



Removal of Brilliant Green and Direct Blue Dyes from Wastewater Dependently on the Polarity of Isothiouonium Polyurethane Foam

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ABSTRACT

Polyurethane foam functionalized with isothiuronium group (ITPUF) was prepared and characterized using infrared and ultraviolet/visible spectra, bulk conductivity, iodine number, methylene blue value, zero point charge, and elemental analysis. The new sorbent has a highly capacity and good stable in acidic and alkaline solutions. The efficiency of ITPUF for removing of hazardous compounds e.g. brilliant green (BG) and direct blue (DB) dyes from wastewater were investigated with the batch and dynamic techniques. The percentages of dyes removed (80-100%) from wastewater were at pH range 2-10 and 1-7 within 3-5 min. Freundlich, Langmuir, Temkin, Harkins Jura, and Dubinin-Radushkevich adsorption models were applied to describe the removing mechanism and the equilibrium isotherms data were estimated. The capacity of ITPUF for BG and DB were 0.38 and 0.19 mmol/g. The kinetic nature of removing process was analyzed using different mathematical models and that provided the values of second order rate constant (k_2) are 4.43 and 0.45 $\mu\text{mol g/min}$, respectively. The results obtained indicate that confirming the suitability of ITPUF as a new sorbent for removing of dyes from wastewater.

Keywords: Isothiouonium polyurethane foam; Brilliant green; Direct blue; Dyes; Removal

INTRODUCTION

The Damietta industrial areas in Egypt, which is famous for its industries, including furniture, textile dyeing, dye wool, nylon, and silk fibers textile, confectionery, leather, cheese industry, where exports its products to several countries [1-3]. Some of these industries that rely on the use of dyes and toxic substances and harmful ultimately lead to harming the health of humans and the environment [4-6]. The wastes of these industries which contain dyes caused the aesthetic pollution of the purity of the water also harms the environment and caused diseases are carcinogenic. Therefore, the removing of these pollutants from the effluent of dyeing industries before its discharge is very important polluting [7-9].

The adsorption process is one of the most promising and extensively method was used for removing of dyes from industrial wastewater. It is inexpensive method due to regenerate and reuses the adsorbent many times [10-14]. Various materials of adsorbent were used for the removing process; however, a novel, economic, locally available and highly removing capacity is still needed to investigate for the scavenging of dye from wastewater.

Polyurethane foam (PUF) is a good sorbent, which has chemical and physical properties that it is suitable for sorption of organic and inorganic compounds from different environmental samples [15,16]. The importance of PUF as a sorbent is due to its sorption efficiency, low cost, handling and storage [17- 19]. In this work, we prepared a new type of polyurethane foam by modified its matrix with thiol functional then coupling with magnetite nanoparticles through two steps. In the first step, add chlorine (Cl) atom to PUF matrix using Sandmeyer and Meerwein Reactions ($\text{PUF-NCO} + \text{HCl} \rightarrow \text{PUF-NH}_2 + \text{NaNO}_2 \rightarrow \text{PUF-N}_3\text{Cl} + \text{CuCl} \rightarrow \text{PUF-Cl}$) [20]. Then the

PUF chloride is converted to thiols via a S-alkylation of thiourea (PUF-Cl + SC(NH₂)₂ → PUF-SC(NHNH₂) [21]. This multistep, one-pot process proceeds via the intermediacy of the isothiuronium salt. The new sorbent (ITPUF) has offering better surface area and sorption capacity for removing of dyes. The sorption conditions employing batch technique, for the removal of brilliant green and direct blue dyes by the ITPUF including pH, initial concentrations, shaking time and temperature were optimized. The ITPUF can also be recycled many times with no significant decrease in sorption capacity.

EXPERIMENTAL SECTION

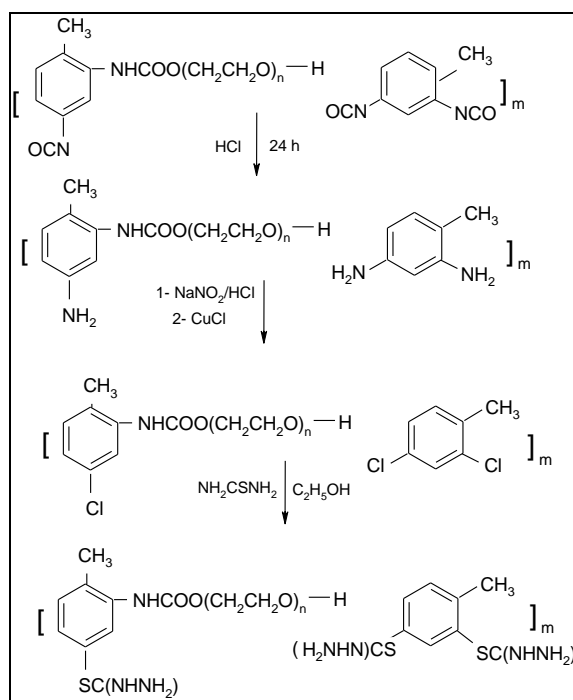
Apparatus

All spectrophotometric measurements were performed on a JASCO (V-630 UV-VIS Spectrophotometer, Japan). The pH measurements were carried out using a Jenway 3510 pH-meter (Beacon Road, Stone, Staffordshire, ST15 OSA, UK).

Reagents and materials

Preparation of ITPUF as following: 10 g PUF was soaked in 1 mol/L of HCl (24 h) to liberate the maximum number of free primary amine groups and then kept in HCl (0.1 mol L⁻¹) in an ice bath. Then the PUF was diazotized by the drop wise addition and vigorous stirring of 50 mL of NaNO₂ (2 mol/L) to form PUF-N₃Cl. Add 50 mL of 0.3 mol/L of CuCl to diazonium salt of PUF at ice bath. Then mix of product of PUF with 15 g thiourea in 200 mL ethanol followed by reflux 2 h at 50 ° C. The ITPUF material was washed with distilled water followed by acetone and finally air-dried (Scheme 1).

Stock solutions of brilliant green (C₂₇H₃₄N₂O₄S, 482.65 g/mol) and direct blue (C₄₀H₂₈N₇NaO₁₃S₄, 965.94 g/mol) were prepared by dissolving of 0.1 g of each dye in 100 mL of distilled water.



Scheme 1

Recommended procedures

The 100 mL conical flasks containing 25 mL of BG and DB dyes solution of known pH, concentration were shaken. The pH of the solution was adjusted using 0.1 M HCl and 0.1 M NaOH solutions. After 60 minutes, the samples of BG and DB dyes were taken out and concentration of remaining dye solution and also the recovering from ITPUF were determined spectrophotometrically.

The removal percentage of dye (E) and capacity of ITPUF (Q, mmol/g), was calculated using the following relationship: $\%E = ((C_o - C)/C_o) \times 100$ and $Q = C_oEV/m$ where C_o and C are the initial and final concentrations of dye in solution, respectively and V (mL) is the volume of the solution and m is the mass of the ITPUF.

RESULTS AND DISCUSSION

Characterization of ITPUF

The FTIR spectra of PUF and ITPUF are shown in Figure 1. The characteristic absorptions peaks of the PUF are observed at 3401.81cm^{-1} (N-H), 2888.8cm^{-1} (C-H), 2258.2cm^{-1} (N=C=O) and 1625.4cm^{-1} (C=O of urethane). In the spectrum of ITPUF, the N=C=O was disappeared and new absorption band appeared at 2036.4cm^{-1} due to -SC(NHNH₂) (isothiuronium) group. The N-H and C-H bands are shifted to 3293.8 and 2863.7cm^{-1} about 108 and 25cm^{-1} that obvious these kinds of peaks of the ITPUF show blue-shift comparing with the corresponding PUF due to the extending of conjugation system after addition of -SC(NHNH₂) group. The results obtained indicate that the surface of ITPUF contains some specific function groups (Table 1) which makes it an efficient sorbent for the extraction of organic dyes. The $\nu_{(\text{NH})}$ of the ITPUF at 3396cm^{-1} was shifted to lower frequencies (3342 , 3253 and 3363cm^{-1}) after sorbed BY, BG and DB, respectively. Also, the absorption band at 2036.4cm^{-1} due to -SC(NHNH₂) is shifted to 2011 and 2071cm^{-1} in the spectra of ITPUF: BY and ITPUF:BG while disappeared in ITPUF:DB. A new absorption bands appeared at 2204 , 2210 and 2237cm^{-1} due to specific groups of dyes (CS=O and C=NC).

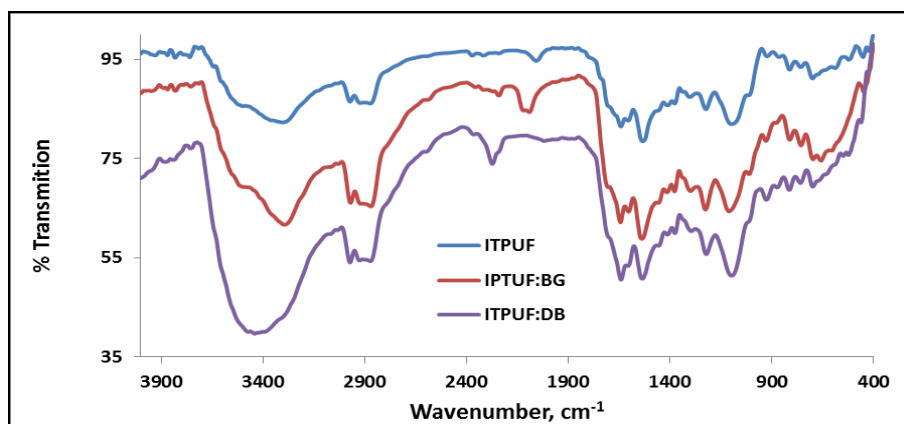


Figure 1: Infrared spectra of ITPUF, ITPUF:BG and ITPUF:DB

The electronic spectra of PUF and ITPUF were recorded in the solid state using Nujol mulls method. Figure 1 shows the absorption spectra and the corresponding data are summarized in Table 1. PUF has absorption bands at 205, 209 and 218 nm assigned to the transitions ($\pi-\pi^*$ and $n-\pi^*$) localized on the conjugated system. These higher energy bands were blue-shifted to 203, 207, 213 nm for ITPUF due to replace the isocyanate group by isothiuronium group. Also, the isothiuronium groups in ITPUF can be detected by the reaction with $\text{Pb}(\text{CH}_3\text{COO})_2$ solution. The spectra of ITPUF were shifted to 237 and 279 nm upon the reaction of lead ions with the ITPUF groups (Figure 2).

Table 1: Properties of ITPUF

Property	ITPUF
C, H, N, S (%)	60.0, 5.8, 8.8, 1.8
IR (cm^{-1})	3293.8, 2863.7, 2036.4, 1633.4
UV-Vis (nm)	203, 207, 213
Basicity (mmol g^{-1})	3.63
Acidity (mmol g^{-1})	0.03
pHZPC	1.9
Iodine number (mmol g^{-1})	3.76
Methylene blue capacity (mmol g^{-1})	0.46

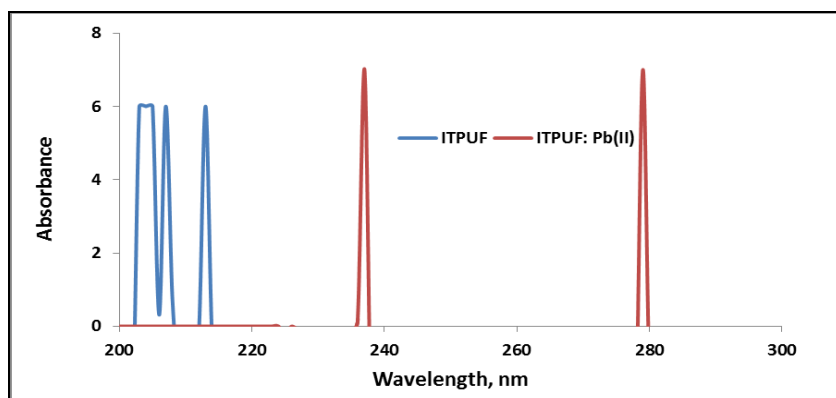


Figure 2: UV spectra of ITPUF and ITPUF after sorbed lead(II) ions

To describe the surface charge of the modified sorbents, the zero charge point (pH_{ZPC}) was determined. The pH_{ZPC} value is based on the membrane-like structure of the ITPUF such as urethane NHCOO , ether CH_2OCH_2 , and terminal $\text{SC}(\text{NHNH}_2)$ groups. The values of pH_{ZPC} for PUF and ITPUF were determined to be 8.9 and 1.9, respectively. Also, the maximum values of ΔpH for PUF and ITPUF are -0.57 and -4.08 at pH 9.7 and pH 10.4, respectively. The obtained results show that the net charge of ITPUF is greater than that of PUF, indicating the high polarity of ITPUF compared with PUF. At pH value < 1.9 , the surface of the ITPUF would be positively charged while at pH value > 1.9 , the surface of the ITPUF would be negatively charged.

The values of electrical conductivity (σ) of PUF and ITPUF are 1.6×10^{-8} and $1.1 \times 10^{-7} \Omega^{-1}\text{m}^{-1}$, respectively (Table 1). This result indicates the ITPUF is more polarity than PUF phase. This result discusses the ability of ITPUF for attracting the acidic and basic dyes according to the polarity of function groups of these dyes.

Acidic and basic sites of the surface of the sorbent were determined using a 0.1 mol/L NaOH and HCl solutions (Table 1). The basic sites of ITPUF are found to be 3.63 mmol g^{-1} . This result shows that the basic sites of ITPUF are higher than PUF due to basicity ($\text{CS}(\text{NH}_2)_2$) group. While the acidic sites of ITPUF (0.03 mmol g^{-1}) are less than PUF (0.4 mmol g^{-1}). By comparing the acidic sites with the basic ones in the ITPUF, it is clear that the total basic sites are greater than those of the acidic ones ($3.63 \text{ mmol g}^{-1} : 0.03 \text{ mmol g}^{-1} = 121 : 1$).

The iodine number gives information about the internal surface area of an adsorbent; since it is assumed to measure the surface area in micropores within pore sizes $\geq 10 \text{ \AA}$. The iodine molecule is relatively small with an area $0.15\text{--}0.42 \text{ nm}^2$ and can enter in the smaller micropores of sorbent particles, providing information about the internal surface. The iodine number of both ITPUF and PUF were calculated to be 3.8 and 1.6 mmol g^{-1} , respectively (Table 1).

The surface ITPUF was also characterized by estimation of methylene blue value (cation exchange capacity). The data revealed that the adsorption capacity of ITPUF and PUF are 0.5 and 0.0 mmol/g . Also, the methylene blue value is proportional to the surface area and pore volume of sorbent, demonstrating that they are interesting probes for the determination of these properties. Indeed, the methylene blue molecule has an area of 2.08 nm^2 and can only enter in large micropores and mesopores.

The percentage of carbon, hydrogen, nitrogen and sulfur of PUF and ITPUF are estimated and shown in Table 1. The results show that PUF contains carbon 64.7%, hydrogen 7.8%, nitrogen 7.9% and oxygen 19.6%. These percentages changed after the coupling between PUF and thiourea to 60.0, 5.8, 8.8, 1.8 and 23.6 for carbon, hydrogen, nitrogen, sulfur and oxygen, respectively. This result shows that sulfur percentage of ITPUF (1.8%) is greater than that of the PUF (0.0%) due to add thiourea. However, the percentages of carbon, nitrogen and oxygen decreased due to the leaching out of some urethane groups.

Optimum conditions for the removal of BG and DB using ITPUF

The initial pH of the solution is one of the main basic factors for removing of BG and DB dyes onto ITPUF due to effects on the activity of functional groups for both ITPUF and tested dyes. The pH of BG and DB solutions was adjusted by using HCl and NaOH solutions. Figure 3 shows that the maximum removal percentages of BG and DB were achieved at pH 2-10 and 1-3, respectively.

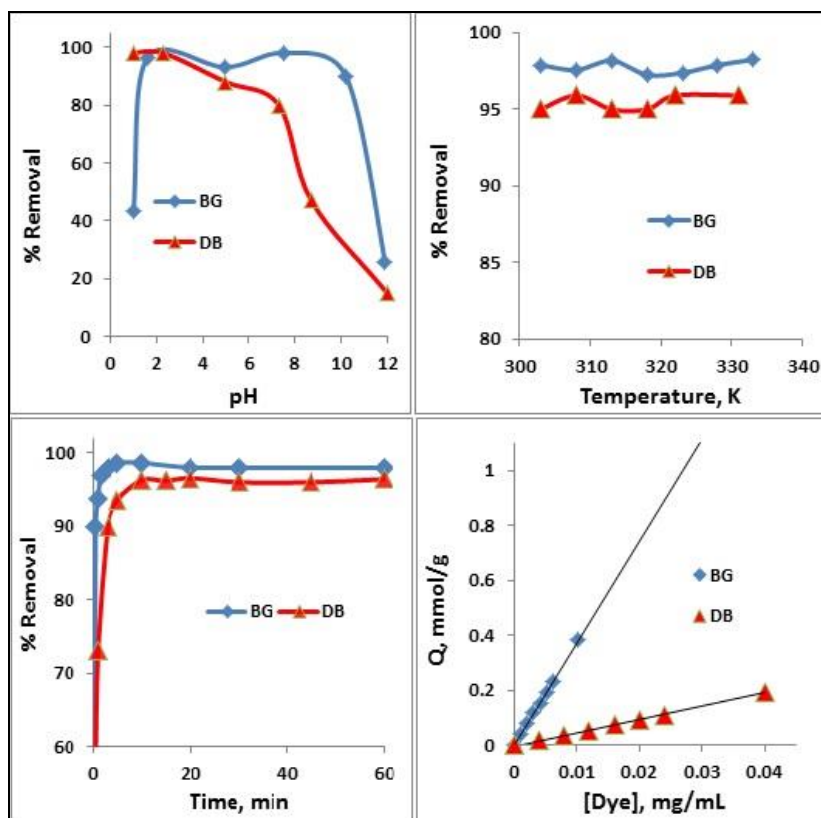


Figure 3: Effect of initial pH on the extraction of dyes onto ITPUF

The effect of temperature on the removal percentages of BG and DB were investigated (Figure 3). The result shows that the removal percentages of BG and DB are slightly effect by increasing the temperature. This result indicates that we can efficiency removal of the tested dyes from hot wastewater–industries (~ 60 °C) by using ITPUF as a novel sorbent.

The effect of shaking time (0.5-60 min) on the sorption of BG and DB (0.004 mg mL^{-1}) dyes onto ITPUF was tested. The time required for completely removal of BG and DB (92-99%) onto ITPUF 3 and 10 minutes, respectively (Figure 3). This rapid sorption rate of tested dyes is due to the strong bond formation with the ITPUF. It was noticed that the initial removal rate of dye is very fast, where ~90% of the total dyes concentration was removal from the tested solutions at the first 3 minutes.

Then the rate slowed down progressively with time and the equilibrium extraction is reached within a period of 5 to 10 min. Initially all the active sited on the surface of ITPUF are vacant and dyes molecules easily occupy these binding sites. With the progress of reaction, the binding sites become saturated and sorption process becomes slower. This result indicates that the removal rate depends on the nature of the reaction between ITPUF and dye molecules.

Figure 3 depicts the effect of the BG and DB concentrations on the batch capacity (Q_B) of ITPUF. The result shows that the good relation curve between the capacity and initial concentration which intercept values are 0.001 and 0.004 for sorption of BG and DB, respectively.

Also, the correlation coefficients of the isotherm curves are 0.999 and 0.998. It is obvious that the increase of BG and DB concentrations is followed by a subsequent increase in the sorption capacity that points to the significant role of dye concentrations on the capacity of the ITPUF.

The values of the batch capacity of the ITPUF for BG and DB were calculated to be 0.38 and 0.19 mmol/g (183.4 and 183.5 mg/g), respectively. The result indicates that the amount of dye sorbed onto ITPUF mainly depends on the dye functional groups not the size of dye.

Sorption mechanism

The sorption behavior of BG at different pH values shows that the maximum removal percentage of BG (96-98%) in a wide range of pH values (pH 2-10) then it was decreased from ~90% (pH 10.2) to 25% at pH 12. This shows that the removal of BG is independent of the medium of the dye solution. The pH_{ZPC} value of ITPUF was approximately 1.9, where over that value the net negative charge on the ITPUF surface.

Accordingly, the electrostatic attraction between cation dye (BG) and functional groups of the ITPUF would take place at pH 2-10 leads to the BG completely removal from the solution at pH 2-10. The surface negative charge of ITPUF was decreased from pH 10-12 this accompanying of the removing of BG. Also, the maximum removal percentage of BG (99%) took place at pH 7-10, these values of pH is corresponding to high charge density of ITPUF. For DB (anionic dyes), the maximum removal percentage of these dyes took place at pH 1-2 due to the electrostatic attraction between DB with ITPUF.

An increasing of pH of DB solutions over pH 2, the removal of these dyes were decreased due to increasing negative charges on the ITPUF surface which results in electrostatic repulsion between DB and ITPUF. The sorption behavior of BG onto ITPUF is reversed than sorption of DB, this result indicates that the sorption process depends on the functional groups of dyes.

This result is due to a difference in functional group of both BG and DB. The average of removal percentage of BG and DB is ~96% while this percentage of dyes onto PUF is 58%. The result clearly emphasized that ITPUF is more efficient than PUF for removing basic and acidic dyes from aqueous solution.

Kinetic studies

The diffusion rates of BG, BY and DB dyes onto ITPUF were measured using Bangham, Weber-Morris and Reichenberg equations

$$[\log \log C_o / (C_o - Q_t) = \log k_o m / 2.303V + \alpha \log t], [Q_t = k_i \sqrt{t}] \text{ and} \\ [Bt = -0.4977 - \ln(1 - F)] \& [F = (6/R)(D_i t / \pi)^{1/2}].$$

The double logarithmic plots of Bangham equation with the time yield perfect linear curves, the correlation values coefficient for sorption of BG and DB are 0.596 and 0.761, respectively (Table 2). This result is showing that the diffusion of BG and DB into pores of ITPUF is involved in the rate controlling step. The values α are 0.011 and 0.097 which show that these values were increased with increasing of the dye size. This result indicates that the pore diffusion rate depend on the size of dye molecules and independent on the functional groups or type of the dyes (acidic or basic dye).

Figure 4 shows that the plot of $t^{1/2}$ vs. Q versus is bad straight line ($R^2 = 0.380$ and 0.485) and this relation not passing through the origin. The k_M values for sorption of BG and DB onto ITPUF are 0.0004 and 0.008 $\text{mmol g}^{-1} \text{min}^{-1/2}$. The diffusion rate of DB > BG, this result is agreement with the result obtained from Bangham model (Table 2).

The correlation values for the relation of t vs. Bt are 0.319 and 0.370 for the sorption of BG and DB, respectively. These values indicate that the bad relationship between t and Bt ; the values of effective diffusion coefficient (D_i) are estimated from the plots of F vs. $t^{1/2}$. The values of D_i of the dyes sorption are 1.9×10^{-7} and 6.8×10^{-9} $\text{cm}^2 \text{min}^{-1}$. Finally, the average values of R^2 are 0.68 , 0.43 and 0.34 for Bangham, Morris-Weber, and Reichenberg models. These values show that Bangham equation is the best model for the description of diffusion mechanism.

Table 2: The diffusion rate for the sorption of brilliant green and direct blue onto ITPUF

Dye	Bangham		Weber-Morris		Reichenberg	
	α	R^2	k_i	R^2	D_i	R^2
Brilliant green	0.011	0.319	0.0004	0.38	1.9×10^{-7}	0.596
Direct blue	0.097	0.37	0.008	0.485	6.8×10^{-9}	0.761

The parameters of pseudo first order $[\log(Q_e - Q_t) = (\log Q_e) - (k_1 t / 2.303)]$ and pseudo second order models $[t/Q_t = (1/k_2 Q_e^2) + (t/Q_e)]$ for the sorption of BG and DB onto ITPUF were estimated. The R^2 values of pseudo first order are 0.385 and 0.113 while the values of R^2 pseudo second order are 0.994 and 0.999 . This shows

that the pseudo second order sorption is predominant. The initial rate constant ($h = k_2 Q_e^2$) of BG and DB are 370.4 and 169.5 min g/ μ mol. The k_2 value of BG (4.43 μ mol g/min) > DB (0.45 μ mol g/min). The values of the half-life ($t_{1/2} = 1/Ck_2$) are 0.23 and 2.22 min for the removal of BG and DB, respectively. The activation energy for the sorption of BG and DB onto ITPUF was estimated ($\Delta E = -RT \ln k_2$). The ΔE values are 30.5 and 36.2 kJ/mol, these values in indicates that the removal process for BG and DB onto ITPUF is chemical adsorption.

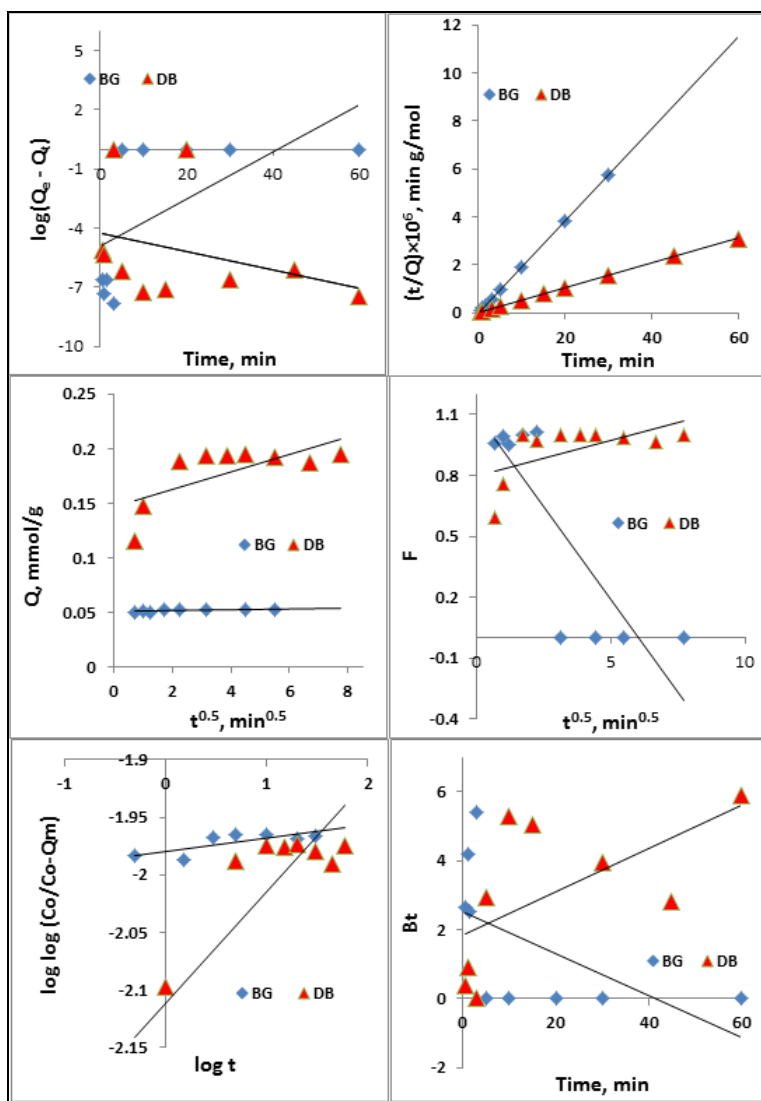


Figure 4: Kinetic models for the removal of dyes onto ITPUF

Isotherm studies

The equilibrium data estimated from the sorption isotherms are also basic requirements to understand the mechanism of the sorption. These data were analyzed using Langmuir [$C_e/Q_c = (1/K_L b) + (C_e/K_L)$], Freundlich ($\log Q = \log K_F + \frac{1}{n} \log C_e$), Dubinin-Radushkevich ($\ln Q_c = \ln K_{D-R} - \beta \varepsilon^2$), Temkin ($Q = B \ln A + B \ln C_e$), and Harkins Jura [$1/Q^2 = (B/A) - (1/A) \log C_e$] models.

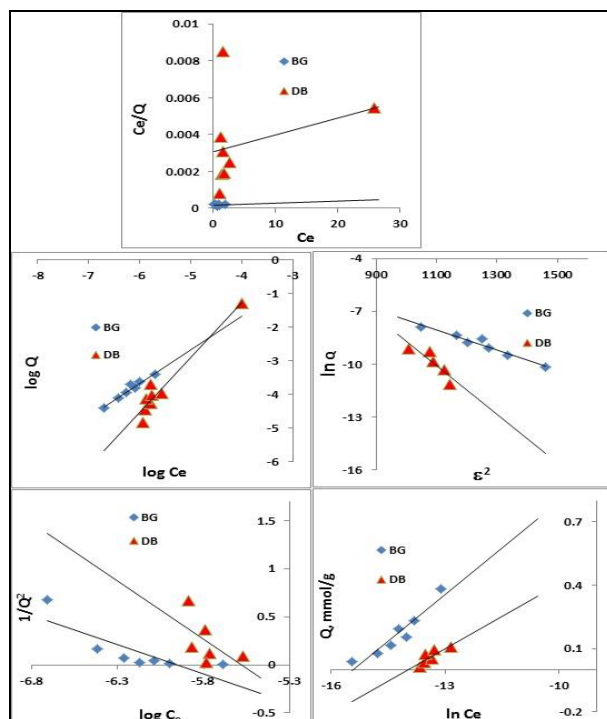


Figure 5: Isotherm models for the removal of dyes onto ITPUF

The Langmuir model plot (C_e vs. C_e/Q_c) for the sorption of BG and DB onto ITPUF is a bad linear relationship which is confirmed by the values of the correlation coefficients (0.052 and 0.104). While the relationship of $\log Q_c$ vs. $\log C_e$ due to Freundlich isotherm model is a good correlation ($R^2 = 0.960$ and 0.943 , Table 3). These results show that the surface structure of the ITPUF is heterogeneous with a non-uniform distribution of heat sorption over the surface.

The R^2 values for Dubinin-Radushkevich model plot ($\ln Q_c$ vs. ε^2) are 0.950 and 0.792; this result is agreement with Freundlich isotherm model. Dubinin-Radushkevich model is based on the surface of ITPUF is no homogeneous or constant adsorption potential. The values of β for sorption of BG and DB are -0.0057 and $-0.0138 \text{ kJ}^2 \text{ mol}^{-2}$, respectively. Also, the sorption free energy values are 9.37 and 6.02 kJ mol^{-1} .

Table 3: Comparison between correlation coefficient for the sorption isotherms models

Dye	Langmuir	Freundlich	Dubinin-Radushkevich	Temkin	Harkins Jura
Brilliant green	0.052	0.96	0.95	0.906	0.669
Direct blue	0.104	0.943	0.792	0.735	0.319

Temkin isotherm model suggests an equal distribution of binding energies over the number of the exchanging sites on the surface. Temkin equation is based on the effect of some direct adsorbate–adsorbate interactive relation on sorption isotherm and due to these interactions the decrease in the heat of the adsorbent of all the molecules in the adsorbed surface is linear rather than algorithmic. B ($B = RT/b$) value is corresponding to the heat of sorption, and A is the equilibrium binding constant. The values of R^2 are 0.906 and 0.735 for Br Y and Br G, respectively suggesting that the experimental data is fitted better to Temkin isotherm model (Figure 5). The values of the correlation coefficient of the Harkins–Jura isotherm model are 0.669 and 0.319 for BG and DB, respectively which indicate that the model is fitted to the obtained data (Figure 5).

Application

Removing of brilliant green and direct blue dyes from wastewater samples, collected from three different places in Damietta Government (Izbat Al-Inaniyyah, Kafr Al-Battikh and Al Adlyaa Cities) by ITPUF was examined for duration of six weeks. A 25 mL aliquot of water sample was spiked with different amounts of tested dyes. Then the solutions were shaken for 30 min, the remaining concentration of dyes in the supernatant solution was determined. The removal percentage of dyes from the water samples was 95-100%. The results show that the ITPUF is a suitable sorbent proven to be useful in removing both acidic and basic dyes from environmental samples. The RSD% values are found to be in the range of 1.2-3.3% (n=6) which is considered relevant (less than 10%) for real samples. The obtained data conferred susceptible accuracy of the developed method based on the satisfactory values of RSD.

CONCLUSIONS

Polyurethane functionalized with isothiuronium groups was synthesized and applied for the treatment of wastewater samples containing brilliant green and direct blue dyes. Though the ITPUF contain both acidic and basic groups it is mainly acidic in character and has a pH_{ZCP} value of 1.9. The sorbent was proven efficient for the removal of BG and DB with a sorption capacity of 183.4 and 183.5 mg/g at pH values of pH 2-10 and 1-7, respectively. The investigated dyes were completely recovered (98-100%) within 10 min. The experimental kinetic data were well-fitted to the pseudo-second order supporting a chemisorption mechanism as evident by the shift of the FTIR bands of the functional groups of the ITPUF after dye sorption. The faster adsorption kinetic data may be useful for environmental technologies in designing dyes removal from wastewater plants. To describe the sorption mechanism, different sorption isotherm models were applied, namely, Freundlich, Langmuir, Temkin, Harkins Jura, and Dubinin-Radushkevich adsorption. The sorption of both dyes was concluded to be favorable process and their removal was mainly based on association mechanism. The synthesized ITPUF is a promising material for environmental remediation, since it could be used for the removal of other anionic and /or cationic dyes from different water samples.

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