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Adsorption characteristics of Direct Red 23 azo dye (onto powdered tourmaline



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KEYWORDS

Dye; Tourmaline; Adsorption; Decolorization **Abstract** The high electric field on the surface of tourmaline particles has a potential of enhancing electrostatic reactions during adsorption. However, information concerning the adsorption characteristics of dyes onto tourmaline is currently unavailable. In the present study, the behavior and efficiency of powdered tourmaline (PT) in removing the diazo Direct Red 23 (DR23) dye from aqueous solution were investigated. The observations from batch adsorption experiments indicated that the adsorption was more favorable under low adsorbate surface loading, low pH, high temperature, and low ionic strength conditions. A homogeneous particle diffusion model (HPDM) was used to characterize the process, and the rate of adsorption was found to be controlled by intra-particle diffusion. An activation energy of 4.54 kcal/mol was calculated, suggesting that the adsorption proceeded with a low energy barrier and that a physisorption was involved. The functional groups binding anionic DR23 on the PT particles were also identified. A maximum adsorption capacity of 153 mg/g was determined according to the Langmuir isotherm. The PT was subjected to a total of 5 regeneration runs without losing much of its dye-adsorption capacities. Due to its low price, abundant availability, and superb adsorption capacity, PT has a great potential for use as an effective adsorbent in removing DR23 from aqueous solutions.

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1. Introduction

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The wastewater of textile industries is usually heavily colored due to the contamination by dyeing chemicals. The color of dyes in water is highly visible which can be visually detected at low concentrations (Weng et al., 2013a). Azo dyes are the largest and most important dye class of synthetic organic dyes (Tunc et al., 2013). The molecules of azo dyes are characterized by the bearing of azo-groups (–) in association with aromatic rings (naphthalene and/or benzene). They may also carry sulfonic groups (Behnajady et al., 2007). Many azo dyes are thought to be carcinogenic to human when ingested. They can also

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be harmful to aquatic organisms. Without proper treatment, a dyeladen wastewater can pose significant threats to human health, as well as the integrity of aquatic ecosystems (Weng and Tsai, 2016). Due to complex molecular structures and their synthetic origin, azo dyes are usually non-biodegradable and don't decompose naturally (Robinson et al., 2001). Conventional biological processes are usually inadequate for the treatment of dye under stringent effluent standards (Weng et al., 2013b).

The development of advanced oxidation processes (AOPs) for the treatment of trace organic contaminants has gained much attention. AOPs such as Fenton, persulfate, and photocatalyst, have been shown to be promising in removing color in dye-laden wastewaters (Avetta et al., 2014; Ribeiro et al., 2015; Su et al., 2011; Weng et al., 2014; Weng and Huang, 2015; Weng and Tsai, 2016; Yola et al., 2014a, 2014b; Zhang et al., 2014). However, concerns such as the release of residual radical oxidants and the possibilities of producing toxic degradation products remain for the application of these processes. Moreover, the effectiveness of these oxidants can be significantly undermined in the presence of radical scavengers in wastewater (Ribeiro et al., 2015).

Adsorption has been proven to be efficient in removing dve molecules from wastewater (Achmad et al., 2012; Ardejani et al., 2007; Atar et al., 2008, 2011; Atar and Olgun, 2009; Fathi et al., 2015; Holliman et al., 2008; Konicki et al., 2012; Liu et al., 2015; Olgun and Atar, 2009; Somasekhara Reddy et al., 2017; Wang et al., 1998; Weng and Pan, 2006; Weng et al., 2009; Weng et al., 2013a). Owing to its superior adsorption performance, activated carbon (AC) in the form of powder, granular, fiber and cloth has been extensively used as adsorbents for a wide variety of trace organic pollutants (Ayranci and Duman, 2009; Duman and Ayranci, 2006; Huang and Blankenship, 1984). However, due to high costs of the material and its regeneration, a general application of AC in wastewater treatment has been limited so far, particularly in the underdeveloped countries (Weng and Wu, 2012). Nonetheless, adsorption remains a simple and effective process for the removal of synthetic dyes, among other organic toxins, in wastewater when appropriate adsorbents are used. Attempts for the search of low cost and high capacity adsorbents continued for the past decades (Duman et al., 2015a, 2015b).

Tourmaline is a naturally-occurring borosilicate mineral with complex and variable compositions. It occurs in the forms of Fe tourmaline (schorl), Mg tourmaline (dravite), and alkali tourmaline depending on the relative abundance of these elements (Harraz and EL-Sharkawy, 2001). Tourmalines are widely available distributed in metamorphic formations, but are abundant in certain aplites and pegmatites. Tourmaline possesses some unique properties similar to ferroelectrics, including the emission of far infrared rays, the existence of spontaneous polarization and permanent poles, and therefore the formation of electric dipoles (Ruan et al., 2004; Yu et al., 2016). The occurrence of an electric field with 106-107 V/m intensity on the surface of micron-sized tourmaline is widely recognized (Yeredla and Xu, 2008). Owing to such unique properties, tourmaline has been used for the enhancement of some photocatalytic decontaminants. For example, Yu et al. (2016) used tourmaline to enhance the photocatalytic activities of TiO2 nano semiconductors through its obstruction on the recombination of electron-holes to prevent aggregation of the nanoparticles.

Tourmaline is a mixed Fe(II)–Fe(III) bearing mineral, and therefore can function as a catalyst in the breakdown of synthetic dyes. In particular, the presence of Fe(II) in Fe-bearing tourmaline significantly enhances the production of active radicals (Wang et al., 2013) from Fenton's reaction. Furthermore, the electric field on the surface of tourmaline may induce Fe^{3+} ions to Fe^{2+} ions in aqueous solutions. This process enhances the oxidation of organic molecules in a conventional Fenton process (Yu et al., 2014). Recent studies have also found that tourmalines are capable of absorbing uranyl molecules (Guerra et al., 2012a) and divalent metals (Guerra et al., 2012b; Liu et al., 2013) in aqueous media. Other studies have also found that phosphates are sorbable to La-modified tourmaline (Li et al., 2015). The high electric fields on the surface of tourmaline particles promote enhancement of electrostatic interactions during adsorption. Therefore, tourmalines have great potentials for application in the adsorptive removal of ionic textile dyes from wastewater, and a closer examination of their adsorption behaviors is of great interest.

The purpose of this study was to investigate the potential application of tournaline for the adsorptive removal of dyes, in particular diazo direct dye, from aqueous solutions. Experiments have been conducted using tournaline for removal of diazo direct dye Direct Red 23 (DR23) from aqueous solutions. DR23 was chosen as a target chemical because it is the most frequently used anionic dye in the textile industry. Key parameters affecting adsorptive behaviors of tournaline on DR23 were studied, including temperature, pH, and ionic strength of the solution, as well as surface loadings of the adsorbate. The fitting of experimental data to the kinetic and isotherm models has been tested. The DR23 adsorption capacity of tournaline was compared with other adsorbents reported in literatures. Efficiency of regeneration of the tournaline adsorbent was also evaluated. Findings of this study provide useful information on the applicability of this natural material as an adsorbent for the treatment of dye-laden wastewaters.

2. Materials and methods

2.1. Materials

A water-soluble anionic direct azo dve, viz, Direct Red 23 (DR23, Fig. 1) manufactured by Sigma-Aldrich (USA) was used as the adsorbate. All chemical reagents used were of analytical grade. Powdered Tourmaline (PT) with a particle size smaller than 0.074 mm (passing No. 200 ASTM sieve) was purchased from the Inner Mongolia Embellish Lung Chemical Co., China. The cost for the PT is 400 USD/ton. The PT as purchased was used without pretreatment. Major properties of the powder were determined using pertinent techniques viz. X-ray diffraction (XRD), scanning electron microscope (SEM), and specific surface area (SSA) measurements. BET-N₂ (Brunauer, Emmett, Teller) SSA and average pore volume were determined using a surface area analyzer (SSA-4200C, Beijing oda Electronic Technology Co., China). Crystal structure of the tourmaline was determined using a XRD analyzer (DX2700, Dandong Fangyuan Instrument Co., China). A SEM (JSM-6700F, JEOL, Japan) was used to determine surface morphology of the tourmaline. A Fourier transform infrared spectroscopy (FTIR, spectrometer Nicolet Avatar 370DTGS, Thermo, USA) covering a wave number between 400 and 4000 cm^{-1} was used to identify the functional groups



Figure 1 Molecular structure of DR23.

on the tourmaline particles before and after adsorption. A laser particle size analyzer (Bettersize 2000, Dandong Baxter Instrument Co., China) was used for the determination of particle sizes.

The point of zero charge (pH_{zpc}) is a fundamental surface property of hydrated adsorbents. The pH_{zpc} of PT was determined in accordance with Srivastava et al. (2011). Solutions of a constant ionic strength of 0.01 mol/L NaCl were prepared. The pH of the solutions was adjusted using either 0.1 mol/L HCl or NaOH to various values within a range between 2.0 and 12.0. At each pH, a volume of 50 mL of the solution was transferred to a test tube, followed by the addition of 1.0 g PT. The resultant solution was then shaken for 2 h before its pH was measured. A graph between pH_{final} and pH_{initial} of the solution was plotted and pH_{zpc} of the adsorbent was determined from the inflection point of the "pH_{final} vs pH_{initial}" curves.

2.2. Analysis

The concentration of DR23 in solutions was determined from its absorbance at a wavelength of 507 nm using a UV–visible spectrophotometer (Thermo Scientific Evolution 201, USA). A calibration curve was established to correlate measured absorbance with the concentration of DR23.

2.3. Kinetic adsorption experiments

Batch adsorption experiments were conducted to characterize dynamic behaviors of the adsorption process and to quantify the adsorption rates. The effects of adsorbent dosage and solution temperature were also investigated. The procedures adopted are summarized as follows. A 1 L solution of fixed DR23 concentration $(1.0 \times 10^{-4} \text{ mol/L})$ and an ionic strength of 0.01 mol/L NaCl were prepared. The pH of the solution was adjusted to 3.0 using HCl or NaOH as necessary. A known amount of PT was added to the solution. The resultant solution was agitated at 800 rpm using a mechanical stirrer (Shin-Kwang, Taiwan) under room temperature (25 °C) for 3 h. Volumes of 5 mL each were taken from the agitated solution at a fixed interval and filtered immediately through 0.45 µm membranes (Advantec, Japan). The residual concentration of DR23 in the supernatant of each solution was then determined. Each run of the experiment was triplicated with average values used for data analysis. To compensate for the adsorption from glass beakers and membrane filters, blank tests without PT addition were conducted in parallel. Experiments using procedures as described were also conducted with various adsorbent concentrations (0.8-4.0 g/L) to evaluate the effect of adsorbent dosage on adsorption rate. The effect of temperature on adsorption kinetics was investigated using temperatures of 5, 15, 25, 35, and 45 ± 0.5 °C by immersing the mixtures in a water bath.

The amount of DR23 adsorbed by PT at a contact time t (q_t) was calculated from the following:

$$q_t = \frac{(C_i - C_t)}{W} \tag{1}$$

where C_i and C_t (mol/L) are respectively the initial concentrations of DR23 and a concentration at contact time *t*, and *W* is the dosage of PT (g/L).

2.4. Equilibrium adsorption experiments

Procedures for the test of adsorption equilibrium as affected by solution pH were as follows: a 1-L solution with an ionic strength of 0.01 mol/L NaCl and a DR23 concentration of 2.0×10^{-5} mol/L were prepared; volumes of 100 mL each of the solution were transferred to 125-mL polyethylene (PE) bottles; initial pH of the samples was adjusted to cover a range between 2.0 and 10.5 using either HCl or NaOH; a given amount of PT (1.0 g/L) was added to each of the samples; the sample bottles were then shaken on a reciprocal shaker for 3 h at 150 excursions/min under a temperature of 25 °C. The contact time was determined based on the results from kinetic experiments and was found to be adequate for reaching an equilibrium. The pH of the mixed liquors was recorded at the end of contact time; the mixed liquors were filtered through 0.45 µm membranes (Advantec, Japan) and residual DR23 in the filtrate was determined. Textile wastewater often contains high concentration of ions. The effect of such ions on DR23 adsorption was evaluated using solutions of various NaCl concentrations (0-0.05 mol/L).

2.5. Regeneration experiments

The cost of commercial powdered tourmaline is 400 USD/ton. The cost of PT can be significantly lower when used with regeneration. The efficiency of regeneration was evaluated using five consecutive cycles. Each cycle (adsorption-desorption) consisted of an adsorption equilibrium test followed by a desorption test. Procedures similar to the adsorption tests as described in Section 2.4 were adopted except that a DR23 concentration of 4.0×10^{-5} mol/L and a PT concentration of 4.0 g/L were used. After completion of the adsorption equilibrium test, the mixed liquor was centrifugally separated at 7500 rpm (6040g) for 10 min (Hsiangtai CN-10001, Taiwan). The concentration of residual dye in the supernatant was then determined. The DR23-saturated-PT was transferred immediately to a solution with an initial pH of 11.0 and proceeded with the desorption test. The mixture was agitated on a reciprocal shaker for 1 h at 150 excursions/min under a temperature of 25 °C. The PT was separated again from the mixture by centrifugation upon completion of desorption, and concentration of the desorbed dye in the supernatant was determined.

3. Results and discussion

3.1. Characterization of the powdered tourmaline

Crystal phase confirmation of the tourmaline powder was carried out using XRD (Fig. 2). The diffraction peaks were at 13.8°, 21.0°, 22.0°, 25.5°, 26.7°, 30.3°, 34.7°, 44.3°, 47.1°, 55.3°, 57.7°, 61.5°, 63.9°. The tourmaline was determined to have a chemical formula of Na(Fe²⁺, Fe³⁺)₃Al₆(Si₆O₁₈) (BO₃)₃(OH)₄. It is classified as schorl, consistent with its relatively high iron content. Morphology of the PT is shown in Fig. 3. The image shows that PT particles formed aggregates of various sizes and shapes. Surface characteristics of the particles were examined using FTIR. Fig. 4 shows the FTIR spectra of bare and DR23 loaded PT particles. The absorption at 3563.6 cm⁻¹ is attributed to O–H bond stretching. The peak



Figure 2 XRD pattern of powdered tourmaline.



Figure 3 Scanning electron microscope image (magnification \times 7500) showing the surface morphology of powdered tourmaline.

at 1156.8 cm⁻¹ was caused by the stretching vibration of C–C bonds. And the band at 1034 cm⁻¹ was a result of stretching vibration of the Si–O–Si bonds (Li et al., 2015). The FTIR analysis reveals a definite chemical structure of the tourmaline. The spectra of OH band shifted prominently after adsorption when the tourmaline particles were loaded with DR23 molecules, suggesting that the OH functional group was likely to have participated in dye binding. Judging from the FTIR spectra, it is concluded that the chemical nature of tourmaline remained virtually unchanged after dye adsorption.

The basic properties of PT are listed in Table 1. The value of pH_{zpc} as determined was 6.6, which is close to those of iron rich minerals such as α -FeOOH (7.6), Fe₂O₃ (6.5), and α -Fe₂O₃ (7.0) (Stumm and Morgan, 1996; Zhang et al., 2016). The surface of PT was positively charged at a pH below 6.6



Figure 4 FTIR spectra of powdered tourmaline before and after DR23 adsorption; letters in red are the functional groups likely involved in DR23 binding.

Table 1 Major properties of powdered tourname.	Fable 1	Major	properties	of powder	ed tourmaline.
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Parameters	Value
Particle size distribution (µm)	
D_{10}	1.272
D_{50} (the median diameter)	6.451
D_{90}	19.52
pH	5.87
pH _{zpc}	6.6
BET specific surface area (m^2/g)	7.34
Pore volume (cm^3/g)	0.0152
Pore size (Å)	8.29
Density (kg/m ³)	3.10×10^{3}

providing a favorable condition for adsorption of the anionic DR23 dye. A median diameter (D_{50}) of 6.451 µm for the particles of PT was obtained and is used for the determination of intra-particle diffusion parameters in the subsequent kinetic studies.

3.2. Kinetic studies

3.2.1. Effect of tourmaline dosage

To determine the required contact time for achieving adsorption equilibrium, experiments were carried out using various tourmaline dosages and a constant initial DR23 concentration. The results (Fig. 5) indicate that the uptake of DR23 by tourmaline particles occurred rapidly at an early stage. The adsorption then proceeded slowly with an equilibrium that was reached within 2.5 h under a surface adsorbate loading (ratio of initial dye concentration and tourmaline dosage) of 2.5×10^{-5} to 1.25×10^{-4} mol/g. The fast initial adsorption was mainly due to a rapid attachment of anionic DR23 molecules to favorable sites on the surface of PT particles through mass transfer. The subsequent adsorption was achieved through molecular diffusion of the dye into pores of the adsorbent (Weng and Pan, 2006).

To characterize adsorption process, the kinetic data were fitted with two empirical models namely the pseudo-first-order



Figure 5 Effect of tourmaline dosage on the adsorption of DR23. Conditions: initial pH 3.0, NaCl 0.01 mol/L, DR23 1.0×10^{-4} mol/L, 25 °C. The dashed lines represent the best fit of (a) pseudo-first-order and (b) pseudo-second-order equation. Surface loading (mol/g) is defined as the ratio between DR23 concentration and tourmaline dosage.

(PFO) and the pseudo-second-order (PSO) models. The Lagergren expression of a PFO model measures the rate of adsorption by assuming that one ion is adsorbed in one adsorption site, and has the form (Lagergren, 1998):

$$q_t = q_e (1 - e^{-k_1 t}) \tag{2}$$

where k_1 (1/min) is the PFO rate constant. The PSO model was proposed by Ho and McKay (1999) based on the adsorption capacity, and can be expressed as follows: (Ho and McKay, 1999):

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{3}$$

where k_2 (g/mol min) is the PSO rate constant.

A graphic software, viz. KaleidaGraph[™] (Version 3.6, Synergy Software, USA), was used to solve for the parameters of a nonlinear equation by calibrating the equation against

experimental data. A normalized standard deviation (s %) was calculated to assess the validity of these models,

$$s = 100 \times \sqrt{\frac{1}{n-1} \times \sum \left[\frac{(q_{t,exp} - q_{t,cal})}{q_{t,exp}}\right]^2}$$
(4)

where *n* is the number of data points, and $q_{t,exp}$ and $q_{t,cal}$ are respectively the observed and model calculated adsorption capacity for a contact time *t*.

Dashed lines in Fig. 5 represent the best fits of both equations with their constants being summarized in the inset of the table. As shown in Fig. 5, both models fit the experimental data well with low standard deviations *s*. By comparing the values of r^2 and *s*, it was determined that the adsorption kinetics was best described by a PSO model. The pseudo rate constant was found to be inversely proportional to surface loadings. As the surface loading increases from 2.5×10^{-5} to 1.25×10^{-4} mol/g, the PSO rate constant k_2 decreases from 2305 to 134.4 g/(mol min). Higher surface loadings result in a lower diffusion efficiency where more ions are competition for a fixed number of activated surface sites; consequently, a lower k_2 value was observed.

3.2.2. Intra-particle diffusion

In order to gain insights into the adsorption mechanisms involved, a homogeneous particle diffusion model (HPDM) as shown in Eq. (5), originally proposed by Boyd et al. (1947), was used to describe the process of diffusive adsorption. In this model, the rate-limiting step is usually described by either an intra-particle diffusion or a film diffusion mechanism:

$$X(t) = 1 - \frac{6}{\pi^2} \sum_{Z=1}^{\infty} \frac{1}{Z^2} \exp\left[\frac{-Z^2 \pi^2 D_p t}{r_0^2}\right]$$
(5)

where X(t) is the fractional attainment at time t, i.e., $X(t) = q_t/q_e$, D_p (m²/s) is the effective diffusion coefficient, r_o is the radius of PT particles assumed to be spherical (6.451 × 10⁻⁶ m), and Z is an integer. For 0 < X(t) < 1, a simplified equation can be obtained for the adsorption on spherical particles:

$$X(t) = \left[1 - \exp\left[-\frac{\pi^2 D_p^2 t}{r_0^2}\right]\right]^{\frac{1}{2}}$$
(6)

A further formula deformation gives the following:

$$-\ln(1 - X^{2}(t)) = \frac{2D_{p}\pi^{2}}{r_{0}^{2}}t = 2k_{p}t$$
(7)

where k_p is the diffusion rate constant (1/s) and $k_p = \frac{D_p \pi^2}{r_0^2}$. Eq. (7) was used for the calculation of effective intra-particle diffusivity (D_p (m²/s)) from the experimental data. In the first step, a graph (Fig. 6a) of $-\ln(1 - X^2(t))$ vs t was developed. The values of k_p under different PT dosages were obtained from the slopes of the fitted lines, and the values of effective diffusion coefficient, D_p (m²/s), can then be obtained from $D_p = \frac{k_p r_0^2}{\pi^2}$.

Eq. (8) can be used when the rate of adsorption is controlled by liquid film diffusion (Valderrama et al., 2008):

$$X(t) = 1 - \exp\left[-\frac{3D_f C_e}{r_0 \delta C_r}\right]$$
(8)



Figure 6 Homogeneous particle diffusion plots for DR23 adsorption onto PT (a) $-\ln(1 - X^2(t))$ vs t plots; (b) $-\ln(1 - X(t))$ vs t plots.

where D_f is the film diffusion coefficient (m²/s) in the liquid phase, and C_e (mol/L) and C_r (mol/L) are respectively the equilibrium concentrations of DR23 in solution and in solid phases. δ is the thickness of liquid film which was assumed to be 10⁻⁵ m according to Yu and Luo (2014).

A further formula deformation of Eq. (8) gives the following:

$$-\ln(1 - X(t)) = k_f t$$
 (9)

where k_f is the diffusion rate constant (1/s) and $k_f = \frac{3D_f C_e}{r_0 \delta C_f}$. The values of k_f were obtained from Fig. 6a. The film diffusion coefficient can then be calculated from $D_f = \frac{k_f r_0 C_r}{3C}$.

The results of linear regression analysis for Eqs. (7) and (9) are shown in Table 2. In general, both intra-particle and film diffusion kinetic data correlate well with HPDM as judged from the high r^2 values. The intra-particle diffusion coefficient increased slightly with an increasing of PT dosage. A higher

PT dosage provides more active sites for dye adsorption, and therefore, a higher rate of DR23 diffusion and adsorption. Additionally, Michelson et al. (1975) suggested that film diffusion is in control at D_f values ranging from 10^{-10} to 10^{-12} (m²/s), while intra-particle diffusion is the rate-limiting step at D_p values in the range of 10^{-15} to 10^{-18} (m²/s). In this study, D_f values in the order of 10^{-12} (m²/s) for film diffusion. Conversely, the D_p values in the order of 10^{-18} (m²/s) for intra-particle diffusion. The results indicate that the intra-particle diffusion controls the sorption of DR23 onto PT particles, which is in agreement with the PSO kinetic model.

3.2.3. Effect of temperature

The temperature dependence of DR23 adsorption is shown in Fig. 7a where dashed lines correspond to the best fit of PSO equations. Adsorption data ranging from 5 to 45 °C were well represented by the PSO equations as judged from the high correlation coefficient (i.e., $r^2 > 0.970$) and low s values. The PSO rate constant, k_2 , increased from 122.3 to 339.5 g/mol min as the temperature rose from 5 to 45 °C, indicating that the adsorption of DR23 onto PT is more favorable and faster at higher temperatures. An increase in temperature elevates the driving force of diffusion across the boundary layer of an adsorbing particle and raises the rate of diffusive adsorption within its pores (Weng and Wu, 2012). The increasing DR23 adsorption with temperature suggests an endothermic reaction of the adsorption.

The activation energy (E_a) of DR23/PT adsorption system was determined using the Arrhenius Equation (Eq. (10)):

$$\ln k_2 = (\ln A) - \frac{E_a}{RT} \tag{10}$$

where A is a pre-exponential factor related to molecular collision, R is the universal gas constant (1.987 cal/mol K), and T is the absolute temperature (K). From the Arrhenius plot of $\ln k_2$ versus 1/T (Fig. 7b), an E_a of 4.54 kcal/mol was determined for the adsorption system. The low E_a value suggests that the DR23/PT adsorption proceeded with low energy barriers and can be achieved at relatively low temperatures. The activation energy for physical adsorption is generally smaller than that of chemisorption. A typical value of E_a ranges from 1.2 to 12 kcal/mol, as compared with 14.3 to 191 kcal/mol for chemisorption (Doğan et al., 2009; Chegrouche et al., 2009). Therefore, the adsorption of DR23 onto PT is primarily a physical process as judged from the relatively low E_a .

3.3. Equilibrium study

3.3.1. Effect of pH

The pH dependence of DR23 adsorption was investigated using a series of experiments with initial pH of the solutions

Table 2 Diffusion parameters of adsorption DR23 onto PT using homogeneous particle diffusion model

Puble 2 Diffusion parameters	s of adsorpti		using no.	mogeneous purchere u	indision model.		
Surface loading (mol/g)×10 ⁻⁴	PT (g/L)	$k_p \times 10^{-4} \; (1/s)$	r^2	$D_p \times 10^{-16} ({ m m^2/s})$	$k_f \times 10^{-4} \ (1/s)$	r^2	$D_f \times 10^{-14}$
1.25	0.8	0.825	0.951	0.870	3.03	0.972	0.544
1.00	1.0	0.860	0.921	0.905	3.10	0.983	0.801
0.50	2.0	1.485	0.969	1.560	4.67	0.964	12.70
0.25	4.0	1.160	0.984	1.755	5.00	0.924	18.70



Figure 7 Effect of temperature on the adsorption of DR23. Conditions: tourmaline 1.0 g/L, initial pH 3.0, NaCl 0.01 mol/L, DR23 1.0×10^{-4} mol/L. The dashed lines represent the best fit of a pseudo-second-order equation.

ranged from 2.5 to 10.5. An initial DR23 concentration of 1×10^{-4} mol/L and a PT dosage of 1 g/L were used for all experiments conducted at a temperature of 25 °C. As shown in Fig. 8, the adsorption of DR23 increased sharply as pH varied from 7.0 to 2.5. The adsorption is favored under acidic conditions owing to the formation of positively charged PT surfaces and fewer competitions from OH⁻ ions.

Complexation and electrostatic interaction play important roles in determining the efficiency of an adsorption process (Weng et al., 2001; Budyanto et al., 2015). Upon hydration, hydroxyl groups form on the solid surface of an adsorbent (Huang and Stumm, 1973):

$$S_{PT} - OH_2^+ \leftrightarrow S_{PT} - OH + H^+$$
(11)

$$S_{PT} - OH \leftrightarrow S_{PT} - O^- + H^+$$
 (12)

where $S_{PT} - OH_2^+$ and $S_{PT} - OH$ are respectively the protonated and neutral hydroxyl groups on the surface of hydrated PT. The binding of DR23 ions with functional groups such as OH from PT, can be expressed as follows:

$$2S_{PT} - OH_2^+ + Dye^{2-} \leftrightarrow (S_{PT} - OH)_2 - Dye^{2-}$$
$$+ 2H^+; \text{ for } pH$$
$$< pH_{zpc}(6.17)$$
(13)

$$2S_{PT} - OH + Dye^{2-} \leftrightarrow (S_{PT} - OH)_2 - Dye^{2-}; \text{ for } pH > pH_{zpc}$$
(14)



Figure 8 Effect of pH on the adsorption of DR23. Conditions: tourmaline 1.0 g/L, NaCl 0.01 mol/L, DR23 1.0×10^{-4} mol/L, contacting time 3 h, 25 °C.

where $(S_{PT} - OH)_2 - Dye^{2-}$ is a binuclear bonding complex due to hydrogen bonding between the dye and the surface functional group of PT. pHzpc is a primary indicator on the deprotonation of an amphoteric surface functional group (Weng et al., 2008). At a solution pH lower than the pH_{zpc} of PT (6.17), the positively charged PT surface $(S_{PT} - OH_2^+)$ provides sites favoring the adsorption of anionic DR23 molecules because the coulombic electrostatic interaction force occurs quite readily under such a condition. At higher pH levels, more OH⁻ ions are available to compete with the anionic DR23 for available sites on the surface of PT. Additionally, fewer attractive surface functional groups $(S_{PT} - OH_2^+)$ occur under high pH levels. The factors collectively contributed to the low DR23 adsorption observed in high pH solutions. The experimental data also indicated that a small amount of dye was adsorbed at pH levels higher than 6.6. The adsorption may be attributed to the occurrence of a neutral surface hydroxyl functional group S_{PT} – OH which provided active sites for dye adsorption. The high electric fields on the surface of tourmaline may also have promoted electrostatic interactions, and the adsorption of DR23.

3.3.2. Effect of ionic strength on the isotherm

Dye wastewaters, particularly those of textile industries, often contain high level of soluble salts. Therefore, a knowledge on the interferences from these ions is necessary for a proper assessment of the efficiency of an adsorbent. In this study, a series of adsorption isotherm experiments were conducted under NaCl concentrations ranging from 0 to 0.05 mol/L. The effect of ionic strength on adsorption isotherm is shown in Fig. 9. In general, the amount of DR23 adsorbed decreases with increasing NaCl concentrations.

The two commonly used adsorption isotherms, viz. Freundlich and Langmuir equations, were adopted for the DR23/PT system. The adsorption on a heterogeneous surface



Figure 9 Effect of ionic strength on the adsorption isotherm of tourmaline for DR23. Conditions: NaCl 0.01 mol/L, DR23 1.0×10^{-4} mol/L, contacting time 3 h, initial pH 3.0, 25 °C. The dashed lines represent the best fit of (a) Freundlich isotherm and (b) Langmuir isotherm.

is commonly characterized using an empirical Freundlich equation, which takes the form of Freundlich (1906)

$$q_e = K_f C_e^{1/n} \tag{15}$$

where q_e is the amount of DR23 adsorbed (mol/g) per gram of tourmaline at equilibrium, C_e is the residual DR23 concentration (mol/L), K_f is the Freundlich isotherm constant (mol/g)· (mol/L)^{-1/n} related to the adsorption capacity of an adsorbent, and n is an adsorption intensity related to the strength of the reaction. On the other hand, a Langmuir isotherm describes quantitatively the formation of a monolayer adsorbate on the surface of the adsorbent (Langmuir, 1918)

$$q_e = \frac{K_L Q_m C_e}{(1 + K_L C_e)} \tag{16}$$

where K_L is the adsorption affinity constant (L/mol), and Q_m is the maximum DR23 adsorption capacity (mol/g). A standard error *s* was used to determine the validity of a specific isotherm equation:

$$s = 100 \times \sqrt{\frac{1}{n-1} \times \sum \left[\frac{(Q_{e,exp} - Q_{e,cal})}{Q_{e,exp}}\right]^2}$$
(17)

Fig. 9a shows the data of adsorption isotherms as fitted using Eq. (15). The Freundlich isotherms suggested a decreased adsorption capacity of PT with an increasing ionic strength of the solution. As a rule of thumb, a value of n between 1 and 10 indicates a favorable sorption process (Goldberg, 2005). According to data shown in the inset table of Fig. 9a, values of *n* for I < 0.05 mol/L are smaller than 10, indicating that the sorption of DR23 onto tourmaline is a favorable one. The data also show that an increase in ionic strength led to a decrease in K_f and an increase in n, implying that ionic strength of the solution can reduce the favorability of adsorption.

The adsorption isotherm data were well represented using the Langmuir equation as judged from the relatively high coefficients of correlation (i.e., $r^2 > 0.959$) (Fig. 9b). The calculated Langmuir constants are listed in the inset table of Fig. 9b. In general, the value of Q_m decreases with increasing ionic strength.

Ionic strength is a key parameter defining the electrical double layer (EDL) of a hydrated particle (Weng and Pan, 2006). The thickness of an EDL $(1/\kappa (1/m))$ can be determined from the following:

$$\frac{1}{\kappa} = \left(\frac{2F^2I \cdot 1000}{\varepsilon \varepsilon_0 RT}\right) \tag{18}$$

where *I* is the ionic strength (mol/L), *F* is the Faraday constant (96,500 C/mol), *R* is the universal gas constant (8.314 J/(-mol K)), *T* is the absolute temperature (K), ε is the dielectric constant of water (78.5), and ε_0 is the vacuum permittivity (8.854 × 10¹² (C/V m)). A linear relationship between Q_m/K_f and the thickness of EDL was established using experimental data (Fig. 10). As can be inferred from Eq. (18), an increasing ionic strength of the solution results in a reduced EDL thickness and an increased number of indifferent ions approaching the adsorbent surface (Weng and Wu, 2012). The introduction of salts (indifferent ions) into a colloidal–interfacial system leads to a screening effect produced by the surface charge on the hydrated particulates (Álvarez-Merino et al., 2005). An increase in NaCl concentration initiates such a screening effect



Figure 10 The relationships between EDL thickness and maximum adsorption capacity of tournaline for DR23.



Figure 11 Regeneration test for DR23 adsorption onto tourmaline. Conditions for all cycles: tourmaline 4.0 g/L DR23 $4.0 \times 10^{-5} \text{ mol/L}$, NaCl 0.01 mol/L, DR23 $1.0 \times 10^{-4} \text{ mol/L}$, contacting time 3 h, 25 °C, initial pH 3.0 for adsorption, initial pH 11.0 for desorption (contacting time 1 h).

which masks the favorable interactions between the negatively charged DR23 and the positive surface charges of tourmaline. Furthermore, the additional Cl^- ions tend to compete with DR23 for the active sites on tourmaline when salts are introduced. The adverse effects of elevated ionic strength on the intended adsorption can be explained by the intensified screening and competition from such ions, as illustrated by the results of this study.

3.4. Regeneration test of PT

As shown in Fig. 11, the adsorption capacity of PT deteriorated gradually with regeneration. The removal efficiency of DR23 by PT is 100% at the 1st cycle. It declined to 49% at the 5th cycle. The efficiency of DR23 desorption from PT also deteriorated with regeneration. A complete decolorization was achieved on the first test cycle using fresh PT while only 89% of the adsorbed dye was desorbed. Some of the dye molecules may have trapped deep inside the aggregates of tourmaline particles and were not readily desorbable in alkaline solutions. The result shows that the PT losses only 51% of its adsorbing capacity after 5 consecutive cycles.

3.5. Comparison of various adsorbents for DR23 adsorption

The adsorption capacities (Q_m) of various adsorbents for DR23 are compared in Table 3. The Q_m of PT is significantly higher than those of TiO₂ and the low-cost adsorbents. Although the magnetic multi-walled carbon nanotubes nanocomposite (MCNN) exhibits a higher adsorptive capacity, its application in the treatment of dyeing chemicals has been limited due to prohibitively high costs of the material. On the other hand, the low-cost adsorbents listed cannot be regenerated as PT or other regenerable adsorbents. Moreover, tourmaline is a relatively abundant mineral which can be obtained in large quantities at reasonable prices. Due to its low cost, reusability, and high adsorption capacity, PT has a high potential for application in the adsorptive removal of color from dye-laden wastewaters.

4. Conclusions

Powdered tourmaline is a highly efficient adsorbent in removing diazo direct dye DR23 with an adsorption capacity much higher than those of low-cost adsorbents reported in literatures. The efficiency of DR23 adsorption by PT is sensitive to the surface loading of adsorbent, and the temperature, pH, and ionic strength of dye-laden solutions. A proper control of these parameters is necessary in maximizing the efficiency of such an adsorptive system. The chemical structure of tourmaline is maintained after application, with OH being the major surface functional group for dye adsorption. A quick initial adsorption of DR23 by PT is achieved through physisorption, which is followed by a stage of slower molecular diffusion. Powdered tourmaline is effective for DR23 removal. It is also abundantly available and highly regenerable. It has great potentials for application in the treatment of colored textile effluents.

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Table 3 The maximum DR23 adsorption capacity of different adsorbents.						
Adsorbent	$Q_m ({ m mg/g})$	pH	Temp. (°C)	Refs.		
Powdered tourmaline	153.0	3.0	25	This study		
Magnetic multi-walled carbon	172.4	< 7.0	30	Konicki et al. (2012)		
nanotubes-Fe ₃ C nanocomposite						
Cationized sawdust	65.8	6.5	30	Hebeish et al. (2011)		
Corn stalks	27.0-52.0	3.0	25	Fathi et al. (2015)		
Uncaria gambir extract	26.7	2.0	30	Achmad et al. (2012)		
Rhizophora apiculata bark	21.6	< 7.0	30	Tan et al. (2010)		
Orange peel	10.7	2.0	25	Ardejani et al. (2007)		
Rice husk	2.4-4.4	-	25	Abdelwahab et al. (2005)		
TiO ₂	2.2-35.2	< 4.5	-	Holliman et al. (2008)		

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