Coffee waste as potential adsorbent for the removal of basic dyes from aqueous solution

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Abstract−We evaluated the adsorption performance of coffee waste (CW), collected from coffee shops, for the removal of two basic dyes, toluidine blue (TB) and crystal violet (CV), from aqueous solutions. Batch adsorption experiments were conducted under different conditions including contact time, initial concentration of dye, pH, sorbent dosage and temperature. The Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) isotherms were tested to examine the adsorption behavior. The equilibrium data were well fitted by Langmuir isotherm model. The kinetic study indicates that adsorption follows the pseudo second-order model. The maximum adsorption capacity was found to be as high as 142.5 mg/g for TB and 125 mg/g for CV, which makes CW a prospective adsorbent for the removal of basic dyes from aqueous solution.

Keywords: Adsorption, Coffee Waste, Basic Dyes, Isotherm, Kinetics

INTRODUCTION

The release of dyes from the textile industry is a major environmental problem. Colored water can affect plant life, and thus an entire ecosystem can be destroyed by the contamination of various dyes in water. Some dyes are toxic and carcinogenic. This dictates the necessity of dye containing water to undergo treatment before disposal to the environment.

Various processes of dyes removal are used, such as biological, oxidation, chemical precipitation and membrane separation [1,2]. But these processes do not show significant effectiveness or economic advantage when the solute concentrations are very low.

Adsorption is one of the most effective and attractive methods for the treatment of dye-containing wastewater [3,4]. Activated carbons are the most widely used adsorbents, but their widespread use is still restricted by their inherently high costs [5,6]. To decrease the cost of treatment, some attempts have been made to find low cost alternative adsorbents. The reported adsorbents are clay material, siliceous materials, zeolites, agricultural wastes, industrial waste products, biosorbents etc. [7,8].

On the other hand, coffee has become an established beverage in the world. In Tunisia, as example, the consumption is on the order of 8390 tons in 2010 (INS Tunisia). Aside from some unimportant losses, all these quantities of coffee end up in the form of coffee grounds in the discharges. Developing technology to reuse coffee grounds for useful purposes would help convert this large amount of waste into a new resource. The production of biofuels such as ethanol [9] and biodiesel [10] and use as an adsorbent for the removal of heavy metal [11,12], dyes [13], and pesticides [14] from wastewater are some of the applications under consideration.

A survey of the literature shows that adsorption studies using treated (e.g., activated carbon) or untreated coffee waste are mainly made with coffee husk [15] or spent coffee grounds [16], which are generated from the processing of coffee. However, the use of waste from coffee shops is scarce. Azouaou [11] studied the adsorption of cadmium by untreated coffee waste and found adsorption capacity of 15.65 mg/g, while Kysas found maximum adsorption capacity of 70 mg/g and 45 mg/g for Cu(II) and Cr(VI), respectively [17]. Recently, Kyzas [13] studied the performance of untreated coffee waste on the removal of a reactive dye and basic dye and obtained high maximum adsorption capacity of 179 and 295 mg/g, respectively. Interestingly, he demonstrated that the adsorbent can be used for the treatment of real textile effluent with ten cycles of adsorption-desorption [18]. This stimulated us to study the performance of coffee waste that did not undergo additional treatment for the removal of dyes from aqueous solutions. Thus, we focused on the removal of two basic dyes, toluidine blue (TB) and crystal violet (CV), chosen as models, at different key parameters such as pH, adsorbent dosage, contact time, initial dye concentration, ionic strength and temperature.

MATERIALS AND METHODS

1. Materials

The coffee waste (CW), collected from a coffee shop, was washed several times with boiled distilled water to remove any adhering dirt and color until pH was reached 6.1 in the residual liquid. The CW was then dried in the oven at 60 °C for 24 h, ground and sieved to obtain a particle size <250 μm. The product was stored in airtight container for further use.
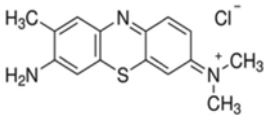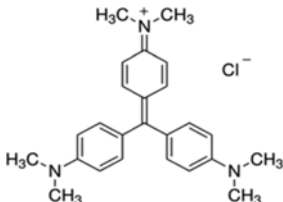
2. Chemicals

The characteristics and chemical structure of Toluidine blue and Crystal violet are listed in Table 1. To prepare various solutions at desired concentrations from the stock solution, distilled water was used for dilution. Various experimental conditions are summarized in Table 2.

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Table 1. Characteristics and chemical structure of dyes

Dye name	Toluidine Blue	Crystal violet
Abbreviation	TB	CV
Color index number	52040	42555
Molecular formula	$C_{15}H_{16}ClN_3S$	$C_{25}H_{30}ClN_3$
Molecular weight	305.8 g/mol	408 g/mol
λ_{max} (nm)	623	590
Chemical name	3-Amino-7-(dimethylamino)-2-Methylphenothiazin-5-ium chloride	Hexamethylpararosaniline chloride
Molecular structure		

Table 2. Effect of parameters on the adsorption of CV and TB onto CW

	Parameters			
	Concentration dye (mg/L)	pH	Adsorbent dosage (g/L)	Temperature (°C)
Effect of pH	40	**3-11**	5	20
Effect of adsorbent dosage (g/L)	40	6	**0.1-10**	20
Effect of concentration dye (mg/L)	**80-400**	6	5	20
Effect of ionic strength	40	6	5	20
Effect of temperature (°C)	40	6	5	**20-50**

3. Characterization of Coffee Waste

The techniques used to characterize the CW include Fourier transform infrared spectroscopy (FTIR), Boehm titration and pH point of zero charge (PZC). The FTIR analysis was done with a Fourier transform spectrophotometer model IRAffinty-1 SHIMADZU. The spectra of the CW before and after adsorption were in the range of 4,000-400 cm^{-1}.

The determination of surface functional groups was based on the Boehm titration method [19]. The number of the basic sites was calculated from the amount of HCl that reacted with the coffee adsorbent. The various free acidic groups were derived using the assumption that NaOH neutralizes carboxyl, lactone and phenolic groups, Na_2CO_3 neutralizes carboxyl and lactone and $NaHCO_3$ neutralizes only carboxyl groups. The excess of base or acid was then determined by back titration using NaOH (0.10 mol/L) and HCl (0.10 mol/L) solutions.

The point of zero charge (PZC) was evaluated according to titration procedure described in literature [15,16,20]. Three aqueous solutions of different pH values (3, 6 and 11) were prepared. Several amounts of CW (0.05%, 0.1%, 0.5%, 1.0%, 3.0%, 7.0% and 10.0% w/w) were added to 20 mL of each solution. The aqueous suspensions containing different amounts of the adsorbent were let to equilibrate for 24 h under agitation (220 rpm) at 20 °C. The pH of each solution was then measured. The pH was determined as the converging pH value from the pH versus adsorbent mass curve.

4. Equilibrium Studies

Equilibrium studies were carried out by contacting xed amount of CW (0.50 g) with 100 mL of dye solution of different initial concentrations in 250 mL stopper conical asks at room temperature (20±

2 °C) and pH of 6. The initial and equilibrium concentrations of dye were analyzed by UV-vis spectrophotometer (Shidmadzu model UV-1601, Japan) at a wavelength of maximum absorbance. The amount of adsorption at equilibrium, q_e (mg/g), was calculated from the following equation:

$$q_e = (C_i - C_e)\frac{V}{W} \tag{1}$$

where C_i and C_e are the initial and final (equilibrium) concentrations of dye (mg/L), respectively, V the volume of dye solution (L) and W is the weight of the adsorbent used (g). The dye removal percentage was calculated as follows:

$$\% \text{ Dye removal} = \frac{C_i - C_e}{C_i}100 \tag{2}$$

RESULTS AND DISCUSSION

1. Characterization of Adsorbent

The experimental titration curves for PZC determination are presented in Fig. 1. These results indicated the PZC value was 5.5±0.2. For pH values above 6, there was a predominant negatively charged surface of CW. At lower pH values, the surface charge may get mainly positively charged. The functional groups at the surface of CW characterized by the Boehm method were: carboxylic 0.225 mmol/g, phenolic 0.27 mmol/g, lactonic 0.015 mmol/g and basic 0.1 mmol/g.

2. Influence of Initial pH

The solution pH is an important parameter in the adsorption process as it may affect the surface charge of adsorbent and the ioniza-
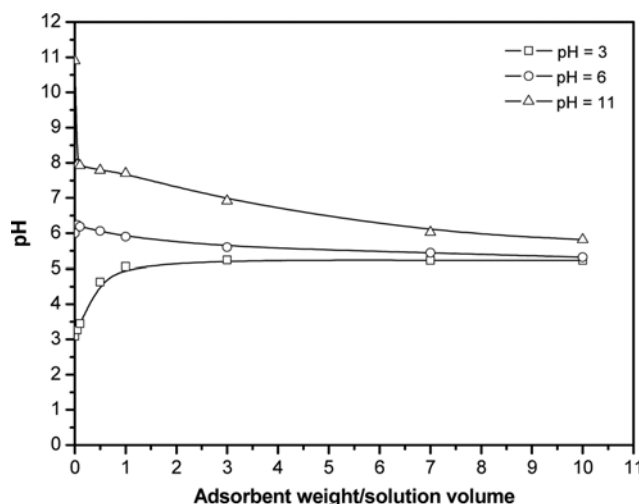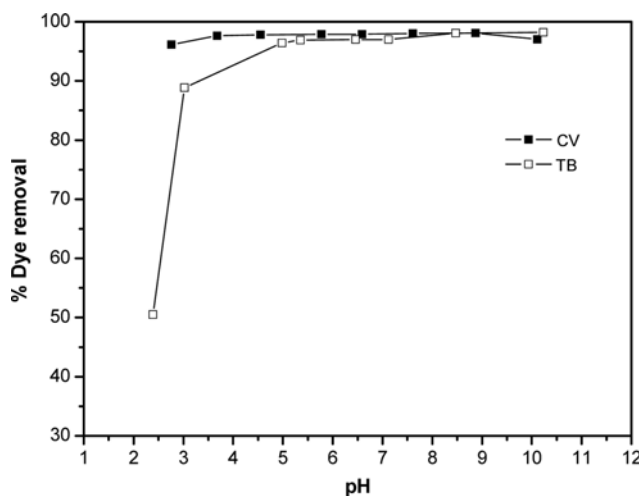
Fig. 1. Determination of PZC for the coffee waste.

Fig. 2. Effect of pH on the adsorption of CV and TB onto CW.

Fig. 3. Effect of adsorbent dosage on the adsorption of CV and TB onto CW.

tion degree of the dye. Fig. 2 shows the effect of pH of solution on the adsorption of TB and CV onto CW. In the case of TB, the adsorption capacity increased from 50 to 95% with the increase of pH from 2.3 to 5 and thereafter remained almost constant. As initial pH of TB solution decreased below the PZC, the number of negatively charged adsorbent sites decreased and positively charged sites increased, which does not favor the adsorption of positively charged TB cations due to electrostatic repulsion [21]. At higher pH, negatively charged adsorbent sites increased, enhancing the adsorption of cationic dyes. A similar behavior was obtained for the removal of basic dye from aqueous solutions using spent tea leaves [22]. In the case of CV, the adsorption capacity in the range of pH studied presented a slight increase with increasing the pH, but no significant differences were observed. A similar behavior has been reported by other CV adsorptions studies [23-25].

3. Effect of Adsorbent Dosage

To investigate the effect of adsorbent amount, the adsorption of TB and CV was measured at seven different adsorbent concentrations at an initial dye concentration of 40 mg/L. Fig. 3 shows that with the increase in adsorbent dosage from 0.1 to 2 mg/L the per-
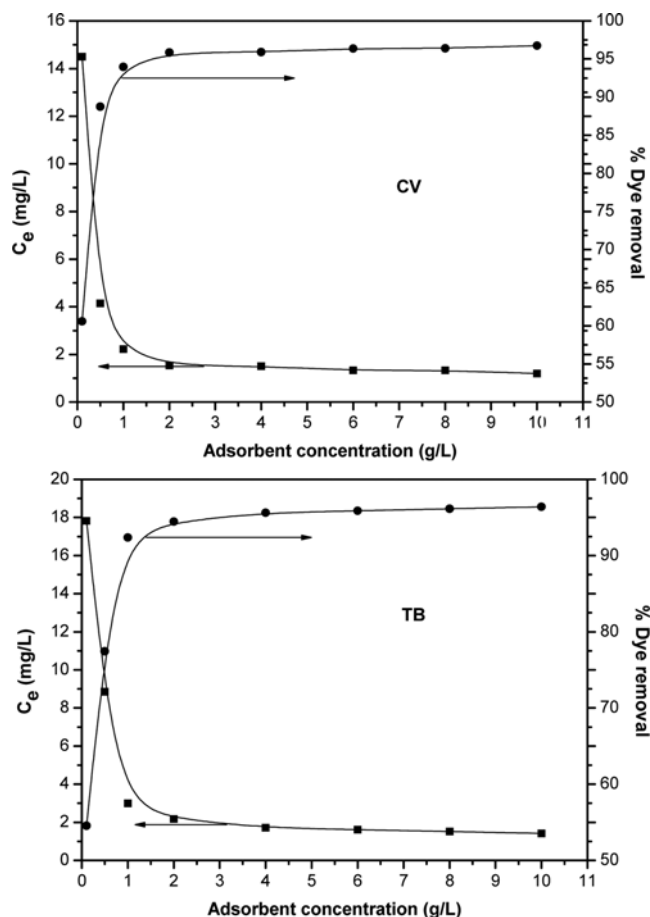
cent removal of dyes increased from 55 to 96% and from 60 to 97% for TB and CV, respectively. Above 2 g/L of sorbent dose the sorption equilibriums of dyes were reached. This can be attributed to increased surface area resulting from the increase in adsorbent mass, thus increasing the number of active sites. Similar behavior for the effect of adsorbent concentration on TB and CV adsorptions capacity was reported in the literature for other types of adsorbents [16, 23-25]. Based on the results presented in Fig. 3, the remaining experiments were conducted for an adsorbent dosage of 5 g/L.

4. Effect of Initial Concentration and Contact Time

The effect of initial dye concentration (80-400 mg/L) for the removal of TB and CV is shown in Fig. 4. The results show that the sorption rate of dye was extremely rapid and the time required for equilibrium adsorption was almost 20 min since no change in the adsorbed amount was detected afterward. The variation in the extent of adsorption with initial dye concentration may be because the dye ions were absorbed by the vacant sites on the surface of CW, when the exterior surface of CW reached saturation. Generally, when adsorption involves a surface reaction process, the initial adsorption is rapid. Then, lesser adsorption follows, as the available adsorption site gradually decreases, which is consistent with former studies reported earlier [14,26-28]. Due to such quick adsorption rate it can be inferred that chemisorption is predominant in this adsorption process; a Dye-CW contact time of 60 min was selected in further adsorp-
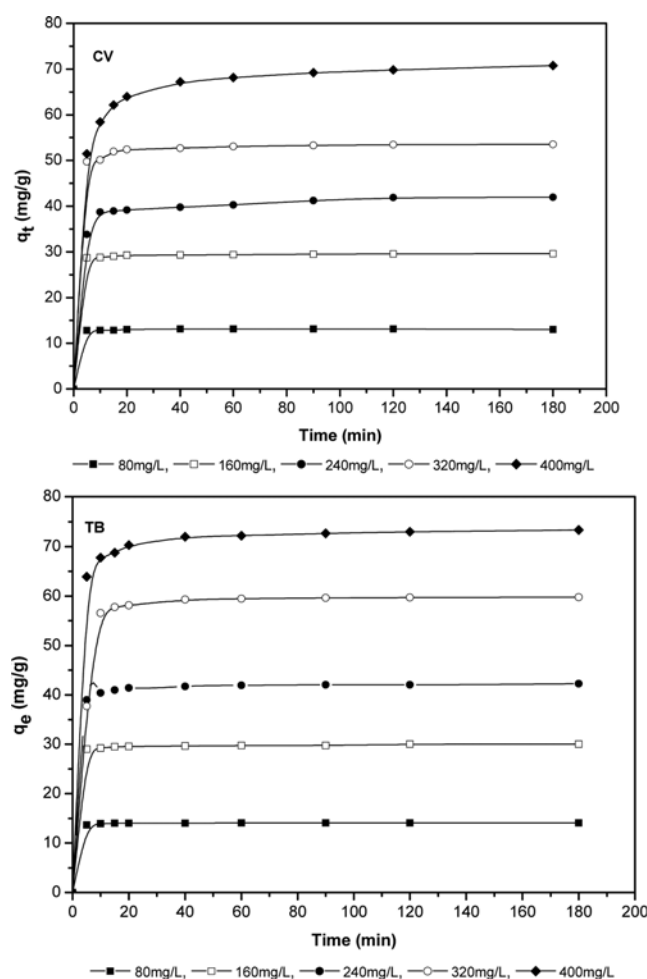
Fig. 4. Effect of initial dye concentration and contact time on the adsorption of CV and TB onto CW.

tion experiments to be sure that equilibrium state had been reached. Also, the adsorption capacity at equilibrium increased from 14.0 to 73.3 mg/g for TB and from 13 to 70.6 mg/g for CV with an increase in the initial dye concentration from 80 to 400 mg/L.
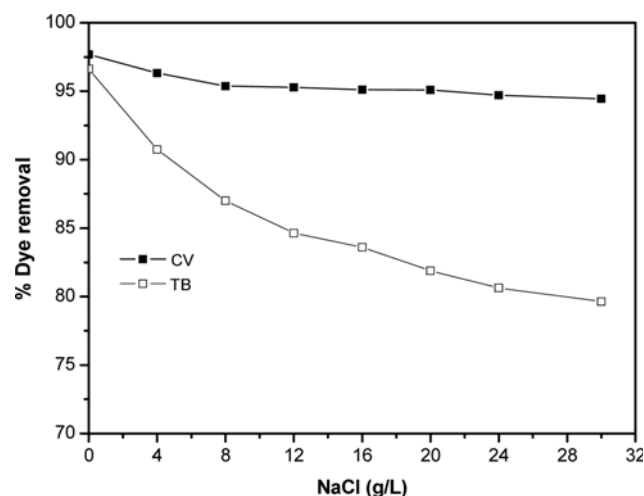

Fig. 5. Effect of NaCl concentration on the adsorption of CV and TB onto CW.
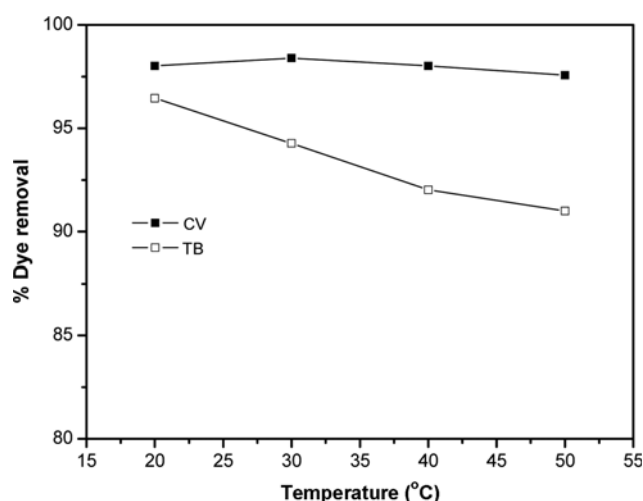

Fig. 6. Effect of temperature on the adsorption of CV and TB onto CW.

5. Effect Ionic Strength

The effect of ion strength salt on the adsorption of dyes was studied by addition of different amounts of sodium chloride (from 0 to 30 g/L). Fig. 5 shows that the reduction of percentage of dye removal reached 17% for TB and 2% for CV as salt concentration increased from 0 to 30 g/L. This could be related to the competition of TB cation and Na^+ for the sorption sites [29]. The effect of ion strength on sorption of CV was less important.

6. Effect of Temperature

The temperature dependence of TB and CV sorption onto CW was studied at initial concentration of 40 mg/L and pH 6. As shown in Fig. 6, the percentage removal of dye decreases slightly from 96% to 91% for TB when the temperature increases from 20 to 50 °C. In the case of CV the variation is negligible. The observed decreases in the adsorption capacity with an increase of temperature indicated that a low temperature is in favor of dye removal by adsorption onto CW. This phenomenon indicates that the adsorption process is exothermic. Similar behavior has been reported in the literature [11,30].

7. Adsorption Isotherm

The equilibrium adsorption isotherm is important in the design of adsorption systems. The adsorption isotherm describes how adsorbates interact with adsorbents and therefore it is critical in optimizing the use of adsorbents. The equilibrium data of dye adsorption on to coffee waste were explored using the isotherm model of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich. The applicability of the isotherm models to the adsorption study within the experimental conditions (concentration range 20-900 mg/L, adsorbent dose 5 g/L, temperature 20±2 °C, contact time 20 min and stirring speed 220 rpm) was judged by the correlation coefficient R^2 value of each plot. The higher the R^2 values indicate the fit.

7-1. Langmuir Isotherm

The Langmuir isotherm, which is the most popular isotherm model, is used to describe the adsorption process where the occupancy occurs at on one adsorption site at an energetically homogeneous range of adsorption sites. The following is the Langmuir isotherm equation [31]:

$$q_e = \frac{q_m bC_e}{1+bC_e} \tag{3}$$

Table 3. Isotherm parameters for adsorption of CV and TB onto CW

Adsorption isotherm	Adsorption constant	Type of dyes	
		TB	CV
Langmuir	q_m (mg/g)	142.5	125
	b (mg/L)	0.039	0.047
	R^2	0.99	0.985
Freundlich	n	1.785	2.096
	K_L (mg/g)	8.306	9.624
	R^2	0.954	0.907
Temkin	A	1.016	1.546
	B	22.24	17.32
	R^2	0.953	0.975
D-R	q_{mD-R} (mg/g)	82	68
	β_{D-R} (mol^2/j^2)	$2\ 10^{-6}$	$4\ 10^{-7}$
	E (j/mol)	500	1118
	R^2	0.746	0.721

where q_e is the amount of dye adsorbed mg/g, q_m the maximum adsorption capacity (mg/g), C_e the equilibrium concentration of dye adsorbed (mg/L) and b is the Langmuir constant (L/mg).

A plot of q_e against C_e gave a fitted curve, and the Langmuir constants were generated from the plot of sorption data (Table 3). The Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given by Eq. (4) [32]

$$R_L = \frac{1}{1+bC_e} \tag{4}$$

where b is the Langmuir constant, and C_0 the initial concentration dye (mg/L). R_L value indicates the adsorption nature to be either unfavorable ($R_L>1$), favorable ($0<R_L<1$), ($R_L=1$) or irreversible ($R_L=0$)

R_L values calculated for all concentrations for dyes revealed that the entire adsorption process was favorable for two dyes since their values were in the range of $0<R_L<1$.

7-2. Freundlich Isotherm

The Freundlich isotherm is an empirical equation assuming that the adsorption process takes place on heterogeneous surface systems in which it is characterized by the heterogeneity factor 1/n. The Freundlich equation is expressed as [33]:

$$q_e=K_F C_e^{1/n} \tag{5}$$

where q_e is the solid phase adsorbate in equilibrium (mg/g), C_e the equilibrium liquid phase concentration (mg/L), K_F and n are the Freundlich equilibrium coefficients. The value of n gives information on favorability of adsorption process and K_F is the adsorption capacity of the adsorbate.

A plot of q_e against C_e gave poor curves, indicating that the adsorption process did not follow the model. The values of the Freundlich equilibrium coefficients K_F and n were generated from the plot of sorption data in Table 3. The parameter 1/n ranging between 0 and 1 measures the adsorption intensity or surface heterogeneity.

7-3. Temkin Isotherm

The Temkin model is based on the assumption that the heat of adsorption will decrease linearly with the increase of the coverage

of the adsorbent' the Temkin model is expressed [34] as:

$$q_e=Bln(A_TC_e) \tag{6}$$

$$B = \frac{RT}{b_T} \tag{7}$$

A_T is the equilibrium binding constant corresponding to the maximum binding energy, B, related to the heat of adsorption, q_e the experimental adsorption capacity (mg/g) and C_e is the concentration of dye adsorbed at equilibrium (mg/L). In Eq. (7) $1/b_T$ indicates the adsorption potential of the adsorbent, R is the universal gas constant (8.314 J K^{-1} mol^{-1}) and T is the temperature in Kelvin (K).

A plot of q_e against C_e indicates a linear decrease in adsorption energy as the adsorption sites are filled. The heat of adsorption of all the molecules in the layer decreases linearly with surface coverage due to adsorbent-adsorbate interactions. It assumes also that adsorption is characterized by uniform distribution of binding energies up to a maximum value.

7-4. Dubinin-Radushkevich (D-R) Isotherm

The Dubinin-Radushkevich model [35] is used to estimate the characteristic porosity and the apparent free energy of adsorption. It helps to determine the nature of adsorption processes whether physical or chemical. The D-R sorption is more general than the Langmuir isotherm because it does not assume a homogeneous surface or constant sorption potential.

The non-linear presentation of the D-R isotherm equation is as follows:

$$q_e=q_m \exp(-\beta\varepsilon^2) \tag{8}$$

where q_e is the amount of dye molecules (mol/L), q_m is the maximum adsorption capacity (mol/g)), β is the activity coefficient related to adsorption mean free energy mol^2/j^2, and ε is the Polanyi potential given by

$$\varepsilon=RTln\left(1+\frac{1}{C_e}\right) \tag{9}$$

A plot of q_e against ε^2 gave nonlinear graphs (figure not shown). The adsorption mean free energy, E (kj/mol) is given as:

$$E = \frac{1}{(2\beta)^{0.5}} \tag{10}$$

The mean free energy gives information about chemical or physical adsorption. With the value of $8<E<16$ kJ/mol, the sorption process follows chemical ion-exchange, while for the values of $E<8$ kJ/mol, the sorption is of a physical nature.

The parameters obtained of the four models were calculated and represented in Table 3. By comparing the correlation coefficients, it can be concluded that Langmuir isotherm provides a good model for the sorption system, which is based on monolayer sorption onto a surface containing a finite number of identical sorption sites. The maximum adsorption capacity of TB and CV at 20 °C was found to be 142.5 mg/g and 125 mg/g, respectively. The comparison of adsorption capacity of the coffee waste with that of various adsorbents is given in Table 4. The coffee waste, an available and cheap by-product, can be used as a potential material to minimize the concentration of TB and CV from aqueous solution.

The values of the parameter R_L indicate that the adsorption is fa-

Table 4. Comparison of the adsorption capacity of basic dyes with different various adsorbent

Adsorbents	Dyes	Sorption capacity q_m (mg/g)	References
Spend coffee grounds	Methylene blue	18.73 (25 °C)	[16]
Untreated coffee residue	Remazol blue RN	12.92 (25 °C)	[13]
	Basic blue 3G	18.81 (25 °C)	[13]
Coffee husks	Methylene blue	90.1 (30 °C)	[15]
Spend tea leaves	Methylene blue	300.05 (30 °C)	[22]
Rejected tea	Methylene blue	147 (30 °C)	[36]
Tea waste	Methylene blue	85.6 (27 °C)	[37]
Coffee waste	Toluidine blue	142.5 (20 °C)	This work
Coffee waste	Crystal violet	125 (20 °C)	This work
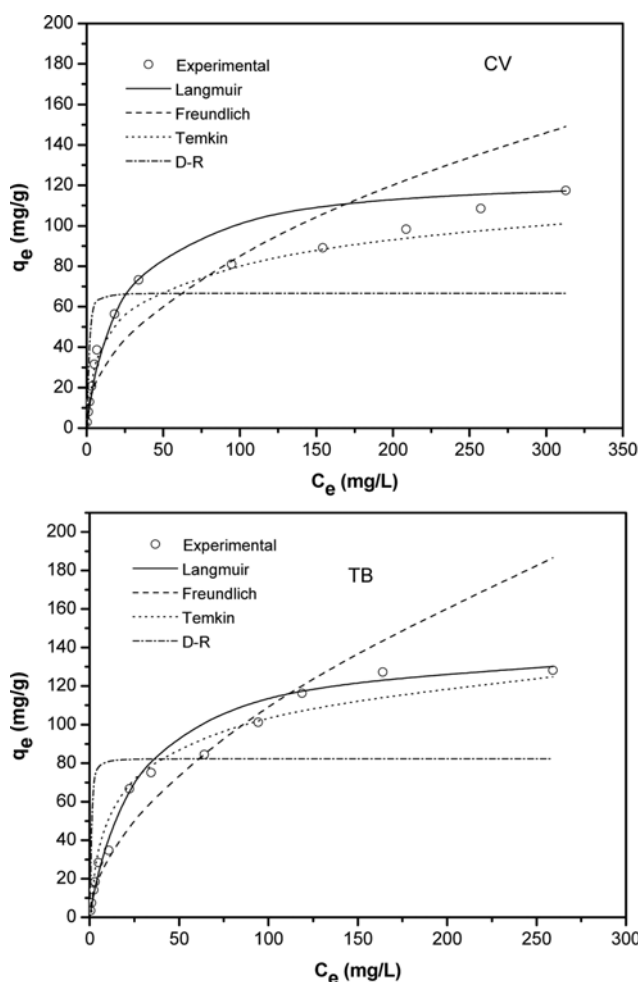
Fig. 7. Isotherm modeling of CV and TB on the adsorption onto CW at 20 °C.

vorable ($0 < R_L < 1$). These were found to be 0.274-0.064 for CV and 0.258-0.060 for TB in the concentration range studied, and the value of the free energy estimated from the D-R model E<8 kJ/mol indicating that adsorption process is of physical nature.

The isotherm profiles of TB and CV are shown in Fig. 7. It is obvious that the experimental results are well represented by the Langmuir isotherm.

8. Adsorption Kinetic Models

To investigate the mechanism of adsorption of the two basic dyes,

Table 5. Pseudo-second order kinetic constants for the adsorption of CV and TB onto CW

Dye	C_o (mg/L)	Pseudo-second-order kinetics				
		$q_{e, exp}$ (mg/g)	$q_{e, cal}$ (mg/g)	k_2 (g mg min^{-1})	R^2	Δq (%)
TB	80	14.090	14.285	0.544	1	1.46
	160	30.04	30.303	0.081	1	0.91
	240	42.272	43.478	0.044	1	0.34
	320	59.763	62.5	0.014	0.999	4.85
	400	73.387	76.923	0.013	1	2.07
CV	80	13.016	13.157	0.028	0.999	1.14
	160	29.619	30.303	0.024	1	2.43
	240	41.944	43.478	0.037	0.999	3.74
	320	53.528	55.555	0.032	1	4.01
	400	70.761	71.428	0.005	1	0.99

TB and CV, on CW, the constants of sorption and intraparticle diffusion were determined in terms of the pseudo-first-order [38] and, pseudo-second-order [39-41]. The linear pseudo-first-order equation is given as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{11}$$

where q_e and q_t are the amount of dye adsorbed (mg/g) at equilibrium and at time t (min), respectively; k_1 is the rate constant of pseudo-first-order equation. Plots of q_t against t, at 20 °C, were plotted (Figure not shown).

The pseudo-second-order kinetic equation can be represented by the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{12}$$

where k_2 is the rate constant of pseudo-second-order equation. Table 5 reports the results of parameters from the plots of pseudo-second-order kinetic model for adsorption of TB and CV on CW. From Table 5, the calculated values of R^2 are equal or near unity for pseudo-second-order kinetic model. These suggested that the pseudo-second-order adsorption mechanism was predominant and that the overall rate of the dye adsorption process appeared to be controlled by chemical process involving valency forces through sharing or exchange of electrons between sorbent and sorbate [42].

The suitability of the kinetic model to describe the adsorption

process was validated by the normalized standard deviation, Δq (%) defined as:

$$\Delta q(\%) = 100 \sqrt{\frac{\sum [(q_{t,exp} - q_{t,cal})/q_{t,exp}]^2}{n-1}} \quad (13)$$

where n is the number of data points, $q_{t,exp}$ and $q_{t,cal}$ are the experimental and calculated adsorption capacities, respectively. The pseudo-second-order kinetic model yielded the best fit, with highest correlation coefficients and lowest normalized standard deviation, Δq values, which ranged between 0.34% and 4.85% for TB and from 0.99% and 4.0% for CV concentration dye ranging from 80 to 400 mg/L.

9. Thermodynamics Parameters

A study of temperature dependence for adsorption process gives information on whether the reaction is spontaneous or not, with aid of thermodynamic parameters such as change in Gibbs free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0), the thermodynamic of adsorption reaction towards spontaneity can be evaluated. These parameters were calculated using the following equations:

$$\Delta G^0 = -RT\ln(K_0) \quad (14)$$

$$\ln K_0 = -\frac{\Delta G^0}{RT} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (15)$$

where R is the universal gas constant (8.314 J K^{-1} mol^{-1}), T is the absolute temperature (K) and K_0 is the distribution coefficient equals to q_e/C_e.

The plot of $\ln K_0$ against 1/T (Fig. 8) yields à straight line, from which ΔH^0 and ΔS^0 were calculated from the slope and intercept, respectively. The thermodynamic parameters obtained at various temperatures investigated for 40 mg/L dyes concentrations are represented in Table 6. The negative values of free energy ΔG^0 at all temperatures indicate the spontaneous nature and the feasibility of the adsorption process. Increase in value of ΔG^0 with increase in temperature suggests that at lower temperature the adsorption is easier. The negative value of standard energy change ΔH^0 implies that the adsorption is exothermic, whereas the negative value of ΔS^0 suggests that the dyes decreased randomness at the solid/solution interface.
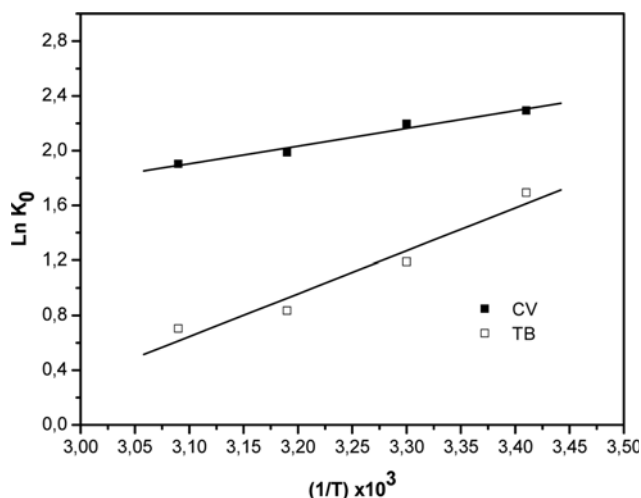

Fig. 8. The plots of $\ln K_0$ against 1/T.

Table 6. Thermodynamic parameters for the adsorption of CV and TB onto CW

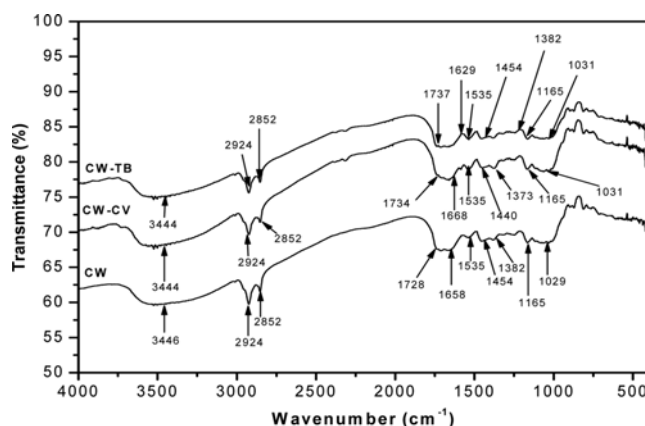| Dye	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol)	ΔG^0 (kJ/mol)			
			293 K	303 K	313 K	323 K
CV	−10.825	−0.017	−5.616	−5.439	−5.261	−5.083
TB	−26.307	−0.076	−3.939	−3.176	−2.413	−1.560

Fig. 9. FTIR spectral characteristics of CW before and after adsorption.

10. FTIR of CW

The spectra of coffee waste before and after the adsorption of dyes are shown in Fig. 9. The functional group and the corresponding infrared absorption frequencies are reported in Table 7. The FTIR spectroscopic analysis showed a broad band at 3,446 cm^{-1} representing bonded -OH groups on the surface of CW. The broad band is attributed to inter-and intra-molecular hydrogen bonding of polymeric compounds (macromolecular associations), such as alcohols, phenols and carboxylic acids, as in pectin, cellulose and lignin [43, 44]. The peaks at 2,924 and 2,852 cm^{-1} are caused by C-H vibration, whereas the adsorption peaks at 1,728 cm^{-1} are assigned to the resulting carboxyl linkage derived from xanthenes derivatives such as caffeine [45]. The absorption bands at 1,658, 1,535 and 1,454

**Table 7. FTIR spectral characteristics of CW before and after adsorption**

| Frequency (cm^{-1})			Assignment
Before adsorption	After adsorption CV	After adsorption TB	
3446	3444	3444	Bonded O-H groups
2924	2924	2924	C-H groups
2852	2852	2852	CH$_2$ groups
1728	1734	1737	C=O stretching
1658	1668	1629	COO groups
1535	1535	1535	N-H group
1454	1440	1456	CO groups
1382	1373	1382	COO$^-$
1165	1165	1165	C-O-C stretching
1029	1031	1031	C-O stretching

cm^{-1} indicate, respectively, the presence of COO of carboxyl, secondary amine group N-H and C-O groups on the adsorbent surface. Bands in the range of 1,382 cm^{-1} are attributed to COO$^-$ symmetric stretching vibration. Another absorption band appearing around 1,165 and 1,029 cm^{-1} could be attributed to the stretching, C-O stretching of ether group and C-O stretching of COOH [46]. The FTIR spectra of dyes (CV and TB)/CW showed that peaks expected at 3,446, 1,728, 1,658, 1,454, 1,382 and 1,029 cm^{-1} had shifted, respectively, to 3,444, 1,734/1,737, 1,668/1,629, 1,440/1,454, 1,373/1,382 and 1,031 cm^{-1} due to CV and TB adsorption. These indicate that corresponding functional groups (-O-H, C=O, COO, C-O, N-H and C-O) are involved in the mechanism of dye adsorption.

11. Biosorption Mechanism

There are many factors that may influence the biosorption behavior, such as dye structure and size, biosorbent surface properties, steric effect and hydrogen bonding, and van der Walls forces. To explain the possible biosorption mechanism, the PZC played an important role. The surface of coffee waste adsorbent may become mainly positively charged.

$$CW \xrightarrow{(pH<5.5)} CW^+$$
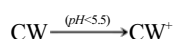
Increasing the pH of the solution (pH>5.5), the surface of CW is charged negatively

$$CW \xrightarrow{(pH>5.5)} CW^-$$
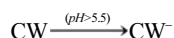
In aqueous solution, the cationic dye is dissociated as

$$D-N^+Cl^- \longrightarrow DN^+ + Cl^-$$

On the basis of the FTIR spectrum and active site analysis, shifts or changes of FTIR peaks indicate interactions of the solute with functional groups on the surface. It was shown that these dyes were adequately adsorbed for optimum pH, which may be due to the formation of surface hydrogen bonds between the hydroxyl and the carboxylate groups on the CW surface and the nitrogen atoms of dye as suggested in Fig. 10. Similar behavior has been reported in the adsorption of 4-chloro-2-methyl phenoxy acetic acid pesticide using coee waste from aqueous solution [14].

The interaction between dye and CW can be due to the interaction bonding between the nitrogen containing amine groups of dye and CW surface and electrostatic interaction between the cationic dye (due to the presence of N$^+$ of dye) and negatively charged CW surface in basic medium.

$$CW-OH \text{ (Phenolicgroups)} \longrightarrow CW-O^-$$
$$CW-O^- + DN^+-Cl \longrightarrow CW-O-DN + Cl^-$$
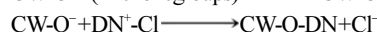
In alkaline conditions, where full deprotonation dominates, the interaction between adsorbent and dye is completely controlled by electrostatic and coulombic strong forces, between the negatively charged functional groups of CW and the constant localized positive charge of the cationic dye.

$$CW-COO^- + DN^+ \longrightarrow CW-COO^-DN^+$$

CONCLUSION

Coffee waste (CW) has been proven to be an effective low-cost adsorbent for the removal of TB and CV from aqueous solutions. The maximum adsorption capacities were 142.5 for TB and 125 mg/g for CV, which was considered high for untreated material. However, the amount of dye adsorbed was varies with initial solution pH, initial dye concentrations, contact time and adsorbent dosage. The equilibrium data were better described by Langmuir model in comparison to Freundlich, Temkin and Dubinin-Radushkevich (D-R) isotherm models. The pseudo-second order kinetic model fits very well with the dynamical adsorption behavior of TB and CV dyes and the adsorption process is exothermic. The remarkable results obtained in this study prompt us to use the coffee waste as an adsorbent for the treatment of textile effluent real. But this requires an adequate effluent pretreatment to prevent clogging of adsorbent.

Fig. 10. Proposed mechanism for the biosorption of CV (a) and TB (b) onto CW.

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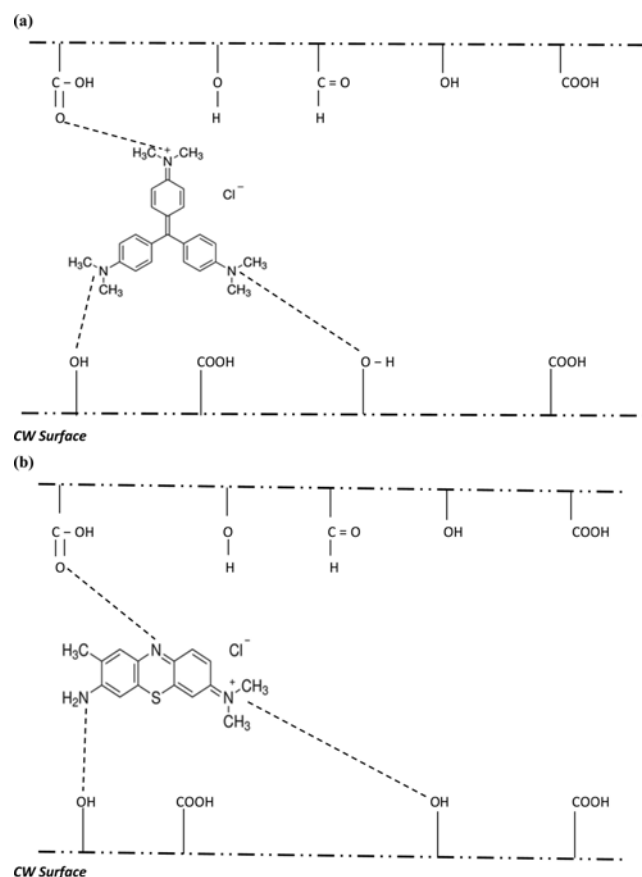
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