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Batch Studies for Methylene Blue Removal and Recovery by Untreated Coffee Residues

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Abstract: This paper reports the practicability of using coffee residues to remove widely used basic dyes like MB (Methylene Blue) from wastewaters. The effect of different batch system parameters, namely stirring speed, pH, initial dye concentration and contact time were studied. Moreover, in continuous fixed-bed column systems, the effects of parameters such as bed-depth, flow rate and initial dye concentration were examined. The experimental batch systems data were simulated using (a) Freundlich, Langmuir and Sips isotherm models and (b) 1st order, 2nd order, and intra-particle kinetic models. The results revealed that the MB is fairly adsorbed on coffee residues. This process could be a low cost technique for the removal of basic dyes from aqueous systems.

Key words: Adsorption, desorption, column, MB (Methylene Blue), coffee residues, wastewaters.

1. Introduction

Many industries, such as paper, plastics, food, printing, leather, cosmetics and textile, use dyes in order to color their products [1]. In textile industries about 10-15% of the dye gets lost in the effluent during the dyeing processes which are harmful products and may cause cancer epidemics [2]. Dyes usually have a synthetic origin and complex aromatic molecular structures which make them more stable and more difficult to biodegrade [3]. The industrial runoffs are usually discarded into rivers and lakes, altering the biological stability of surrounding ecosystems [4]. Therefore, removal of dyestuffs from wastewater has received considerable attention over the past decades [5].

In wastewater treatment, various methods applied to remove dyes include photocatalytic degradation [6], membrane separation, chemical oxidations [7] and electrochemical process. Among the above mentioned techniques of dye removal, the process of adsorption gives the best results as it can be used to remove different types of coloring materials [8].

Adsorption onto activated carbon is the most widespread technology for the removal of pollutants from water and wastewaters. The disadvantage of activated carbon is its high cost [9]. Hence, it is of pivotal importance thence of low-cost substitute absorbents to replace activated carbons. Various types of untreated biomass have been reported to have a use in dye removal: peanut husk, palm kernel fibre [10], *Turbinaria turbinate* alga, graphene, defatted jojoba and sugar beet pulp [11]. The sorption efficiency of several adsorbents is presented in Table 1.

Further, numerous pretreated lignocellulosic materials are used to remove dyes in water and wastewater. Pyrolyzed date pits, date stones and *Turbinaria turbinate* alga have proved to be effective adsorbents.

2. Materials

Coffee residues and others similar byproducts like coffee husks and coffee grounds have been investigated to remove various dyes and heavy metals from aqueous solutions. Coffee husks have been used for the removal of Cu (II), Cr (VI), Cd (II) and Zn (II),

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coffee grounds for Nylosan Red N-2RBL and degreased coffee bean for Malachite Green. It is reported that the removal of Remazol Brilliant Blue RN and Basic Blue 3G is using coffee residues, focusing on batch processes and not on continuous systems [12].

In the current study, the adsorption capacities of coffee residues to remove MB (Methylene Blue) from aqueous solutions were investigated. Both batch and continuous fixed-bed-column systems were investigated. As regards the fixed-bed-column systems filed with coffee residues, various bed-depths, flow rates and initial dye concentrations were examined for the first time.

3. Methods

Coffee residues, a low-cost material acquired from different cafeterias in the city of Piraeus (Greece) were used as adsorbent. This adsorbent was washed with distilled water and dried at 110 °C for 24 hrs to remove the humidity.

The dye used herein in batch and column experiments was MB ($C_{16}H_{18}ClN_3S{\cdot}3H_2O$, molecular weight = 373.90×10^{-3} $kg{\cdot}mol^{-1}$) supplied by Sigma-Aldrich. A stock solution was prepared by dissolving a specific amount of MB (humidity 22%) in distilled water. Working solutions were 3-140 $mg{\cdot}L^{-1}$. MB concentrations were determined by measuring the absorbent values in each experiment with HACH DR4000U UV-VIS spectrophotometer at $\lambda = 664$ nm.

Isotherms were obtained from batch experiments. Accurately weighted quantities of approximately 0.5 g coffee residues were transferred to 0.8 L bottles, where 0.5 L adsorbate solution were added. The temperature was 23 °C, the MB initial concentration ranged from C_0 = 1.5 $mg{\cdot}L^{-1}$ to 150 $mg{\cdot}L^{-1}$. The bottles are sealed and mechanically agitated for a period of 7 days. The 7-day period was determined after optimization analysis, with agitation periods varying from 4 hrs to 14 days, to ensure that nearly equilibrium conditions were achieved. The final concentrations were determined. Concentrations (before and after equilibrium) from each bottle represented one point on the adsorption isotherm plots. The pH was near 7.5.

Batch experiments were carried out at stirring speeds from 65 to 664 rpm, pH varied from 1.54 to 12.9, the adsorption temperature varied from 23 to 70 °C, initial dye concentration from 3 to 140 $mg{\cdot}L^{-1}$ for a maximum contact time up to 95 min. Samples were taken at 5 minutes intervals and the MB concentration was measured. The reactor, containing V = 1 L aqueous solution of dye was placed in a water bath to maintain constant temperature at the desired level.

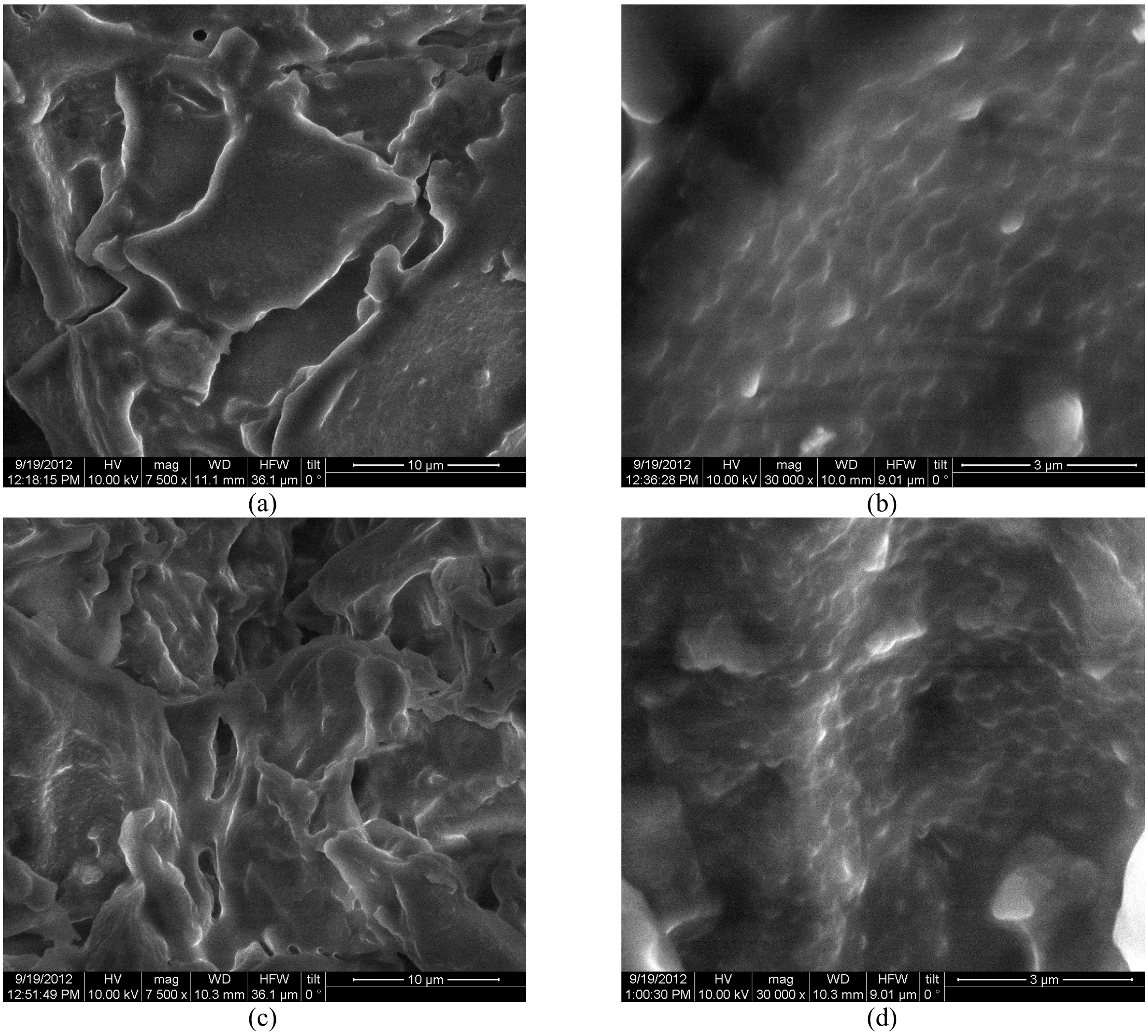
The study of the coffee residues by SEM (Scanning Electron Microscopy) was conducted at the Institute of Materials Science, National Centre for Scientific Research ‘Demokritos’, using an FEI Inspect SEM.

The concentration of output solution was measurement at λ = 664 nm and using HACH DR4000U UV-vis spectrophotometer. Finally, pH measurements were made using a digital pH meter, Multi Lab model 540.

4. Results

The SEM micrographs for coffee residues before and after MB adsorption are presented in Fig. 1. The coffee residues particle in Fig. 1(a) with magnification 7,500X shows some pores. The surface texture of this particle is relatively rough as it can be observed in Fig 1(b) with magnification 30,000X. The adsorption conditions were C_0 = 140 $mg{\cdot}L^{-1}$, t = 95 min, m/V = 1 $g{\cdot}L^{-1}$, agitation speed = 664 rpm. The texture of the coffee residues particles after MB adsorption in Fig. 1(d) is rougher comparing to the same material before MB adsorption, presented in Fig. 1(b). This fact indicates the swelling effect on the lignocellulosic particles after MB adsorption.

Three isotherm models including Freundlich (1906), Langmuir (1916) and Sips (1948) [13] equations were



(a) (b) (c) (d)

Fig. 1 SEM analysis for coffee residues.

used to fit the experimental data. Freundlich isotherm model assumes that the surface of absorbent is where heterogeneous and polymolecular layer adsorption takes place. This model can be described byEq. (1):

$$q = K_F \cdot (C_e)^{\frac{1}{n}} \tag{1}$$

where q is the amount adsorbed per unit mass of the adsorbent (mg·g^{-1}), C_e is the equilibrium concentration of MB adsorbed (mg·L^{-1}), K_F [(mg·g^{-1})(L·mg^{-1})$^{1/n}$] is the Freundlich isotherm constant related to adsorption capacity and n is the Freundlich isotherm constants related to adsorption intensity. In cases where the isotherm experimental data approximates the Freundlich equation, the parameters K_F and n can be estimated either by plotting log$q$ versus logC_e either by NLRA (Non-Linear Regression Analysis). The linear form of the Freundlich isotherm model can be defined by Eq. (2):

$$\log q = \log K_F + \frac{1}{n} \log C_e \tag{2}$$

The Langmuir (1916) isotherm model is given as:

$$q = \frac{K_L q_m C_e}{1 + K_L C_e} \tag{3}$$

Moreover, this equation in linearized form is:

$$\frac{1}{q} = \left(\frac{1}{q_m}\right) + \left(\frac{1}{K_L \cdot q_m}\right) \cdot \left(\frac{1}{C_e}\right) \tag{4}$$

where K_L is the Langmuir constant related to the energy of adsorption (L·mg^{-1}) and q_m is the amount of MB adsorbed (mg·g^{-1}) when saturation is attained. In cases where the isotherm experimental data approximates the Langmuir equation, the parameters K_L and q_m can be estimated either by plotting $1/q$ versus $1/C_e$ either by NLRA.

Numerous studies incorporate another important parameter, R$_L$, namely the separation factor. The value of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$) and is expressed by Eq. (5):

$$R_L = \frac{1}{1 + K_L \cdot C_0} \tag{5}$$

where C_0 is the initial dye concentration (mg·L^{-1}) and K_L is the Langmuir constant (L·mg^{-1}).

Sips (1948) [13] isotherm model is a combination of the Langmuir and Freundlich isotherm type models and is expected to describe heterogeneous surface better. The Sips equation is presented by Eq. (6):

$$q = \frac{q_m \cdot (K_L \cdot C_e)^{1/n}}{1 + (K_L \cdot C_e)^{1/n}} \tag{6}$$

where K_L (L·mg^{-1}), q_m (mg·g^{-1})is the Langmuir constants and n the Freundlich constant. These parameters can be estimated by NLRA.

MB adsorption isotherms experimental data for untreated coffee residues are presented in Fig. 2. The theoretical curves are estimated for the above mentioned three models. The parameter values of these models are shown in Table 1. These parameters were obtained by NLRA. The SEE (Standard Error of Estimate) was calculated in each case as Eq. (7):

$$SEE = \sqrt{\sum_{i=1}^{n'} (y_i - y_{i,theor})^2 / (n' - p')} \tag{7}$$

where y_i is the experimental value of the depended variable, $y_{i,theor}$ is the theoretical or estimated value of the depended variable, n' is the number of the experimental measurements and p' is the number of parameters (the difference $n - p'$ being the number of the degrees of freedom.

The fitting of the Sips adsorption model to the present data was the most satisfactory for MB adsorption, better than the other two isotherm models, as shown by the corresponding SEE-values given in Table 1. The fitting of the Langmuir's adsorption model to the present data was also satisfactory but to a lesser degree than the Sips model. The R_L values were found to be 0.236-0.935, i.e. $0 < R_L < 1$ for all MB concentrations C_0 in the range of 3-140 mg·L^{-1}.

In order to make adsorption mechanism more clear, the adsorption data were fitted using the pseudo-first order, the pseudo-second order and the intra-particle diffusion kinetic model.

The Lagergren (1898) [12] non-linear pseudo-first order equation is given as Eq. (8):

$$q - q_t = q \cdot e^{-k \cdot t} \tag{8}$$

where q and q_t (mg·g^{-1}) are the amounts of MB dye adsorbed per unit mass of the adsorbent at equilibrium time ($t \rightarrow \infty$) and adsorption time t (min), respectively, while k (min^{-1}) is the pseudo-first order rate constant for the adsorption process. Moreover:

$$q = (C_0 - C_e)V/m \text{ and } q_t = (C_0 - C)V/m \tag{9}$$

where C, C$_0$ and C$_e$ (mg·L^{-1}) are the concentrations of MB in the bulk solution at time t, 0 and ∞, respectively, while m (g) is the weight of the adsorbent used, and V (mL) is the solution volume. Further modification of Eq. (9) in logarithmic form gives:

Table 1 Isotherms' parameters of Methylene Blue dsorption on coffee residues.

	K_F[(mg·g^{-1})(L·mg^{-1})$^{1/n}$]	n	K_L (L·mg^{-1})	q_m (mg·g^{-1})	SEE
Freundlich	3.555	1.612			2.397
Langmuir			0.0230	78.90	2.197
Sips		1.195	0.0111	109.27	2.168

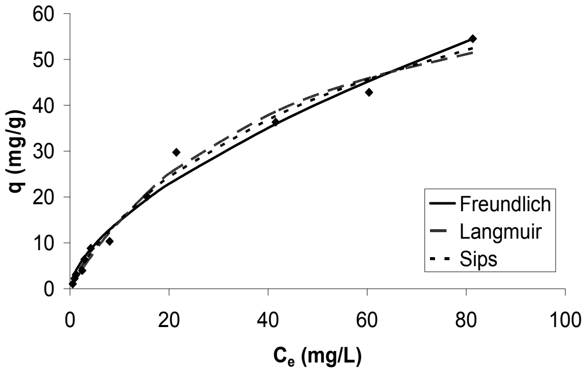


Fig. 2 Isotherm's parameters of adsorption of coffee residues.

$$ln(q-q_t)=lnq-k\cdot t \tag{10}$$

The pseudo-second order equilibrium adsorption model equation is given as Eq. (11):

$$q_t = q-\left[q^{-1}+k_2 t\right]^{-1} \quad \text{or} \quad q_t = q-\frac{1}{\frac{1}{q}+k_2 t} \tag{11}$$

where k_2 (min^{-1}) is the rate constant of second order adsorption.

The intra-particle diffusion model based on the theory proposed by Weber and Morris (1963) [9] is expressed as Eq. (12):

$$q_t = c+k_p\cdot\sqrt{t} \tag{12}$$

where k_p [mg (g·min$^{0.5}$)$^{-1}$] is the intra-particle diffusion rate constant and c (mg·g^{-1})is a constant related to the thickness of boundary. A value of c close to zero indicates that diffusion is the only controlling step of the adsorption process.

The stirring speed was studied between 65 and 664 rpm at constant dye concentration 14 mg·L^{-1}, pH equals 7 and stirring time of 95 min. The correlation between the first-order rate constant k for the MB absorption by coffee residues is shown in Fig. 3. The rate constant is generally increasing with stirring speed up to 200 rpm were a level-off is reached.

According to the literature, the pH of the aqueous solution is one of the most important parameters of the adsorption process. The effect of the initial pH on the MB adsorption onto coffee residues is illustrated in Fig. 4. The range of pH studied was from 2 to 12. As can be seen the rate constant increases linearly by pH increasing.

The effect of initial MB concentration on adsorption on coffee residues is shown in Fig. 5. The kinetic parameters of the above mentioned three kinetic models were estimated using NLRA and are presented in Table 2. As can be seen, the SEE values are lower for the intra-particle diffusion kinetic model indicating better fitting to the experimental data. In addition the pseudo-second order kinetic model had better fitting that the pseudo-first one.

The temperature variation from 20 °C to 70 °C on MB uptake by coffee residues revealed that increase in temperature of the process enhanced better adsorption of MB from bulk solution. The conditions under which they became the experiments with different temperature were pH = 8, the initial concentration was 14 mg·L^{-1},

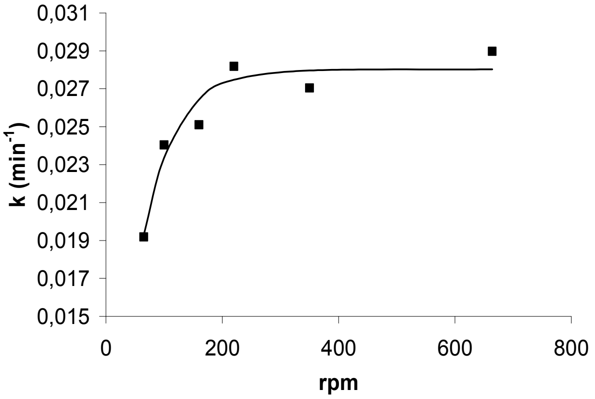


Fig. 3 Effect of stirring speed.

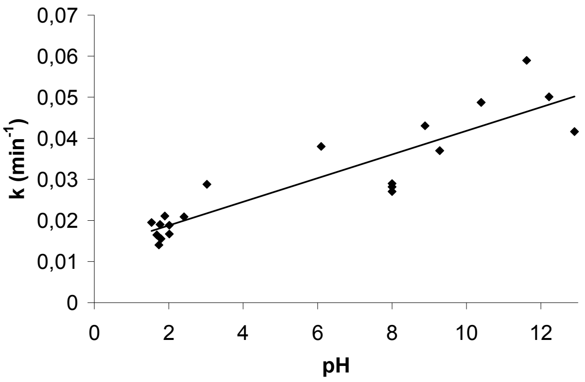


Fig. 4 Effect of pH.

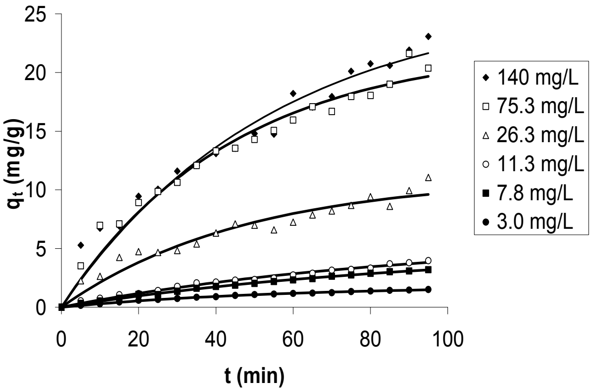


Fig. 5 Effect of initial MB concentration.

the stirring speed was 600 rpm and the dose of coffee residues was 1 g. Increase in temperature increased entropy of the system which yielded more chances of adsorption. The change in adsorption rate constant k as a function of adsorption temperatures is presented in Fig. 6.

The rate constant k of the Lagergren model follows the Arrhenius law:

$$k = p \cdot exp(-E / RT) \tag{13}$$

The activation energy E (kJ·mol^{-1}) for the adsorption of MB on untreated coffee residues can be estimated by linear regression of *lnk* on *1/T*. This activation energy was found to be 27.4 kJ·mol^{-1} or 6.57 kcal·mol^{-1}. The frequency factor of Eq. (13) was p = 1,236 min^{-1}. Consequently, the intra-particle diffusion, which is a physical process, is probably the controlling step of the adsorption process. The parameters of fixed—bed column systems for coffee residues are shown in Table 3.

This study is a research on the adsorption capacity of the coffee residue and its application to industrial scale. There is object for further research to determine the coffee residues quantity by region distribution and corresponding exploitation by industrial scale unit.

The MB adsorption capacity for various lignocellulosic materials found in the literature was compared to the coffee residues adsorption capacity estimated in the present work (Table 4). The adsorption capacity of the coffee residue was better than the adsorption capacity of other waste biomass such as peanut husk, *turbinaria turbinate alga*, and wheat straw. The adsorption capacities of various coffee residues/byproducts found in the literature are shown in Table 5. The coffee residues adsorption capacity found in the present work was close to the average of the Freundlich and Langmuir capacities, i.e., K_F and q_m respectively, reported in the literature.

The present study is a part of continues involvement of our Research Group in the study of wastewater treatment using original and modified (pretreated) lignocellulosic biomass as potential adsorbents. Previous study of our Group gave Langmuir capacity q_m = 38.7 mg·g^{-1} for pine sawdust, significantly lower comparing to q_m = 78.9 mg·g^{-1} for the coffee residues studied in the present work.

Table 2 Kinetic parameters of Methylene Blue adsorption on coffee residues.

C_0 (mg·L^{-1})	140	75.3	26.3	11.3	7.8	3.0
First order						
k	0.0183	0.0227	0.0211	0.0113	0.0107	0.0176
q_e	28.78	22.26	11.11	5.79	4.98	1.82
SEE	1.2827	0.9917	0.7150	0.1271	0.0515	0.0243
Second order						
K_2	0.000376	0.000604	0.001139	0.000796	0.000823	0.004587
q_e	37.81	30.99	15.42	9.27	8.18	2.74
SEE	1.1818	0.8594	0.6563	0.1198	0.0488	0.0209
Intra-particle diffusion						
c	-1.05	-0.70	-0.29	-0.49	-0.49	-0.16
k_p	2.3371	2.1586	1.0365	0.4275	0.3647	0.1706
SEE	0.9196	0.6165	0.5137	0.1945	0.1613	0.0535

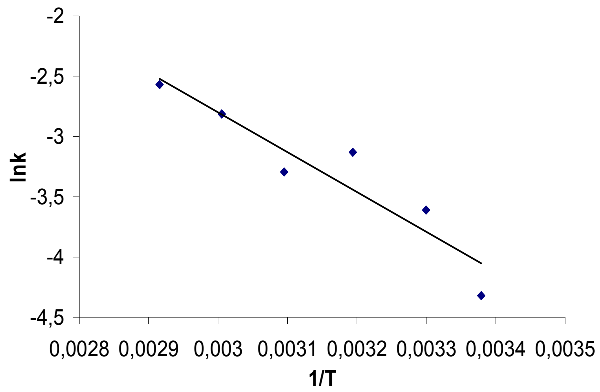


Fig. 6 Effect of temperature.

Table 3 Column models parameters of Methylene Blue adsorption on coffee residues.

	C_i (mg/L)	Q (mL/min)	*n*	N (mg/L)	K	Q_0 (mg/g)	SEE
x = 15cm							
Bohart-Adams	165	20	2.000	42,798	0.000080	96.90	2.3110
Clark	165	20	1.612	40,522	0.000060	91.76	2.3053
Bohart-Adams	130	40	2.000	29,317	0.001400	66.39	0.4876
Clark	130	40	1.612	26,317	0.000100	59059	0.6402
Bohart-Adams	150	70	2.000	31,482	0.000250	71.29	5.8235
Clark	150	70	1.612	28,382	0.000220	64.27	5.1515
Bohart-Adams	145	80	2.000	24,745	0.000210	56.03	7.5229
Clark	145	80	1.612	20,673	0.000180	46.80	6.3513
Bohart-Adams	800	20	2.000	46,166	0.000020	104.54	38.2861
Clark	800	20	1.612	33,869	0.000010	76.69	32.5900
Bohart-Adams	1,600	10	2.000	30,224	0.000010	68.44	102.8607
Clark	1,600	10	1.612	22,024	0.000010	49.87	93.8242
Bohart-Adams	1,600	20	2.000	36,641	0.000020	82.97	103.0998
Clark	1,600	20	1.612	25,017	0.000020	56.64	903.4492
x = 25 cm							
Bohart-Adams	150	70	2.000	38,290	0.000160	86.65	4.0545
Clark	150	70	1.612	35,501	0.000130	80.34	3.7795
Bohart-Adams	800	20	2.000	21,788	2.25E-05	49.30	62.5900
Clark	800	20	1.612	16,007	1.98E-05	36.20	56.0000
Bohart-Adams	550	40	2.000	32,847	8.61E-05	74.30	17.6150
Clark	550	40	1.612	30,028	7.51E-05	68.00	14.6410

Table 4 Methylene Blue adsorption capacity for various lignocellulosic materials.

Adsorbents	Pretreatment	$K_F[(\mathrm{mg{\cdot}g^{-1}})(\mathrm{L{\cdot}mg^{-1}})^{1/n}]$	*n*	$q_m(\mathrm{mg{\cdot}g^{-1}})$	$K_L(\mathrm{L{\cdot}mg^{-1}})$
Activated carbon fibers	Chenmical vapor deposition modified	120.000	1.460	478.00	0.3750
Cocoa	carbonized, burn	40.850	8.090	212.77	0.2690
(The *obroma cacoa*) shell	activated				
Coffee residues	-	3.555	1.612	78.90	0.0230
Commercial activated carbon		-	-	370.40	1.0500
Cotton stalk	-	50.440	6.150	147.06	0.0249
Cotton stalk	sulfuric acid treated	202.210	1.810	555.56	0.6207

Table 4 continued

Adsorbents	Pretreatment	K_F[(mg·g^{-1})(L·mg^{-1})$^{1/n}$]	n	q_m(mg·g^{-1})	K_L(L·mg^{-1})
Cotton stalk	phosphoric acid treated	157.910	16.150	222.22	14.516
Date pits activated carbon	Pyrolyzed, $FeCl_3$ activated	74.871	4.670	249.46	0.0830
Date stones activated carbon	Pyrolyzed, $ZnCl_2$ activated	71.190	3.440	369.38	0.0429
Enteromorph a prolifera activated carbon	$ZnCl_2$ activated	236.230	3.720	270.27	1.2300
Graphene	-	90.920	5.710	153.85	1.4400
Jojoba (defatted)	-	1.132	1.054	167.00	0.0009
Palm kernel fiber	-	8.670	1.770	95.40	0.0317
Peanut husk	-	16.650	3.270	72.13	0.0850
Pine sawdust	Autohydrolyzed	15.680	2.582	88.02	0.1072
Pistachio hull	-	112.300	4.200	389.00	0.0960
Posidonia oceanic (*L.*) dead leaves activated carbon	Carbonized, $ZnCl_2$ activated	112.120	2.740	217.390	1.7000
Sugar beet pulp	-	12.520	1.990	244.600	0.0149
Sugar beet pulp	-	2.777	10.128	714.290	0.0039
Tea (rejected)	NaOH modified	40.870	2.110	242.110	0.1300
Turbinaria turbinaria alga	-	14.000	2.310	63.000	0.1830
Turbinaria turbinaria alga	pyrolyzed	40.000	3.030	163.000	0.1040
Turbinaria turbinaria alga	pyrolyzed, physically activated	105.000	3.630	411.000	0.0830
Turbinaria turbinaria alga	pyrolyzed, chemically activated	137.000	5.670	345.000	0.136
Wheat straw	Acid hydrolyzed	10.950	1.010	20.410	0.663

Table 5 Adsorption capacity of various coffee residues/byproducts.

Adsorbents	Adsorbates	K_F[(mg·g^{-1})(L·mg^{-1})$^{1/n}$]	n	q_m(mg·g^{-1})	K_L(L·mg^{-1})
Coffee grounds chemically activated carbon	Nylosan Red N-2RBL	-	-	367	0.077
Coffee grounds chemically activated carbon	Methylene blue	-	-	181.8	0.109
Coffee husk-based activated carbon	Remazol brilliant Orange 3R dye	3.747	3.608	66.76	0.401
Coffee husks	Methylene blue	2.567	1.29	90.09	0.0226
Coffee grounds	Methylene blue	51.926	3.30	18.73	0.2687
Coffee bean (degreased)	Methylene green	2.03	0.511	55.3	0.0935
Coffee residues	Remazol brilliant Blue RN	11.84	2.53	175	0.009
Coffee residues	Basic Blue 3G	36.61	3.12	240	00.041
Coffee husks	Cu(II)	3.702	5.01	7.496	0.4232
Coffee husks	Cd(II)	3.188	5.05	6.854	0.3124
Coffee husks	Zn(II)	2.721	6.07	5.565	0.2238
Coffee husks	Cr(II)	2.353	3.65	6.961	0.1805
Coffee residues	Methylene blue	3.555	1.612	78.90	0.0230

5. Conclusions

The use of coffee residues is an innovative technique using waste biomass from urban and rural areas in and Industrial Ecology framework. Also, that is an index of the sensitivity of citizens for the rational management of waste and their contribution to sustainable development. The present work proves the viability of using coffee residues to remove basic dyes like MB from wastewaters. The effect of different system parameters on (a) batch and (b) continuous fixed-bed column systems were studied. The experimental systems data were simulated using the most commonly used isotherm and kinetic models. The continuous fixed-bed column results proved that the MB is practically adsorbed on coffee residues giving maximum Bohart and Adams capacity N = 46,166 $mg \cdot L^{-1}$ or q_0 = 104.5 $mg \cdot g^{-1}$ for bed-depth 15 cm, initial dye concentration 800 $mg \cdot L^{-1}$ and flow rate 20 $mL \cdot min^{-1}$. These results provide evidence for suggesting this low cost residue for the removal of basic dyes in industrial scale applications.

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