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Using tea bag filter as a sufficient cellulosic membrane for removal of Safranin-O dye from water: adsorption and density functional theory studies

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ABSTRACT

Safranin-O dye is recognised as a harmful material for both of human health and the environment. Due to that, proposing a simple, efficient, and low-cost method for the purification of water from Safranin-O dye was our main goal. Tea bag filter as a cellulosic membrane was tested as an adsorbent for the removal of Safranin-O from water by applying the batch equilibrium method at pH = 11.0. The adsorption studies were carried out based on contact time, adsorbent mass, adsorbate concentration, and pH (pH_{PZC} of the adsorbent was also determined). These studies revealed in general that tea bag filter is good candidate as a sufficient membrane for removal of Safranin-O dye from water at pH = 11.0 due to its uptake capacity (%), time of adsorption (very short time with equilibrium time ~90–120 s), and regeneration efficiency (around 95%, indicating the reversibility of sorption process without loss of binding efficiency). The isothermal behavior and the adsorption kinetics of Safranin-O dye on the surface of tea bag filter with respect to the temperature, and the initial mass of tea bag filter were also investigated. The obtained results revealed that the experimental data of the adsorption showed good correlation with both of Langmuir and Freundlich isotherm equations (although the correlation of data with Langmuir isotherm equation is more pronounced with respect to their R^2 values), and the adsorption process is best explained by the pseudo-second-order model. The molecular electrostatic potential maps for both of cellulose and Safranin-O based on density functional theory calculations was investigated in order to determine the charge-dependent properties and the probable interaction between the adsorbent (cellulose) and the adsorbate (Safranin-O). The results indicate that the interaction is mainly due to the hydrogen bonding between the two molecules.

Keywords: Water treatment; Cellulosic membrane; Tea bag filter; Safranin-O dye; Adsorption studies

1. Introduction

Cellulose is a polysaccharide compound with carbon, hydrogen, and oxygen atoms having common structure $[C_x(H_2O)_y]$, and is made up of a number of D-anhydroglucose pyranose (simply glucose units). These glucose units jointly form a fundamental cellulose unit, known as β-1,4-glycosidic bonds (Fig. 1a) [1]. Cellulose is widely available in nature as

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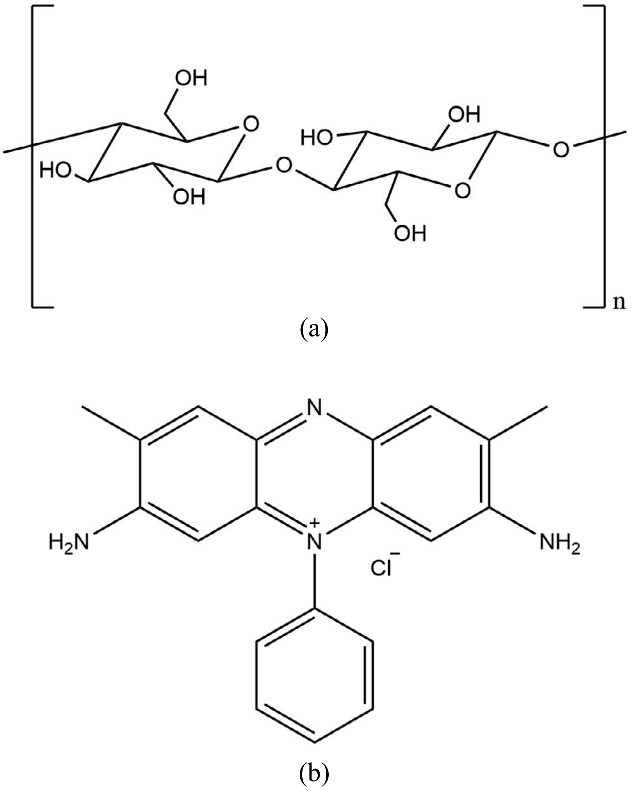
it represents one of the major components of the cell wall plants. The major sources of cellulose are fibers of various plants, like wood, flax, jute, hemp, cotton, and many more. Cellulose consists of 45%–50% wood [2], and is an important source of our dietary fiber. Cellulose is used in manufacturing of paper, some kinds of clothes, film, plastic, and also as an alternative source of energy. Agricultural materials and their wastes normally have high cellulose content. These materials have been already used without any modifications as adsorbents for removal of different heavy metals, dyes, and other pollutants. Along with cellulose, agricultural materials have considerable amounts of hemicelluloses, pectin, lignin, etc.; they are physically or chemically modified, and produced sufficient adsorbents [3]. Bagasse is a cellulose-rich material (50%) that contains hydroxyl and phenolic groups. It has been used in the field of water treatment as an adsorbent (in both treated and untreated forms). Khan et al. [4] investigated using sugar cane bagasse as an adsorbent for removal of Cr(VI) ions from water based on the effect of pH; they obtained promising results [4]. Recently, waste bagasse (obtained from sugar industry) has been treated with sodium hydroxide, and produced a new adsorbent. This adsorbent has been used sufficiently for removal of Cr(VI) and Ni(II) ions from waste water [5]. Wood sawdust is an abundant waste of wood industry. This material contains nearly (45%–50%) cellulose and polyphenolic groups. Wood sawdust and some derivatives have been widely used in the adsorption of heavy metal [5]. Likewise, Sharma and Forster [6] tested a kind of sawdust as adsorbent for Cr(VI) eradication, and encouraging results were obtained (the adsorption capacity of sawdust was 39.7 mg/g). Researchers tried to use phosphate-treated sawdust as a membrane for removal of Cr(VI), Ni(II), Cu(II), and Zn(II) ions [3]. They noticed a significance change in adsorption capacity of the raw and treated sawdust. Rice husk contains 32.24% cellulose. This material is widely used as an adsorbent for the removal of heavy metals from water with good adsorption capacity [7]. In this context, Chuah et al. [8] observed that Co, Ni, Cu, Zn, As, Cd, Au, Hg, and Pb, were successfully remediated by rice husk. In the first two cycles, the regeneration efficiency was about 97%–95.4%. This indicates the reversibility of sorption process without loss of binding efficiency [9]. Column study with raw and treated rice husk has been conducted by Mohan and Sreelakshmi [10]. The adsorption rate and capacity were double in case of the treated rice husk compared to raw one. Another study performed by Verma et al. [11] proposed the mechanism for the removal of Cr(VI) ion from waste water using coconut husk as a biosorbent.

Modified cellulose has been also used as adsorbents or membranes for the removal of many substances (adsorbates and contaminates) [11,12]. Chemically modified (with quaternary ammonium groups) cellulose from flax shive was used by Wang and Li [12] for the removal of reactive red 228 dye from aqueous solution. Interestingly, high adsorption affinity was observed by this kind of materials which had an uptake capacity of 190 mg/g of the dye at 20°C. This was even higher than the chemically modified cellulose by anhydrides used by Zhou et al. [13]. This study investigated the removal capacity of the prepared materials toward malachite green from aqueous solution. The study revealed that the maximum adsorption capacities for the removal of malachite green on the modified cellulose were 370 and 111 mg/g, respectively, and the adsorption process followed the Langmuir model in both cases. This kind of materials is used as effective adsorbents for the removal of other substances [14].

Tea bag, is a small, porous, sealed bag or packet, basically containing tea leaves or the leaves of other herbs, which is immersed in water to steep and make an infusion. Tea bags are commonly made of filter paper or food-grade plastic, or occasionally of silk cotton or silk. The tea bag performs the same function as a tea infuser [15,16].

Dyes are some kind of substances that can be used to impart color to other materials, such as paper, foodstuffs, and textiles. Commercially, the synthetic dyes are widely used around the world. Dyes are released into water as a consequence of a numerous industrial applications (for examples: textile, ink, printing, dyeing, and some other related industries) [17]. The organic dyes affect all living beings, harmfully. Most of the dyes released into the water are generally toxic and carcinogenic. Dyes can cause skin irritation, allergic diseases, and cancer [18]. Furthermore, dyes can inhibit the penetration of sunlight into the water, which may hamper the stream's quality of life [19]. Safranin-O dye (the chemical structure of this dye is shown in Fig. 1b, while the physicochemical properties are expressed in Table 1) is one of the most known dyes; this dye is already used in different application areas, especially in dyeing silk, cotton, leather, wool, and paper [20]. Stability and/or structural complexity of Safranin-O dye create problems for biodegradation [21]. This dye has the ability to damage the nucleic acid of microorganisms, along with mutagenicity and carcinogenicity. Several



(a)

(b)

Fig. 1. Molecular structures of cellulose (a) and Safranin-O (b).

methods (physical, chemical, physicochemical, and biological methods) are used to separate the organic dyes from water [22–24]. Gupta et al. [20] used activated carbon and activated rice husks for removal of safranin-T from water. Preethi et al. [25] adsorbed safranin dye on corncob activated carbon. Chowdhury et al. [26] used sodium hydroxide-treated rice husks for the removal of safranin dye from water. While Malekbala et al. [27] removed safranin from water by using alkali-treated mango seed integuments as an adsorbent.

To the best of our knowledge, and due to our comprehensive search through the literatures, until the present work, no investigation of using tea bag filter as adsorbent for Safranin-O dye had been reported. In this study, tea bag filter was evaluated as a cellulosic membrane for removal of Safranin-O dye from water. The adsorption of Safranin-O onto tea bag filter with respect to the temperature, contact time, and adsorbent mass, and pH were performed following the batch equilibrium method. Both of the kinetics and isothermal behavior of the adsorption of Safranin-O dye by tea bag filter on the basis of the initial mass of tea bag filter, and temperature were also investigated. Moreover, the Langmuir and Freundlich isotherm models were applied to fit the experimental data. The molecular electrostatic potential (MEP) maps for both of cellulose and Safranin-O dye show that the interaction between the two molecules is mainly due to the hydrogen bonding.

2. Experimental part

2.1. Materials and methods

Safranin-O ≥ 85% was purchase from Sigma-Aldrich Co., (Germany). Tea bag filter (Lipton Co., Ltd., UK, pore size range is around 50–60 µm) was characterized by Fourier-transform infrared spectroscopy (FTIR) prior to use. The FTIR spectrum of tea bag filter was compared with that of pure cellulose powder (Fluka, Germany), Fig. S1. FTIR spectra were recorded on a Bruker Optics ALPHA II spectrophotometer (ATR mode). BS-11 thermostated shaker was used in order to shake and thermostat the samples. UV-Vis UV-M90 spectrophotometer was used to measure Safranin-O samples. pH of the solutions were measured using pH meter model: PHS-3C. All the results presented in the text are the average of at least three independent experiments.

Table 1
Physico-chemical properties of Safranin-O dye

IUPAC name	3,7-Diamino-2,8-dimethyl-5-phenylphenazin-5-ium chloride
Chemical formula	$C_{20}H_{19}ClN_4$
Molecular mass	350.85 g/mol
Appearance	Reddish brown in solid state, and red to pink in aqueous solution
Density	1.00 g/mL at 20°C
Melting point	>240°C (decomposed)
Flash point	46°C
Boling Point	~507.14°C
Sensitive	Easily absorbing moisture
Solubility	Easily soluble in water and some organic solvents like methanol, ethanol, and acetone
Hazard statements	H315, H318
Signal word	Danger

2.2. UV-Vis quantitative determination of Safranin-O dye

Pure Safranin-O dye (20 mg) was dissolved in distilled water (1,000 mL). The maximum absorption wavelength was determined. Different concentrations of Safranin-O were prepared by transferring suitable volume of the mother solution into 10 mL calibrated flasks to cover the working range. The absorbance of the solution at the specific λ_{max} = 518 nm was measured against the blank. The absorbance was plotted against concentration to obtain a calibration graph, Fig. S2a. These experiments were repeated again in order to perform a calibration graph in methanol at λ_{max} = 528 nm, Fig. S2b.

2.3. Adsorption studies

2.3.1. Determination of pH_{PZC} of tea bag membrane

The pH of the point of zero charge (pH_{PZC}) of tea bag membrane was determined using pH drift method by adjusting the pH of aqueous solution of sodium chloride (50 mL, 0.01 M) with 1 M aqueous solution of hydrochloric acid or 1 M aqueous solution of sodium hydroxide to a value between 2.2 to 11.8 (pH_i: initial pH). 0.1 g of tea bag membrane was immersed within the solution, and the mixture was shaken for 12 h. The final pH (pH_f) was then measured, and the pH_{PZC} of the membrane was determined by plotting pH_i against pH_f (Fig. 2).

2.3.2. Adsorption of Safranin-O on the tea bag membrane

The adsorption of Safranin-O on the surface of the cellulosic membrane (tea bag filter) was performed via the batch equilibrium method. 50 mL of 20 ppm aqueous solution of Safranin-O (the pH of the solution was adjusted to 11.0 with 1 M aqueous solution of sodium hydroxide) was added to 0.05 g (4.5 cm × 8 cm) of dry cellulosic membrane (pH of

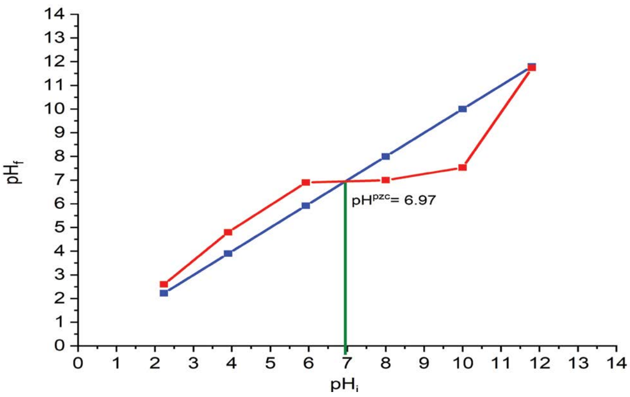


Fig. 2. Determination of pH_{PZC} of tea bag filter using pH drift method.

the solution is 11.0), and the mixture was shaken at different temperatures (30°C, 40°C and 50°C) for specific period of time. The clear solution was measured spectrophotometrically at λ = 518 nm, to determine the amount of Safranin-O remaining in solution. The concentration of Safranin-O dye was calculated from the calibration curve of the dye. The effect of adsorbent mass on the adsorption of Safranin-O was investigated by using different masses of tea bag filter [0.1 g (9 cm × 8 cm), 0.15 g (13.5 cm × 8 cm), 0.2 g (18 cm × 8 cm), and 0.25 g (22.5 cm × 8 cm)] at 30°C.

2.3.3. Adsorption of Safranin-O on the tea bag membrane as a function of pH

The effect of pH on the adsorption of Safranin-O dye by the tea bag membrane was studied: 50 mL of 20 ppm of aqueous solution Safranin-O was adjusted to pH values from 2 to 12. Then, 0.05 g (4.5 cm × 8 cm) of dry cellulosic membrane was added, and the mixture was shaken at 30°C for 120 s. The clear solution was measured spectrophotometrically to determine the amount of Safranin-O dye remaining in solution.

2.3.4. Adsorption isotherms

The adsorption of Safranin-O on the surface of the membrane (tea bag filter) was investigated at pH = 11.0 using the following procedure: 50 mL of aqueous solution of Safranin-O (20, 25, 30, 35 or 40 ppm) was added to dry cellulosic membrane (0.05 g). The mixture was shaken at different temperatures: 30°C, 40°C and 50°C for the equilibrium time. The clear solution was measured spectrophotometrically at λ = 518 nm, to determine the amount of Safranin-O remaining in solution. The concentration of Safranin-O dye was calculated from the calibration curve of the dye.

2.3.5. Mathematical treatments

2.3.5.1. Mathematical equations of mass balance

In order to determine the amount of Safranin-O adsorbed at equilibrium, q_e (Safranin-O dye (mg)/tea bag filter (g)), the mass balance equation [Eq. (1)] was applied in the isotherm experiments:

$$q_e = \frac{\left(C_0 - C_e\right)V}{W} \tag{1}$$

where C_0 (mg/L): the initial concentration of Safranin-O dye; C_e (mg/L): the concentration of Safranin-O dye at equilibrium; V (L): the volume of solution; W (g): tea bag filter mass.

Whilst, in the kinetic experiments, the amount of Safranin-O adsorbed on the surface of the tea bag filter at any time, q_t (mg/g), was obtained from the following equation:

$$q_t = \frac{\left(C_0 - C_t\right)V}{W} \tag{2}$$

where C_t (mg/L): the concentration of Safranin-O dye in solution at any time (t).

2.3.5.2. Isotherm models

Langmuir and Freundlich isotherms are the most common sorption models used to fit the experimental data [28,29]. The Langmuir isotherms model assumes that equilibrium is attained when a monolayer of the adsorbate molecules (Safranin-O dye) saturated the adsorbent (tea bag filter). Eq. (3) displays the linear form of Langmuir model:

$$\frac{C_e}{q_e} = \left(\frac{1}{K_L q_{\max}}\right) + \left(\frac{C_e}{q_{\max}}\right) \tag{3}$$

where $q_{\max}$: adsorption capacity; K_L: a constant related to the affinity between the adsorbate and the adsorbent.

The values of $q_{\max}$ and K_L can be obtained by plotting C_e/q_e vs. C_e. The value of q_e can be determined by applying Eq. (1).

The type of the isotherm basically can be estimated depending upon the R_L value: $0 < R_L < 1$ (favorable), $R_L > 1$ (unfavorable), $R_L = 1$ (linear) or $R_L = 0$ (irreversible), Eq. (4) [30].

$$R_L = \frac{1}{\left(1 + K_L C_0\right)} \tag{4}$$

On the other side, the Freundlich model represents one of the most important isotherms that express the multisite adsorption isotherm which is related to heterogeneous surfaces [31]. The linear form of Freundlich isotherm is shown in Eq. (5):

$$\log q_e = \log K_F + \left(\frac{1}{n}\right)\log C_e \tag{5}$$

where K_F: Freundlich constant and n: Freundlich isotherm exponent constant.

2.3.5.3. Kinetic models

Pseudo-first-order and pseudo-second-order as two common kinetic models are usually applied to fit the experimental data of adsorption. Eq. (6) displays the differential form of the pseudo-first-order kinetic model, whilst Eq. (7) shows the integral equation (boundary conditions: $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_e$) [32]:

$$\frac{dq_t}{dt} = k_1\left(q_e - q_t\right) \tag{6}$$

$$\ln\left(q_e - q_t\right) = -k_1 t + \ln q_e \tag{7}$$

where k_1: the equilibrium rate constant of the pseudo-second-order model (min^{-1}) and t: the time (min).

The differential form of the pseudo-first-order kinetic model is shown in Eq. (8), while Eq. (9) displays the integral equation (boundary conditions: $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_e$) [33]:

$$\frac{dq_t}{dt} = k_2\left(q_e - q_t\right)^2 \tag{8}$$

$$\frac{t}{q_t} = \frac{1}{k_2 \left(q_e\right)^2} + \frac{t}{q_e} \tag{9}$$

where k_2: the equilibrium rate constant of the pseudo-second-order (g/mg·h).

The thermodynamic parameters for the adsorption process ($\Delta G°$, $\Delta H°$, and $\Delta S°$) were calculated using Eq. (10) [33]:

$$\ln K_d = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{10}$$

where R: universal gas constant (8.314 J/mol·K); T (K): the temperature of absolute solution; K_d: the distribution coefficient which could be obtained from Eq. (11):

$$K_d = \left(\frac{C_{\mathrm{Ae}}}{C_e}\right) \tag{11}$$

where C_{Ae} (mg/L): the amount of Safranin-O adsorbed on the surface of tea bag filter at equilibrium; C_e (mg/L): the equilibrium concentration; $\Delta G°$ can be calculated by applying Eq. (12):

$$\Delta G° = -RT \ln K_d \tag{12}$$

2.4. Desorption studies

0.05 g of tea bag filter was loaded with 50 mL of aqueous solution of Safranin-O dye at agitation period of 150 s. Tea bag filter loaded Safranin-O was collected and washed thoroughly with distilled water. The amount of Safranin-O (mg) adsorbed on the surface of tea bag filter was determined using the supernatant Safranin-O concentration. Tea bag filter loaded Safranin-O was treated with 50 mL of pure methanol. The concentration of Safranin-O desorbed from the tea bag filter was determined spectrophotometrically at different times (30, 60, 90, 120, 150, 200, 250, 300, 600, 720, and 1,440 s), and the percentage of desorption of Safranin-O dye was determined by Eq. (13):

$$\text{Desorption}\left(\%\right) = \left(\frac{m_r}{m_0}\right) \times 100\% \tag{13}$$

where m_r (mg): the amount of Safranin-O desorbed and m_0 (mg): the amount of Safranin-O adsorbed.

2.5. Density functional theory calculations

The density functional theory (DFT) approach was used to carry out the MEP calculation on the studied chemicals (cellulose and Safranin-O dye). The B3LYP exchange-correlation function, which comprises Becke's three-parameter exchange function [34], and Lee, Yang, and Parr's correlation function [35] were employed in the DFT computations. The Gaussian 09W [36] Gauss View 5.0 molecular visualization program [37] was utilized in this investigation.

3. Results and discussion

3.1. Determination of pH_{PZC} of tea bag membrane

Basically, $\mathrm{pH_{PZC}}$ of a membrane depends on the chemical and electronic properties of the functional groups on its surface. The results for the determination of $\mathrm{pH_{PZC}}$ are shown in Fig. 2. From Fig. 2 the $\mathrm{pH_{PZC}}$ value of the tea bag membrane is approximately 7.0. Therefore, it seems that there was a negatively charged surface of adsorbent at pH over this value while there was a positively charged surface of adsorbent at pH below this value. These results are quite consistent with that obtained from the study of the effect of pH on the adsorption of Safranin-O dye by tea bag filter.

3.2. Adsorption studies

3.2.1. Rate of adsorption of Safranin-O dye

The adsorption of Safranin-O dye by tea bag filter was performed using a batch equilibration technique as a function of contact time at the optimal pH (pH = 11.0). The effect of agitation period on the adsorption of Safranin-O by tea bag filter adsorbent is displayed in Fig. 3. The obtained results showed that the amount of Safranin-O adsorbed (q_t) increases with time. Furthermore, the rate of Safranin-O uptake decreases gradually with time until attains the pseudo steady state value (equilibrium loading capacity, q_e). The equilibrium time of adsorption was about 100 s, which can be considered as a very fast adsorption process. During the first seconds of the adsorption process, the rate of adsorptions of Safranin-O dye is sharply increased, then continues to increase but with a lower rate until approaches a steady state. Depending upon these results, the adsorption mechanism demonstrates that the intraparticle diffusion is played an important role in the adsorption process. One hundred seconds (very short time) are needed to reach equilibrium. This elucidates the negligible of the resistance of intraparticle diffusion. As soon equilibrium is settled, both of the Safranin-O in solution and Safranin-O adsorbed by the tea bag filter would be in a state of dynamic equilibrium. This behavior indicates that further removal of Safranin-O dye is negligible, and is mainly attributed to the continuous decrease in the concentration driving force. This consequently indicates the

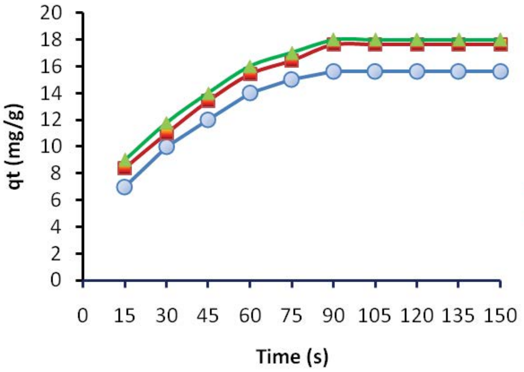


Fig. 3. Amount of Safranin-O adsorbed by the tea bag filter at different temperatures as a function of contact time.

formation of a monolayer of Safranin-O dye on the external surface of the tea bag filter [38,39].

Tea bag filter possesses the following properties which convinced us to consider it as a good adsorbent: (i) insoluble in water even at high temperatures, (ii) cheap and nontoxic, (iii) re-usability with desorption percentage reach to 95%, and (iv) contains a high porosity and high tensile strength that will provide a highly durable and protective layer for any solid adsorbates. Its high air permeability, hydrophilic nature, and fast water absorption (2 s) could overcome the longer extraction times and the poor wettability of the membrane. The target analyte could easily diffuse through the tea bag filter paper and reach the sorbent to enhance the extraction efficiency [40].

3.2.2. Effect of adsorbent mass on the adsorption of Safranin-O dye

The effect of the mass of tea bag filter on the adsorption of Safranin-O dye was studied. Fig. S3 displays that the percentage of Safranin-O removed increases with the increasing of the membrane mass. This can be assigned to the increasing of composite sites available for adsorption.

3.2.3. Effect of pH on the adsorption of Safranin-O dye

The effect of pH on the adsorption of Safranin-O dye by tea bag membrane is displayed in Fig. 4. It can be clearly seen from this figure that the amount of Safranin-O adsorbed by the tea bag filter is increased with increasing the pH until reach the maximum at pH = 11. This result is consistent with that of pH_{PZC}. At low pH (less than 7.0), there will be a positively charged surface of adsorbent, and this makes the membrane to be as a suitable adsorbent for negatively charged adsorbates. As pH increases, there will be a negatively charged surface of adsorbent, and this makes the membrane to be as a suitable adsorbent for positively charged adsorbates like Safranin-O dye. It is worth mentioning that over pH = 11 (strong basic conditions), some of the cellulosic membrane break up and dissolved in solution, and this explains the decease of q_e of Safranin-O dye on the tea bag membrane at pH = 12.

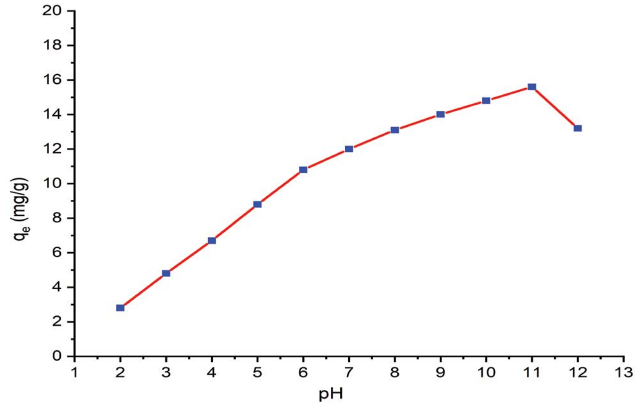


Fig. 4. Amount of Safranin-O adsorbed on the tea bag filter as a function of pH at: T = 30°C and t = 120 s.

3.2.4. Adsorption isotherms

Adsorption isotherms generally provide an imagination about the distribution between the adsorbent and the solution at the equilibrium conditions. Moreover, it reveals the effect of equilibrium concentration on the loading capacity of the adsorbate at different temperatures. Fig. 3 displays the adsorption of Safranin-O dye by tea bag filter at different temperatures (30°C, 40°C and 50°C). The obtained results showed that the loading capacity of adsorbent increases with temperature. This behavior indicates the endothermic nature of the adsorption of Safranin-O dye onto tea bag filter.

The Langmuir and Freundlich isotherm models were used to fit the experimental data of the adsorption of Safranin-O dye by tea bag filter (Figs. 5 and 6, respectively). Based on the correlation coefficient (R^2) values that depicted in Table 2, the obtained experimental data of the adsorption showed good correlation with both of Langmuir and Freundlich isotherm equations, but the best fit of the experimental data was obtained from the Langmuir isotherm model (the R^2 values of Langmuir isotherm model are found to be slightly higher than that of Freundlich isotherm model). The obtained results revealed that the adsorption of Safranin-O dye by tea bag filter is characterized by monolayer coverage of the dye on the outer surface of the filter.

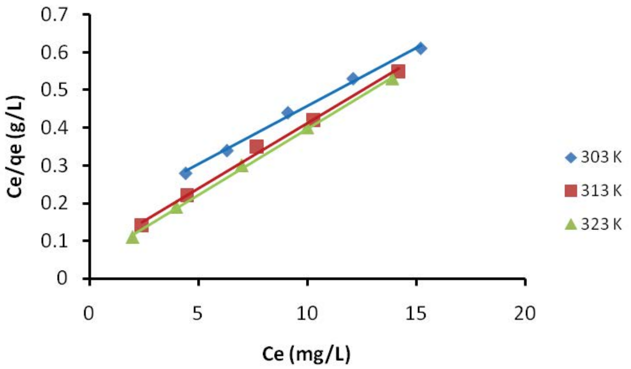


Fig. 5. Linearized Langmuir for the adsorption of Safranin-O by tea bag filter at different temperatures.

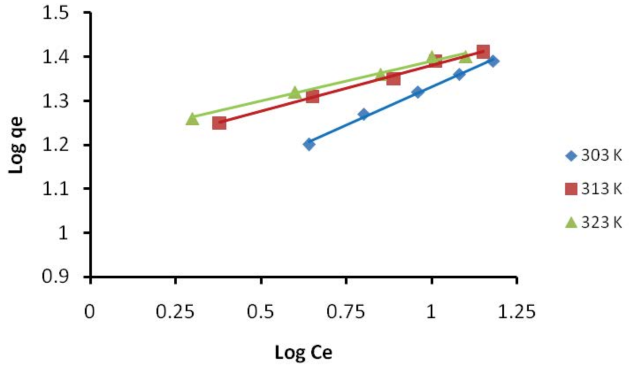


Fig. 6. Linearized Freundlich for the adsorption of Safranin-O by tea bag filter at different temperatures.

Furthermore, the adsorption process has an equal activation energy or homogenous nature for each adsorbed molecule. On the other hand, values of the separation factor (R_L) were in the range $0 < R_L < 1$ (for the range of concentration of Safranin-O dye used in this work), which highly indicates that the adsorption of Safranin-O dye on tea bag filter is favorable. The mechanism of the adsorption of Safranin-O dye on porous tea bag filter might involve the following steps: (i) diffusion of the Safranin-O dye to the external surface of tea bag filter; (ii) diffusion of the Safranin-O dye into the pores of tea bag filter; (iii) adsorption of the Safranin-O dye on the internal surface of tea bag filter.

3.2.5. Adsorption kinetics

It is worth mentioning that in order to examine the mechanism of the adsorption process, pseudo-first-order and pseudo-second-order represent the two major kinetic models that can be used to fit the experimental data of adsorption. Fitting results of the experimental data for the two models are illustrated in Figs. 7 and 8, respectively. Whilst the rate constants and correlation coefficient (R^2) for the two models are shown in Table 3. These figures revealed that the adsorption of Safranin-O dye by tea bag filter is best described by the pseudo-second-order model. This was elucidated based on the values of R^2 (Table 3). The kinetic model of the second-order indicates that the rate limiting step might be chemical adsorption. It is more likely to predict that the adsorption behaviour can involve valency forces through sharing of electrons between Safranin-O dye and tea bag filter [29,38–42]. This was further confirmed by DFT calculations (MEP studies).

Table 2
Calculated values of Langmuir and Freundlich isothermal constants for the adsorption of Safranin-O by tea bag filter

	Langmuir isotherm			Freundlich isotherm		
T (K)	q_{max} (mg/g)	K_L (L/mg)	R^2	$1/n$	K_F (mg/g)	R^2
303	32.26	0.22	0.994	0.347	9.64	0.994
313	29.41	0.52	0.995	0.209	14.83	0.992
323	28.57	0.76	0.994	0.182	16.11	0.986

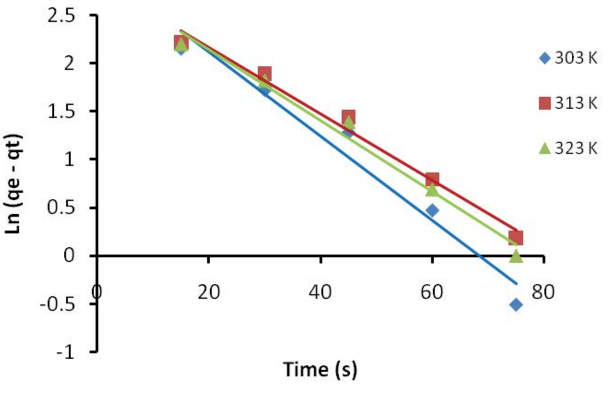


Fig. 7. Pseudo-first-order kinetics for the adsorption of Safranin-O onto tea bag filter at different temperatures.

3.2.6. Adsorption thermodynamics

Almost of the studies related to the adsorption processes that reported so far indicated in general the increasing of the adsorption capacities of the adsorbent with temperature. This confirms that the nature of the adsorption of adsorbate onto adsorbent is endothermic. Similarly, the adsorption capacity of tea bag filter was found to be increased with increase of temperatures. This behavior emphasized that, as temperature increases, the active centers in tea bag filter available for adsorption increase. Due to that, the viscosity of the liquid phase decreases, while the pore size increases; and ultimately enhancing the rate of intraparticle diffusion of solute molecules. This will enhance the adsorption capacity of the tea bag filter. Eqs. (10)–(12) were applied to calculate the thermodynamic parameters ($\Delta H°$, $\Delta S°$, $\Delta G°$ and K_d) of the adsorption process ($\ln K_d$ was plotted against $1/T$ as shown in Fig. 9). This figure revealed that the relationship between $\ln K_d$ and $1/T$ is linear which further confirms the endothermic nature of the adsorption process. The standard free energies ($\Delta G°$) for tea bag filter are negative and decrease as the temperature increases (–8.94 kJ/mol at 303 K, –19.07 kJ/mol at 313 K, and –24.17 kJ/mol at 323 K). The results display the feasibility and spontaneous nature of the process. Moreover, the results exhibit positive values of $\Delta S°$ (780.02 J/mol·K) and $\Delta H°$ (226.56 kJ/mol) for tea bag filter. This was previously proved by the isotherm experiments at different temperatures. The positive values of $\Delta S°$ exhibit the affinity of tea bag filter for Safranin-O dye, as a result of the increased randomness at the interface between the solid liquid phases. These results can suggest a strategy for the adsorption of Safranin-O on the tea bag filter. Adsorption data of some

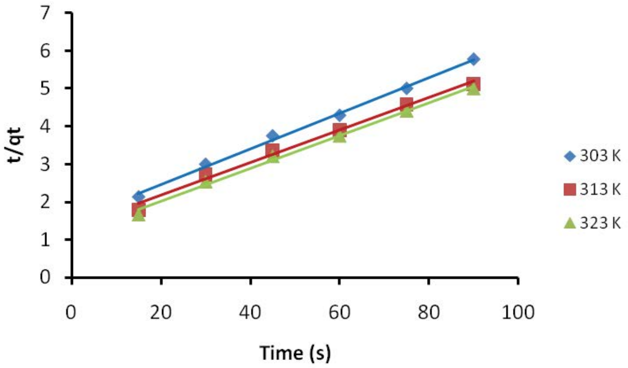


Fig. 8. Pseudo-second-order kinetics for the adsorption of Safranin-O onto tea bag filter at different temperatures.

Table 3
Comparison of the pseudo-first-order and pseudo-second-order models for the adsorption of Safranin-O by tea bag filter.

T (K)	Pseudo-first-order model		Pseudo-second-order model	
	k_1 (s^{-1})	R^2	k_2 (g/mg·s)	R^2
303	0.043	0.964	1.45×10^{-3}	0.996
313	0.034	0.983	1.41×10^{-3}	0.991
323	0.036	0.98	1.61×10^{-3}	0.994

previous studies used cellulose derivatives as adsorbents or Safranin-O dye as an adsorbate are summarized in Table 4.

3.3. Desorption studies

In the recycling processes, the regeneration of adsorbents, and also the recovery of adsorbed material have attracted great interest. Herein, the desorption studies are led us to elucidate: (i) the nature of adsorption process, (ii) recover the Safranin-O dye from tea bag filter, and (iii) regeneration of tea bag filter in order to be further used as an adsorbent. Methanol (100%) as desorption agent was used to carry out the desorption experiments (desorption % was determined at different times). Tea bag filter displays good desorption results. The percentage of desorption is increased gradually with time until reach the maximum desorption 95% within about 8–10 min (Fig. 10). The appearance of the tea bag filter before adsorption, after adsorption, and after desorption are shown in Fig. S4.

3.4. DFT calculations

3.4.1. Molecular electrostatic potential

The MEP surface is represented in three dimensions by molecular electrostatic potential maps. The MEP map is a reliable instrument for investigating chemical reactivity, electrophilic and nucleophilic regions of molecular systems since the surface of the map reveals molecular size, shape, charge distribution, and electrostatic potential value. Different colors, such as red for a negative electrostatic potential, blue for a positive electrostatic potential, and green for a relatively low positive electrostatic potential, denote different electrostatic potentials on the surface [47]. The charge distribution information is used to determine the charge-dependent properties and the interaction of molecules with each other. In the MEP map, the red region refers to an electron-rich region of the molecule that strongly repels outer electrons and has the lowest potential energy. It also indicates the region with electronegative potentials. While the blue region refers to electron-poor region that strongly attracts the outer electrons of the molecule, is positively charged, and has the highest potential energy value [48,49]. The MEP surface of cellulose (as a monomer) was calculated using the DFT/B3LYP/6-311++G (d,p) method/functional, which made by using the file *chk of the optimized

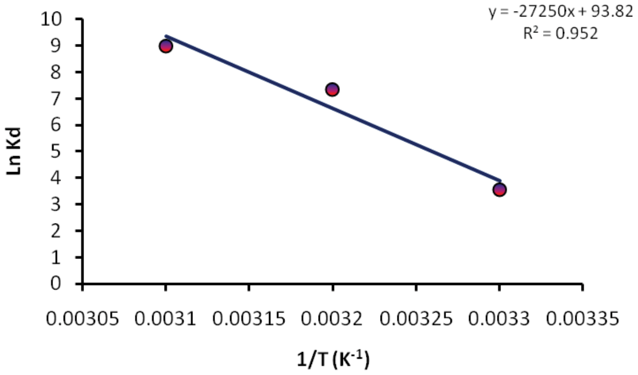


Fig. 9. Variation of thermodynamic parameters with temperature for the adsorption of Safranin-O onto tea bag filter.

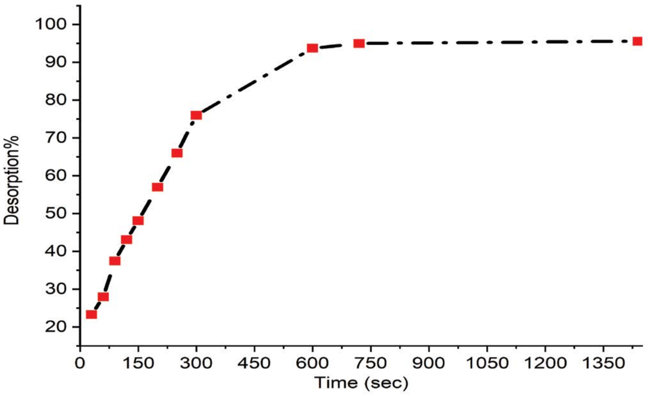


Fig. 10. Percentage of desorption of Safranin-O dye from tea bag filter as a function of time.

Table 4
Adsorption data of some previous studies used cellulose derivatives as adsorbents or Safranin-O as adsorbates.

Adsorbent		Isotherms	q_{max}	References
SPION	SO	L, F	0.79 mg/g	[43]
MWCTN/SPION	SO	L, F	8.42 mg/g	[43]
UCC	SO	L	80.32 mg/g	[44]
PCC	SO	L	96.81 mg/g	[44]
SCC	SO	L	89.53 mg/g	[44]
CAT	Co(II)	L	0.878 mmol/g	[45]
CAT	Cu(II)	L	1.683 mmol/g	[45]
CAT	Ni(II)	L	1.199 mmol/g	[45]
CAT	Cu(II)–Co(II)	L	0.99–0.24 mmol/g	[46]
CAT	Cu(II)–Ni(II)	L	1.13–0.34 mmol/g	[46]
CAT	Co(II)–Ni(II)	L	0.48–0.53 mmol/g	[46]

SPION: Superparamagnetic iron oxide nanoparticles; MWCTN: Multi-wall carbon nanotube; SO: Safranin-O; UCC: Untreated coconut coir; PCC: Phosphoric acid coconut coir; SCC: Sulphuric acid coconut coir; CAT: cellulose trimellitate.

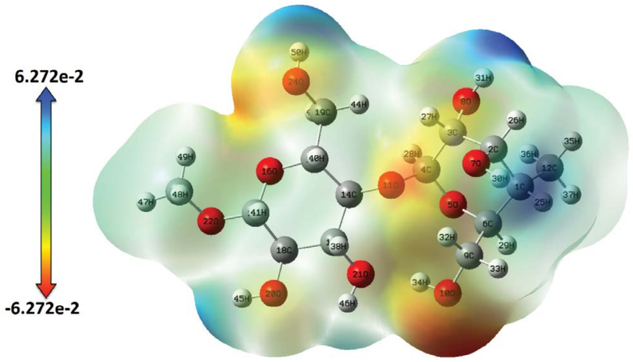


Fig. 11. Molecular electrostatic potential surface of monomer cellulose.

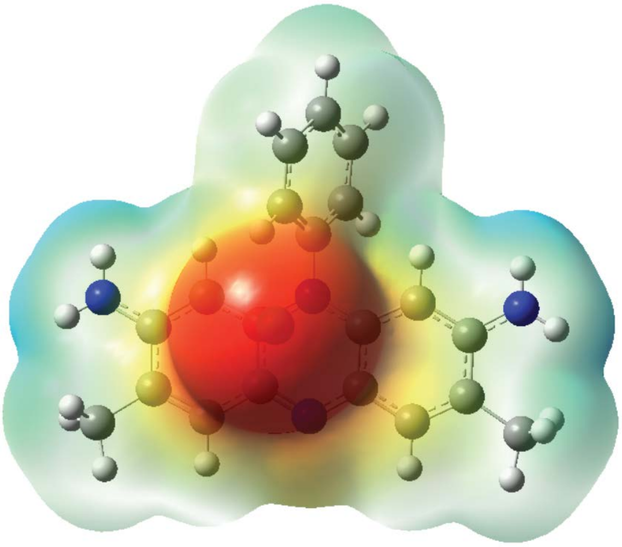


Fig. 12. Molecular electrostatic potential map of the Safranin-O compound.

structure. The resulting MEP surface is shown in Fig. 11. A color scale between –6.272e-2 and 6.272e-2 was obtained. The negative region or dark red points are localized on oxygen atoms (O10, O24 and partially O11 and very little density over other O atoms) of molecule, which are the most favorable places for electrophilic attack. In contrast, the hydrogen atoms, which are the target of the most sensitive nucleophilic attack, were surrounded by the most positive regions or strong blue zones. On the other hand the molecular electrostatic potential map of the Safranin-O compound is given in Fig. 12. It can be realized from this figure that the negative region of the compound is concentrated around the chloride ion, while the positive region is partially located on the hydrogen atoms of the amine group in the phenylephrine ring. This study provides us with some information about the probable places in the two molecules (cellulose and Safranin-O) that may be involved in the interaction between the adsorbent (tea bag filter as a cellulosic membrane) and the adsorbate (Safranin-O dye). This interaction is mainly due to the hydrogen bonding between the two molecules.

4. Conclusions

Tea bag filter is tested as adsorbents for the removal of toxic Safranin-O dye from water using the batch equilibrium method at pH = 11.0 (optimal pH). The adsorption studies were carried out with respect to the contact time and adsorbent mass. Depending upon these studies, tea bag filter exhibited good ability to be as a membrane for removal of Safranin-O dye from water at wide range of pH. Beside this ability and compatibility, tea bag filter displayed the following advantages: (i) insoluble in water even at high temperatures; (ii) cheap and nontoxic, (iii) re-usability with desorption percentage reach to 95%, (iv) contains a high porosity and high tensile strength that will provide a highly durable and protective layer for any solid adsorbates. Its high air permeability, hydrophilic nature, and fast water absorption (2 s) could overcome the longer extraction times. The target analyte could easily diffuse through the tea bag filter paper and reach the sorbent to enhance the extraction efficiency. The isothermal behavior and the kinetic models of the adsorption of Safranin-O dye on the surface of tea bag filter as a function of temperature, and initial mass of the adsorbent were also investigated. The isothermal behavior showed that the experimental data of the adsorption correlates well with both of Langmuir and Freundlich isotherm equations (although the correlation of data with Langmuir isotherm equation is more pronounced with respect to their R^2 values). On the basis of the kinetic models, the adsorption of Safranin-O dye by tea bag filter is best explained by the pseudo-second-order model. Based on the MEP maps, the interaction between the adsorbent (cellulose) and the adsorbate (Safranin-O dye) is mainly attributed to the hydrogen bonding.

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Supporting information

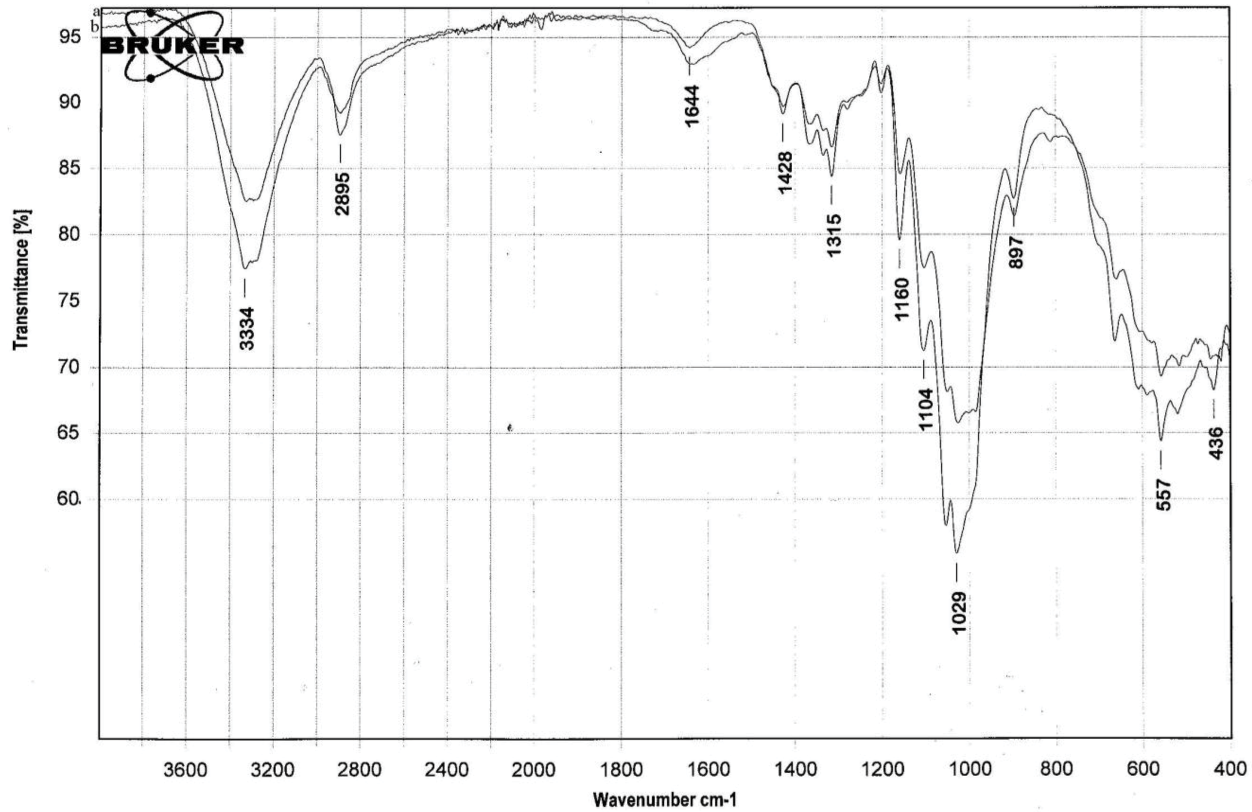

Fig. S1. Fourier-transform infrared spectra of tea bag filter (a) and pure cellulose powder (b).

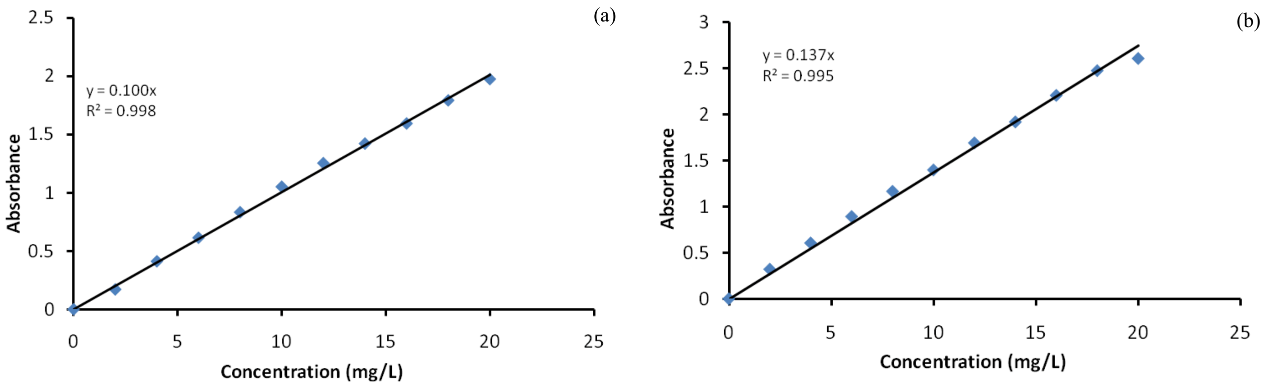

Fig. S2. Calibration curve of Safranin-O in distilled water at 518 nm (a) and in methanol at 528 nm (b).

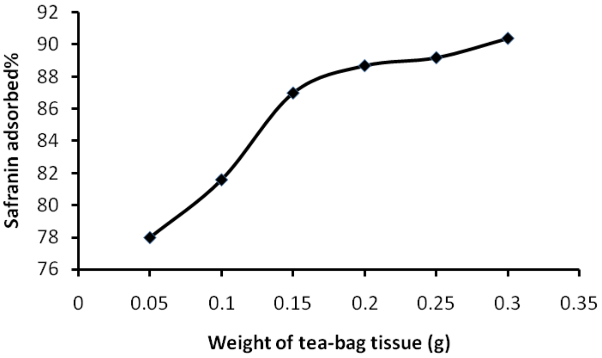

Fig. S3. Effect of tea bag filter weight on the percentage of Safranin-O adsorbed.

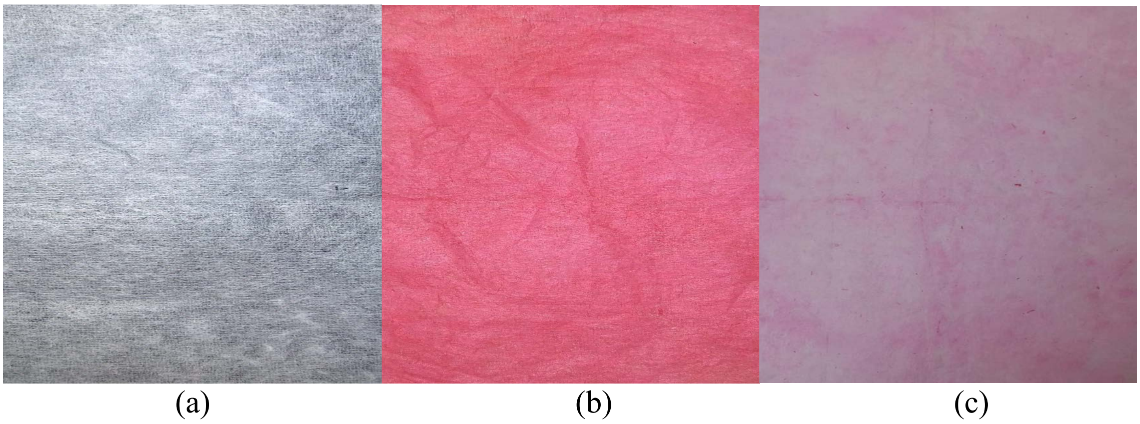

Fig. S4. Appearance of the tea bag filter: (a) before adsorption, (b) after adsorption, and (c) after desorption.