282	1.7200
	b (L/mg)	11.2389	-3.0860
	R^2	0.7830	0.7565
	R_L	0.1447	-0.7283
Freundlich	K_F	0.5631	0.6270
	n	1.5129	1.5694
	1/n	0.6610	0.6372
	R^2	0.8276	0.8094
Dubinin-Radushkevich	q_m (mg/g)	1.7570	2.2560
	β (mol^2/kJ^2)	0.0749	0.0905
	R^2	**0.9248**	**0.8926**
	E	7.3078	6.6482

In addition, this study was continued with the other models such as the Freundlich and Langmuir model. Based on Appendices 3(b) and 3(c), the correlation for both analytes was $R^2 > 0.0800$ which means that β-CD-TDI polymer has a heterogeneous surface. The n values that were calculated represent the Freundlich constant for both analytes were in the range of $2 > n > 1$ thus showing the pseudo-linear of the model. Next, the value of $\beta < 0.1$ calculated from Dubinin-Radushkevich's isotherm (Table 3) for the adsorption of these two analytes indicated a rough surface and multilayer structure. This result aligned with the isotherm data from Freundlich's model which suggested that adsorption of 4-aminobiphenyl and benzidine occurred on the heterogeneous surfaces of β-CD-TDI polymer consisting of many cavities (CD), isocyanate group and imidazolium ring [25]. The fitted isotherm model to the adsorption equilibrium was calculated in the order of Dubinin > Freundlich > Langmuir.

Adsorption thermodynamic

Based on Table 4, the result of ΔG° was calculated to be a negative value for the adsorption of 4-aminobiphenyl (-2.9995, -3.0291 and -3.0482 kJ/mol). A negative value was observed for benzidine at low temperatures (-0.115 kJ/mol) but changed to positive values (0.306 and 1.5954 kJ/mol) as the temperature increased. The result showed that the process is spontaneous for 4-aminobiphenyl at all temperatures however for benzidine only at low temperatures (298 K). As the temperature increased, the process became non-spontaneous for benzidine [28].

Next, the enthalpy value (ΔH) calculated for both analytes showed negative values of -2.6355 J/mol (4-aminobiphenyl) and -12.7129 J/mol (benzidine). These values pointed out that the adsorption process was exothermic. Besides, the negative value of Entropy (ΔS°) for benzidine was due to the decreasing randomness at the solid-solution interface during the adsorption process [29]. In the meantime, the positive value of ΔS° for 4-aminobiphenyl (1.228 J/Kmol) was due to the decrease in degree of freedom at the solid-solution interface of the adsorption process. In conclusion, the adsorption process for 4-aminobiphenyl and benzidine was exothermic and spontaneous for 4-aminobiphenyl at all temperatures while spontaneous at low temperatures and non-spontaneous at high temperatures for benzidine.

Table 4. Thermodynamic parameters for 4-Aminobiphenyl and Benzidine on β-CD-TDI polymer

Analyte	Temperature, (K)	Enthalpy, ΔH^o (J/mol)	Entropy, ΔS^o (J/Kmol)	Gibbs Energy, ΔG^o (kJ/mol)
4-Aminobiphenyl	298			-2.9995
	318	-2.6355	1.2280	-3.0291
	338			-3.0482
Benzidine	298			-0.115
	318	-12.7129	-41.8502	0.3060
	338			1.5952

Method validation: Precision

The analysis was performed five times (*n=5*) and was carried out day-to-day on two consecutive days (*n=2*). All measurements were performed in triplicate. As for precision, the results were reported in the form of relative standard deviation value (RSD) (%). Based on Table 5, the RSD values for 4-aminobiphenyl and benzidine recorded for intra-day were 0.4432 and 0.5487. While for inter-day, the RSD values calculated were 0.5487 (4-aminobiphenyl) and 2.8512 (benzidine).

Reusability study of β-CD-TDI polymer

The reusability study was investigated by using the used polymer for the next analysis. The polymer has been stirred in ACN and dried in the oven for 1-2 hours [5]. Based on Figure 5, the adsorbent can be used after 5 times without significant reduction in the removal efficiency.

Table 5. Precision study by intra-day and inter-day

Analyte	Intra-day (RSD, %)	Inter-day (RSD, %)
4-Aminobiphenyl	0.4432	0.5487
Benzidine	0.6463	2.8512

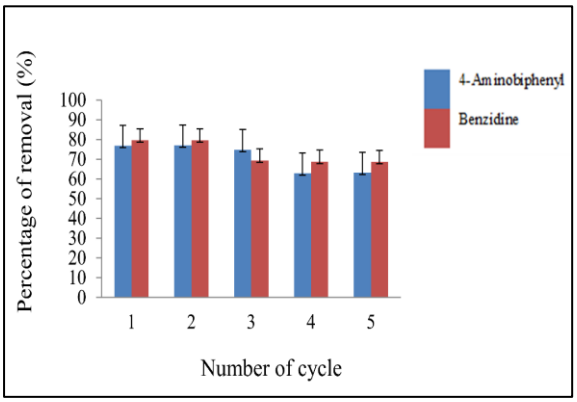

Figure 5. Reusability of removal efficiency on β-CD-TDI polymer in five (5) different cycle

Analysis of real sample

The developed method was applied to real samples to assess the suitability of the adsorbent towards the analytes. There were three different types of batik wastewater collected in Kota Bharu, Kelantan. All the samples underwent several steps of pre-treatment prior to the removal technique using β-CD-TDI polymer. The removal efficiency (%) of 4-aminobiphenyl and benzidine was successfully illustrated in Figure 6 for batik wastewater samples. Based on Table 6, the removal efficiency for 4-aminobiphenyl on the three samples was (A (79.60%), B (66.74%), C (59.82%)) and for benzidine was (A (76.55%), B (72.29%) and C (59.79%)). From the result, the matrix effect in the samples has significantly influenced the removal efficiency for sample C. The presence of biological inert matter in the wastewater which chemically binds with high molecular weight dyestuff could cause low removal efficiency of 4-aminobiphenyl and benzidine in batik wastewater [30]. This is because physical adsorption is only preferable for non-biodegradable matter. Furthermore, the presence of grease, wax and surfactant in the batik wastewater might be the reason for the low removal efficiency in sample C [31]. Besides, the low percentage of removal in the real samples could be related to the complex structure of the synthetic dyes which caused low adsorption of 4-aminobiphenyl and benzidine onto the surface of β-CD-TDI polymer. The complex structure of synthetic dyes used in the batik industry increases their resistance to water, detergents and other washing agents so that the colour does not fade easily [1].

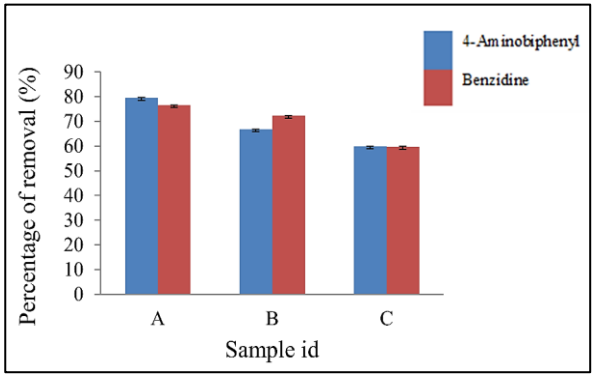

Figure 6. The percentage removal of 4-Aminobiphenyl and Benzidine using β-CD-TDI polymer from batik wastewater samples at room temperature

Table 6. Data on the removal of 4-aminobiphenyl and benzidine from batik wastewater

Sample	**A**		**B**		**C**	
Analyte	**Found (mg/L)**	**Removal ± RSD (%)**	**Found (mg/L)**	**Removal ± RSD (%)**	**Found (mg/L)**	**Removal ± RSD (%)**
4-Aminobiphenyl	11.17	79.60 ± 1.41	35.67	66.74 ± 0.02	17.16	59.82 ± 0.08
Benzidine	7.74	76.55 ± 0.03	27.96	72.29 ± 0.01	11.82	59.79 ± 0.65

Table 7. Comparison of the previous studies for the extraction of AAs in various samples

Method/Adsorbent	**Analytes AA**	**Linearity (mg/L)**	**LODs (µg L^{-1})**	**Detection**	**Sample Matrix**	**RSD (%)**	**References**
NaH_2PO_4	7	3.3-120	2.61-5.33	CE	Wastewater	2.2-6.6	[32]
βCD	9	1.151-223.86	$6.7x10^{-6}$-$4.5x10^{-4}$	MECC	Water	1.6-3.1	[33]
M@CCNs/EE-SPME	6	0.0 013–0.012	0.0013-0.0060	HPLC-DAD	Textile Wastewater	1.1-8.4	[34]
SPE cartridge	24	0.003-0.1	0.05-1.6	UHPLC-MS/MS	Food	0.1-15.9	[35]
β-CD-TDI	2	-	-	UV-VIS	Wastewater	0.01-1.41	This work

Conclusions

β-CD-TDI polymer has been successfully synthesised and characterised using various instruments. The obtained results were compared with native β-CD and TDI. From the FTIR result, the complete polymerization of β-CD-TDI polymer was observed. The morphology analysis by SEM showed the presence of the cross-linker based on the increase of pores on the surface of the polymer simultaneously increasing the roughness on the surface of β-CD-TDI polymer compared to β-CD. The performance of β-CD-TDI polymer in the removal of 4-aminobiphenyl and benzidine from aqueous solution was successfully evaluated. The optimum removal of these analytes was observed at initial concentration; 0.5 mg/L, sorbent dosage; 25 mg, temperature; 298 K, contact time; 120 minutes, pH; 5 and 20% (w/w) of NaCl added. According to the kinetic analysis result, the pseudo second-order equation formed an excellent correlation for the adsorption of 4-aminobiphenyl (0.9995) and benzidine (0.9996). The model of adsorption isotherm that fits with this study is Dubinin-Radushkevich's isotherm. The spontaneity of the study can be investigated through thermodynamic adsorption study. Based on the result obtained, this study was confirmed as exothermic and spontaneous at all temperatures for 4-aminobiphenyl. However, for benzidine, the reaction was only spontaneous at low temperatures (298 K) and became non-spontaneous as the temperature increased. Through this approach, a new method has been successfully developed to remove the studied aromatic amines from wastewater with some advantages such as being environmentally friendly, easily synthesised, good repeatability and good selective separation.

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References

1. Katheresan, V., Kansedo, J., and Lau, S. Y. (2018). Efficiency of various recent wastewater dye removal methods: A review. *Journal of environmental chemical engineering*, 6(4): 4676-4697.
2. El Bouraie, M., and El Din, W. S. (2016). Biodegradation of Reactive Black 5 by *Aeromonas hydrophila* strain isolated from dye-contaminated textile wastewater. *Sustainable Environment Research*, 26(5): 209-216.
3. Toor, S. K., Kushwaha, J. P., and Sangal, V. K. (2019). Adsorptive interaction of 4-aminobiphenyl with mesoporous MCM-41. *Physics and Chemistry of Liquids*, 57(6): 720-732.
4. Kaur, S., Rani, S., and Mahajan, R. K. (2013). Adsorption kinetics for the removal of hazardous dye congo red by biowaste materials as adsorbents. *Journal of Chemistry*, 2013(1): 628582.
5. Anne, J. M., Boon, Y. H., Saad, B., Miskam, M., Yusoff, M. M., Shahriman, M. S., ... and Raoov, M. (2018). β-Cyclodextrin conjugated bifunctional isocyanate linker polymer for enhanced removal of 2,4-dinitrophenol from environmental waters. *Royal Society Open Science*, 5(8): 180942.
6. Liang, Q., Chai, K., Lu, K., Xu, Z., Li, G., Tong, Z., and Ji, H. (2017). Theoretical and experimental studies on the separation of cinnamyl acetate and cinnamaldehyde by adsorption onto a β-cyclodextrin polyurethane polymer. *RSC Advances*, 7(69): 43502-43511.
7. Boon, Y. H., Zain, N. N. M., Mohamad, S., Osman, H., and Raoov, M. (2019). Magnetic poly (β-cyclodextrin-ionic liquid) nanocomposites for micro-solid phase extraction of selected polycyclic aromatic hydrocarbons in rice samples prior to GC-FID analysis. *Food Chemistry*, 278: 322-332.
8. Raoov, M., Mohamad, S., and Abas, M. R. (2013). Synthesis and characterization of β-cyclodextrin functionalized ionic liquid polymer as a macroporous material for the removal of phenols and As (V). *International Journal of Molecular Sciences*, 15(1): 100-119.
9. Navarro, A. E., Hernandez-Vega, A., Masud, M. E., Roberson, L. M., and Diaz-Vázquez, L. M. (2016). Bioremoval of phenol from aqueous solutions using native Caribbean seaweed. *Environments*, 4(1): 1.
10. Garg, V. K., Kumar, R., and Gupta, R. (2004). Removal of malachite green dye from aqueous solution by adsorption using agro-industry waste: a case study of Prosopis cineraria. *Dyes and Pigments*, 62(1): 1-10.
11. El Qada, E. N., Allen, S. J., and Walker, G. M.

(2006). Adsorption of basic dyes onto activated carbon using microcolumns. *Industrial & engineering chemistry research*, 45(17): 6044-6049.

12. Crini, G., and Badot, P. M. (2008). Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature. *Progress in Polymer Science*, 33(4): 399-447.
13. Alam, M. A., Shaikh, W. A., Alam, M. O., Bhattacharya, T., Chakraborty, S., Show, B., and Saha, I. (2018). Adsorption of As(III) and As(V) from aqueous solution by modified *Cassia fistula* (golden shower) biochar. *Applied Water Science*, 8: 1-14.
14. Chandra Srivastava, V., Deo Mall, I., and Mani Mishra, I. (2006). Modelling individual and competitive adsorption of cadmium (II) and zinc (II) metal ions from aqueous solution onto bagasse fly ash. *Separation Science and Technology*, 41(12): 2685-2710.
15. Allen, S. J., Gan, Q., Matthews, R., and Johnson, P. A. (2005). Kinetic modeling of the adsorption of basic dyes by kudzu. *Journal of Colloid and Interface Science*, 286(1): 101-109.
16. Guo, L., Li, G., Liu, J., Yin, P., and Li, Q. (2009). Adsorption of aniline on cross-linked starch sulfate from aqueous solution. *Industrial & Engineering Chemistry Research*, 48(23): 10657-10663.
17. Li, N., Mei, Z., and Wei, X. (2012). Study on sorption of chlorophenols from aqueous solutions by an insoluble copolymer containing β-cyclodextrin and polyamidoamine units. *Chemical Engineering Journal*, 192: 138-145.
18. Kim, E., Jung, C., Han, J., Her, N., Min Park, C., Son, A., and Yoon, Y. (2016). Adsorption of selected micropollutants on powdered activated carbon and biochar in the presence of kaolinite. *Desalination and Water Treatment*, 57(57): 27601-27613.
19. Febrianto, J., Kosasih, A. N., Sunarso, J., Ju, Y. H., Indraswati, N., and Ismadji, S. (2009). Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: a summary of recent studies. *Journal of hazardous materials*, 162(2-3): 616-645.
20. Larsen, E. K., Nielsen, T., Wittenborn, T., Birkedal, H., Vorup-Jensen, T., Jakobsen, M. H., ... and Kjems, J. (2009). Size-dependent accumulation of PEGylated silane-coated magnetic iron oxide nanoparticles in murine tumors. *ACS Nano*, *3*(7): 1947-1951.
21. Ho, Y. S., McKay, G., Wase, D. A. J., and Forster, C. F. (2000). Study of the sorption of divalent metal ions on to peat. *Adsorption Science & Technology*, 18(7): 639-650.
22. Shaarani, F. W., and Hameed, B. H. (2011). Ammonia-modified activated carbon for the adsorption of 2, 4-dichlorophenol. *Chemical Engineering Journal*, 169(1-3): 180-185.
23. López, M. D. M. C., Pérez, M. C., García, M. S. D., Vilariño, J. M. L., Rodríguez, M. V. G., & Losada, L. F. B. (2012). Preparation, evaluation and characterization of quercetin-molecularly imprinted polymer for preconcentration and clean-up of catechins. *Analytica Chimica Acta*, 721: 68-78.
24. Tan, I. A. W., Ahmad, A. L., and Hameed, B. H. (2009). Adsorption isotherms, kinetics, thermodynamics and desorption studies of 2, 4, 6-trichlorophenol on oil palm empty fruit bunch-based activated carbon. *Journal of Hazardous Materials*, 164(2-3): 473-482.
25. Raoov, M., Mohamad, S., and Abas, M. R. (2013). Removal of 2, 4-dichlorophenol using cyclodextrin-ionic liquid polymer as a macroporous material: characterization, adsorption isotherm, kinetic study, thermodynamics. *Journal of Hazardous Materials*, 263: 501-516.
26. Crini, G., Peindy, H. N., Gimbert, F., and Robert, C. (2007). Removal of CI Basic Green 4 (Malachite Green) from aqueous solutions by adsorption using cyclodextrin-based adsorbent: Kinetic and equilibrium studies. *Separation and Purification Technology*, 53(1): 97-110.
27. Pavan, F. A., Dias, S. L., Lima, E. C., and Benvenutti, E. V. (2008). Removal of Congo red from aqueous solution by anilinepropylsilica xerogel. *Dyes and Pigments*, *76*(1): 64-69.
28. Gueu, S., Yao, B., Adouby, K., and Ado, G. (2007). Kinetics and thermodynamics study of lead adsorption on activated carbons from coconut and seed hull of the palm tree. *International Journal of Environmental Science & Technology*, 4: 11-17.
29. Aydın, Y. A., and Aksoy, N. D. (2009). Adsorption of chromium on chitosan: Optimization, kinetics and thermodynamics. *Chemical Engineering Journal*, 151(1-3): 188-194.

30. Lin, S. H., and Peng, C. F. (1994). Treatment of textile wastewater by electrochemical method. *Water research*, 28(2): 277-282.
31. Buthiyappan, A., Raman, A. A. A., and Daud, W. M. A. W. (2016). Development of an advanced chemical oxidation wastewater treatment system for the batik industry in Malaysia. *RSC Advances*, 6(30): 25222-25241.
32. Szabo, B. S., Jakab, P. P., Hegedűs, J., Kirchkeszner, C., Petrovics, N., Nyiri, Z., ... and Zsuzsanna, E. K. E. (2021). Determination of 24 primary aromatic amines in aqueous food simulants by combining solid phase extraction and salting-out assisted liquid–liquid extraction with liquid chromatography tandem mass spectrometry. *Microchemical Journal*, 164: 105927.
33. Wu, J., Huang, Y., and Huang, X. (2022). Efficient trap of polar aromatic amines in environmental waters by electroenhanced solid phase microextraction based on porous monolith doped with carboxylic carbon nanotubes. *Separation and Purification Technology*, 282: 120067.
34. Ye, S., and Huang, F. (2007). Separation of carcinogenic aromatic amines in the dyestuff plant wastewater treatment. *Desalination*, 206(1-3): 78-85.
35. Khawaji, A. D., Kutubkhanah, I. K., and Wie, J. M. (2008). Advances in seawater desalination technologies. *Desalination*, 221(1-3): 47-69.