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Isotherm, kinetic and thermodynamic studies of dye removal from wastewater solution using leach waste materials

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Abstract. In this study, Malachite Green (MG) dye removal from synthetic wastewaters by adsorption process using raw boron enrichment waste (BEW) and it's modifications (with acid and ultrasound) were aimed. 81% MG removal was obtained by BEW at optimum equilibrium conditions (time: 40 min., dosage: 500 mg/dm^3, pH: 5-6, speed: 200 rpm, 298 K). MG removal from wastewaters using acid modified boron enrichment waste (HBEW) was determined as 82% at optimum conditions (time: 20 min., dosage: 200 mg/ dm^3, pH: 10, speed: 200 rpm, 298 K). For ultrasound modified BEW (UBEW), the highest MG removal percent was achieved as 84% at optimum conditions (time: 30 min, dosage: 375 mg/ dm^3, pH: 8, speed: 200 rpm, 298 K).
The equilibrium data of Malachite Green was evaluated for BEW, HBEW and UBEW adsorbents by using sorption isotherms such as Langmuir, Freundlich and Temkin models, out of which Langmuir model (R^2 = 0.971, 0.987 and 0.984) gave better correlation and maximum adsorption capacity was found to be 147.05, 434.78 and 192.30 mg/g, respectively. The adsorption kinetics followed the pseudo-second-order kinetic equation for sorption of MG onto wastes. A look at thermodynamic data reveals that natural sorption is spontaneous and endothermic because of free negative energy exchange and positive change in enthalpy, respectively. The results indicated that boron enrichment waste, and HCl and ultrasound-modified boron enrichment waste served as good alternative adsorbents in dye removal from wastewater.

Keywords: adsorption; malachite green; boron enrichment waste; dye removal; ultrasound

1. Introduction

A lot of industries are working with synthetic dyes and derivatives due to the coloring processes of their products (e.g., leather, textile, paper, foods, plastic, cosmetics, etc.) (Rizzi *et al.* 2017). On an annual basis, over 7×10^5 t of dye waste product isproduced (Gupta *et al.* 2012). If toxic dyes which are very common are discharged to the environment, the life of some organisms is affected with the incidence for aquatic life systems because they are generally very recalcitrant to microbial degradation and can block the penetration of sunlight and oxygen (Buthelezi *et al.* 2012, Rizzi *et al.* 2017).

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There are many physio-chemical methods for treatment of industrial wastewater containing dyes and other pollutants such as coagulation-flocculation (Gadekar and Ahammed 2016), Fenton process (Özdemir *et al.* 2011, Sharma *et al.* 2016), ion exchange (Ali Khan *et al.* 2017), adsorption (Alizadeh and Zeidi 2017, Evliyaogullari *et al.* 2017), membrane separation (Ahmad *et al.* 2002, Jirankova *et al.* 2010), photodegradation (Gupta *et al.* 2011), electrocoagulation (Oden and Sari-Erkan 2018), electrodialysis (Lafi *et al.* 2019) and electrochemical oxidation (Indu *et al.* 2014) etc. Among these methods, adsorption is the most widely used In terms of efficiency, because of its affordability, technical feasibility and social acceptability (Oei *et al.* 2009, Gupta *et al.* 2012). Adsorption techniques are widely preferred because of the high yield and color removal percentage in the treatment of dyed and colored wastewater. Adsorption process has economical and easliy impact when applied in wastewater treatment technology (El-Zahhar and Awwad 2016).

Malahit green is permanent in the environment, and causes an acute toxic effect on a wide variety of land and aquatic organisms. Acute and chronic exposure to the dye is extremely fatal for freshwater fish. It may also cause serious public health hazards and environmental problems. Both clinical and experimental observations suggest that malachite green has been a toxin for many organs (Sartape *et al.* 2017). A significant number of experts has recently been focused on the adsorption technique for the removal of dyes from wastewater onto the diversified industrial waste adsorbent. Various adsorbents have been used for removal different dyes, such as olive pomace (Rizzi *et al.* 2017), ginger waste (Ahmad and Kumar 2010), neem sawdust (Khattri and Singh 2009), organically modified hydroxyapatite (El-Zahhar and Awwad 2016), Limonia acidissima (wood apple) shell (Sartape *et al.* 2017), industrial waste shells of egg (Abdel-Khalek *et al.* 2017), the almond gum (Bouaziz et al. 2017), chemically cross-linked chitosan beads (Chiou *et al.* 2004) , silver nanoparticles (Muthu *et al.* 2016), copper nanowires loaded on activated carbon (Ghaedi et al. 2015).

This study investigated the waste leaching material (BEW) emerging in the enrichment of the boron mine which is very much in our country, the modification of this leaching waste with acid (HBEW) and the use of this leaching waste as an adsorbent through the sound (UBEW). With the waste materials and modifications obtained, Malahit Green (MG) removal from synthetic wastewater was investigated. While determining the equilibrium and optimum conditions for the treatment, conditions such as contact time, adsorbent dose, pH of the solution and mixing speed were taken into consideration. The major innovation of this study is the high color removal efficiency from wastewater with modified and raw boron enrichment waste.

2. Materials and methods

2.1 Preparation and characterization of the adsorbent and reagents

The enrichment leach wastes used in the study (BEW) were obtained from the Eti Mine Works General Directorate, Etibar Bigadiç production of colemanite and Ulexit plant in Balikesir, Turkey. The material was made ready for use after pre-treatment. Boron enrichment plant waste was modified with HCl (HBEW) and ultrasound (UBEW) belonging to increase the surface area of waste.

The main purpose of these modifications is to assist in color removal by increasing the surface activation of the material. The sono-modified process was performed by indirect sonication in an ultrasonic water bath, which was operated at a fixed 35-kHz frequency approximately 60 minutes. Grain size analysis was performed on three waste materials and particle sizes were selected <250

µm.

All chemicals used were of analytical reagent grade and all solutions were prepared with the help of deionized water. pH meter (Hach Multi-HQ40d Instruments) equipped with electrode calibrated by buffer solutions of pH 4.0, 7.0 and 9.2 was used in this study for pH adjustment. A thermal shaking incubator was used for the batch adsorption experiments (ZHWY-200B, Zhicheng Analytical Co., Ltd). The colored solutions were filtered through 0.45-µm membrane filters (Millipore Corp., Bedford, Mass.) after settling. The exact concentration of MG in dye solution was determined using a UV–Vis spectrometer (Hach Lange DR 2800) at a wavelength of maximum absorbance.

2.2 Batch sorption experiments

Adsorption experiments were carried out in batch mode at various temperatures (298-318 K) and shaking speeds (100-400 rpm), using 250 cm^3 shaking flasks containing 200 cm^3 dye at initial concentration (50 mg/dm^3), adsorbent dosages (125-1500 mg/dm^3) and different initial pH values (2-12). After shaking for a selected time, the solutions were filtered through 0.45-µm membrane filters to separate dye solutions from the adsorbent. Absorbance values were measured using a UV–vis spectrophotometer. The solution was scanned from 190 to 900 nm for λmax measurement (618 nm) of dye after adjusting the pH.

The dye concentrations in the solutions were determined at the beginning (C_0) and end (C_e) of the shaking period. The removal percentage (R (%)) of MG as well as the adsorbed quantity on waste materials (q_e (mg/g)) was determined using Eqs. (1), (2) and (3) respectively (Kushwaha *et al.* 2014).

$$\text{R,} \qquad \text{sorption (\%)} = \left[\frac{(Co - Ce)}{Co}\right] x\ 100 \tag{1}$$

The equilibrium amount of dye adsorbed from aqueous solution was determined by the following equation

$$qe = \left[\frac{(Co - Ce)}{W} \text{ x V}\right] \tag{2}$$

$$k_d = \left[\frac{(Co - Ce)}{Ce} \text{ x } \frac{V}{W}\right] \tag{3}$$

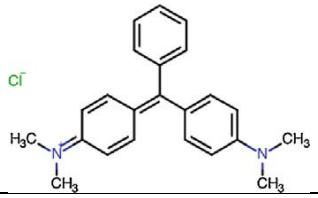
where qe is the amount of dye adsorbed at time t (mg/g adsorbent); W is the adsorbent mass (g); C^0 and C_e are the initial and equilibrium solution concentrations of dye in aqueous solution (mg/dm^3), respectively, and V is the volume of the solution (dm^3)(Chiou *et al.* 2004), the distribution coefficient (K_d)(cm^3/g) (El-Zahhar and Awwad 2016).

Adsorbate. Malachite Green (characteristics given in Table 1) is a basic cationic dye. Different concentrations (0-300 mg/dm^3) of MG were prepared from a stock of 1000 mg/dm^3 solution in distilled water, and the solution pH was adjusted to be neutral using NaOH and H_2SO_4 solutions.

2.3 Surface characterization of adsorbents

Scanning electron microscopy (SEM) helps to analyze the material by scanning the surface with high-energy electrons focusing on a very small piece of the area to create high-resolution images. The three adsorbents were dried in oven at 103 ^{0}C and then stored in a desiccator until to

Table 1 Chemical properties and characteristics of malachite green (Bouaziz *et al.* 2017)

Generic Name	Malachite Green
Chemical Formula	$C_{23}H_{25}N_2Cl$
Molecular weight (g/mol)	364.911
Type of dye	Cationic
λ_{max} (nm)	618
Chemical structure	

use. SEM analysis was performed to investigate the surface morphology of the prepared adsorbents with a Zeiss Evo LS10 instrument. SEM imaging of the adsorbent's surface was carried out with 20.00 kV and at 5 000 (1μm) times of magnification.

2.4 Adsorption Isotherms

The three most frequently used isotherm equations: Langmuir, Freundlich and Temkin equations were tested for the equilibrium data obtained from dye concentration study. The Langmuir adsorption isotherm linear form is represented by Eq. (4)

$$\frac{Ce}{qe} = \frac{1}{(Qmax.b)} + \frac{Ce}{Qmax} \tag{4}$$

where, qe is adsorption capacity and Q_{max} (mg/g) maximum adsorption capacity that describes the formation of a monolayer, whereas b (mg/g) represents binding energy, C_e (mg/dm^3) represents the concentration of MG in solution at equilibrium (Bhatti *et al.* 2017). The linear form of the Freundlich isotherm model is given by Eq. (5)

$$\log q_e = \log K_f + \frac{1}{n.\log Ce} \tag{5}$$

where, n and K_f (mg/g) are the Freundlich constants, adsorption intensity and capacity, respectively. C_e represents the concentration dye in solution (mg/dm^3), q_e is the amount adsorbed per unit mass of the adsorbent (adsorption capacity (mg/g)).

The representation of Temkin isotherm (Tempkin and Pyzhev 1940) is as follows in Eq. (6)

$$q_e = B_T . \ln A_T + B_T . \ln Ce \tag{6}$$

where, B_T =RT/b_T (J/mol) is the Tempkin constant, related to the heat of sorption, A_T (dm^3/g) is the equilibrium binding constant equivalent to the maximum binding energy. R (8.314 J/mol*K) is the universal gas constant, b_T is a variation of sorption energy (J/mol) and T is the absolute solution temperature (Elsharkawy 2017).

2.5 Thermodynamics of adsorption

The thermodynamic parameters include Gibbs free energy change (ΔG^o, kJ/mol), enthalpy change (ΔH^o, kj/mol), and entropy change (ΔS^o, j/(mol*K)) and were calculated using Eqs. (7) and

(8).

$$Ln\ K_D = \ \Delta S/R - \ \Delta H/(R * T) \quad (7)$$

$$\Delta G = \ \Delta H - \ (\Delta S * T) \quad (8)$$

where $K_d = {}^{q_e}/_{C_e}$ the thermodynamic equilibrium constant (cm^3/g) from Eq. (3), R is the universal constant of gas (8.314 J/mol*K), and C_e is the MG concentration at equilibrium (mg/dm^3) (El-Zahhar and Awwad 2016). The values of ΔH^o and ΔS^o were calculated from the slope of the linear plot of ln K_d vs. 1/T (Fig. 4) and the free energy change ΔG^o was calculated from Eq. (8) at 298 K and given in Table 4.

2.6 Kinetics study of adsorption

The kinetics of MG adsorption onto waste materials were analyzed using pseudo-first-order (Dubinin 1965), pseudo-second-order(Radushkevich 1949), and intraparticle diffusion (Weber and Morris 1963) kinetic models. The conformity between experimental data and the model predicted values were expressed by the correlation coefficients (R^2, values close or equal to 1) (Ghaedi *et al.* 2015).

Pseudo-first-order-model. The linear form of the pseudo-first-order (Dubinin 1965) rate equation is given by (9)

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (9)$$

where q_t and q_e (mg/g) are the amounts of the dye adsorbed at time t (min) and equilibrium (mg/g), respectively and k_1 is the rate constant of the equation (1/min).

Pseudo-second-order model. The sorption behavior over the whole adsorption time was predicted by the pseudo second-order model and was estimated using Eq. (10) (Radushkevich 1949, Ghaedi *et al.* 2015).

$$\frac{t}{q_t} = \left(\frac{1}{k_2 . q_e{}^2}\right) + \left(\frac{1}{q_e}\right)t \quad (10)$$

where k_2 (g/mg min) is the rate constant of the second-order equation, q_t (mg/g) is the amount of dye adsorbed at equilibrium (mg/g). Sorption rate constants (k_2) is obtained experimentally by plot of t/qt versus t. The rate constants and R^2 values were calculated.

Intraparticle diffusion model. The intraparticle diffusion model is represented by Eq. (11)

$$q_t = k_{int} . t^{1/2} + C \quad (11)$$

where k_{int} is the intraparticle diffusion rate constant ($mg/g.min^{1/2}$) and C is the intercept. The rate constants of intra particle diffusion havecalculated the plot of dye uptake, q_t, versus the square root of time ($t^{1/2}$).

3. Results and discussions

3.1 Surface characterization of adsorbent samples

The scanning electron microscope is a beneficial instrument for confirmation of surface

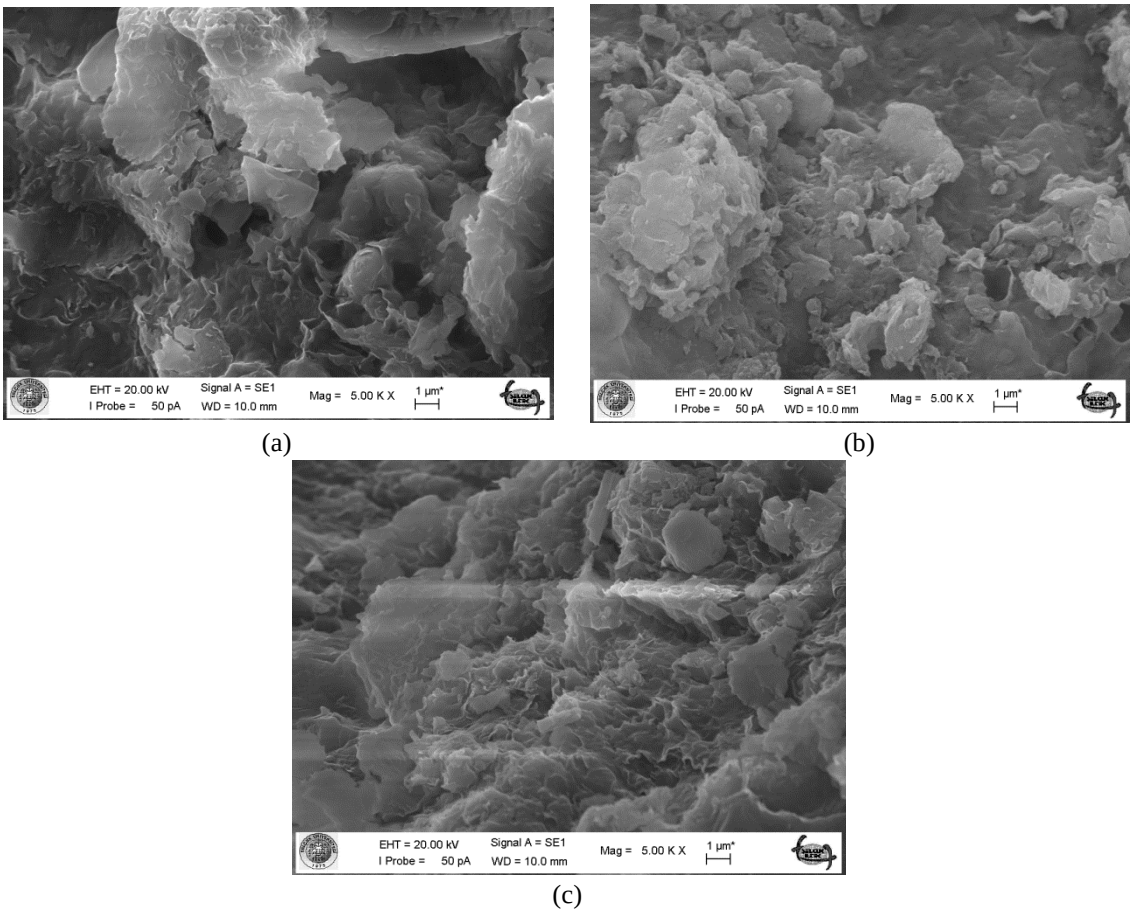


Fig. 1 Scanning electron microscope images of (a) BEW, (b) HBEW and (c) UBEW

morphology and the physical condition of the surface. SEM images of BEW, HBEW and UBEW are given in Fig. 1.

The highest porosity structure is formed on the surface of UBEW as can be seen in Fig. 1. In comparison to BEW and HBEW, a large number of small porous structures were observed on the surface of the material modified by ultrasound (UBEW). The increase in the surface porosity of the materials used also increases the surface activity and adsorption capacity of the material.

3.2 Effect of dose of adsorbent and contact time

MG removal efficiency from synthetic wastewater containing 50 mg/dm^3 of dye using BEW, HBEW and UBEW as adsorbent was investigated. Adsorbents ranging from 125 mg/dm^3 to 1500 mg/dm^3 dosages were added in MG solutions. The properties of adsorbates and adsorbents are quite specific and depend upon their component. The chemical properties of the adsorbate have a profound effect on the adsorption characteristics and performance. The initial dye concentration and contact time between adsorbent and adsorbate species play a significant role in the process of removal of dye from water and wastewater by adsorption at a particular temperature and pH (Khattri and Singh 2009). The adsorption rate is faster at the initial stage and then approximately

10 minutes later reached to a plateau because of the saturation of active surface of materials. After 90 minutes contact time, the dye removal efficiency was fixed and optimum dosage and contact time were determined. Operation criterions were temperature 298 K, original pH value 5-6.5 range, shaking speed 200 rpm and contact time 40, 20, 30 minutes for BEW, HBEW and UBEW, respectively. The optimum removal efficiencies were obtained for adsorbent dosages (500, 200, 375 mg/dm3): 80 %, 81%, and 77 % for BEW, HBEW and UBEW, respectively. The increased adsorption of MG with adsorbent dose could be due to the presence of more adsorption areas with increasing adsorbent dose (El-Zahhar and Awwad 2016). At initial times of adsorption, rapid adsorption occurs with initial contact, indicating the presence of dye. At the higher time probably due to electrostatic repulsion between the adsorbed positive charge adsorbate onto the surface and the available cationic MG in the bulk cause decrease in adsorption (Ghaedi *et al.* 2015). The relationship among adsorption capacity, contact time and removal efficiency are given in Fig. 2(a).

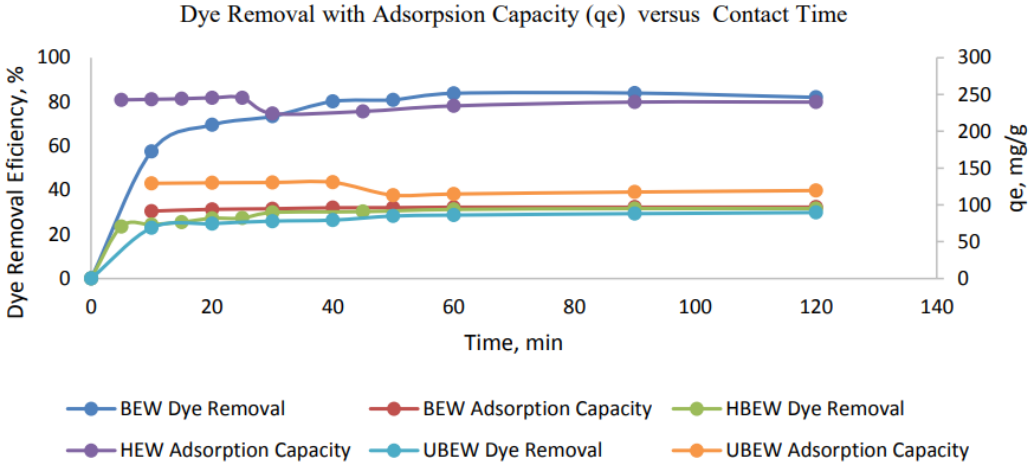
3.3 Effect of the initial pH of the solution

Since pH affects both the behavior of the adsorbate and the load on the surface of the adsorbent, it is one of the most essential parameters to consider in dye removal from aqueous solutions. (Abussaud *et al.* 2016). The pH values of synthetic wastewater were determined by adjusting between 1-13. Fig. 2(c) shows the pH behavior of the three different adsorbents whose dye removal efficiency will be determined. The pH value of the solution is very important for the removal efficiency of malachite green due to the effect of dye molecules on ionization and the surface of the adsorbent. At lower pH, the number of positively charged adsorbent surface sites increased at the expense of the number of negatively charged surface sites (El-Zahhar and Awwad 2016, Sartape *et al.* 2017). pH optimization experiments were performed under the following adsorption conditions: adsorbent dose: 500 mg/dm^3, contact time: 40 minute for BEW; adsorbent dose: 200 mg/dm^3, contact time: 20 minute for HBEW; adsorbent dose: 375 mg/dm^3, contact time: 30 minute for UBEW and other criterions were shaking speed: 200 rpm, temperature: 298 K. The percents of dye removal was achieved as 81%, 82% and 84% for BEW, HBEW and UBEW adsorbents at 5-6, 10 and 8 pH values, respectively.

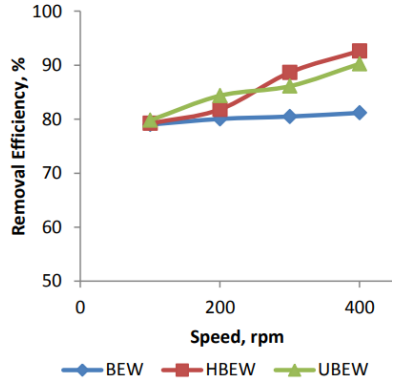
3.4 Effect of shaking speed

Depending on the degree of agitation of the fluid particle system, the adsorption rate is controlled by either film diffusion or pore diffusion. The rinsing rate has a significant effect on the retention of dyes. At low agitation rates, the liquid film around the particle is thicker, and the film diffusion rate is a limiting step. The adsorption kinetics are affected by low mass transfer of the adsorbate to the inner surface of the boot. This results in maximized film diffusion at higher agitation speeds, and therefore, pore diffusion becomes a speed control step.(Khattri and Singh 2009, Abussaud *et al.* 2016).

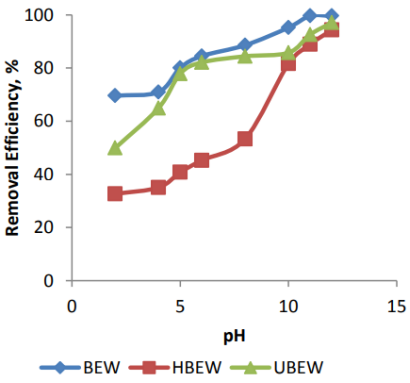
The effect of shaking speed on the uptake of dye onto waste materials was studied by varying the shaking speeds from 100 to 400 rpm, keeping the initial concentration, pH, dosage and other parameters constant. However, in the continuation of the operation the uptake of dye is not greatly affected when shaking speed increases from 200 to 400 rpm, the equilibrium time remains constant, In addition adsorbents can leave uptake of dye at high shaking speed in the system. The obtained results (see Fig. 2 (b)) show that the adsorption of malachite green increased until 400 rpm but the application of high shaking speed has difficulty in water treatment plants, so the



(a) (pH:5-6, temperature: 298 Kelvin, dye concentration: 50 mg/L, shaking speed: 200 rpm)



(b) (pH:5-6, temperature: 298 Kelvin, dye concentration: 50 mg/ dm^3, dosage 500, 200, 375 mg/dm^3, contact time 40, 20, 30 minutes for BEW, HBEW and UBEW, respectively)



(c) (shaking speed:200 rpm, temperature: 298 Kelvin, dye concentration: 50 mg/ dm^3, dosage 500, 200, 375 mg/dm^3, contact time 40, 20, 30 minutes for BEW, HBEW and UBEW, respectively)

Fig. 2 Effects of contact time (a), Effect of shaking speed (b), Effects of pH (c) on dye removal efficiency for BEW, HBEW and UBEW

optimal shaking speed was selected as 200 rpm. Although the best dye removal efficiency (approximately 90-92%) was at 400 rpm, 200 rpm was selected as optimum shaking speed value. This is because it is very difficult to mix wastewater at very high speeds in real field applications and this is considered to cause a lot of energy consumption. HCl-modified boron enrichment waste adsorbent provided the highest level of dye removal. The percents of dye removal were achieved as 81%, 82% and 84% for BEW, HBEW and UBEW adsorbents at 200 rpm values at 298 K, respectively.

3.5 Determination of adsorption isotherms

Adsorption parameters were evaluated by using Langmuir, Freundlich and Temkin isotherm models. Investigation of adsorption isotherms has provided important information to describe how

Table 2 Values of constants of Langmuir, Freundlich and Temkin isotherms for adsorption of malachite green on BEW, HBEW, UBEW

		BEW	HBEW	UBEW
Isotherm Model	Parameters		Values (298 K)	
Langmuir	*qmax* (mg/g)	147.05	434.78	192.30
	KL (L/mg)	270.27	63.69	238.09
	R^2	0.971	0.987	0.984
Freundlich	Kf (mg/g)	38.10	91.47	5.71
	1/n	0.292	0.319	0.26
	R^2	0.810	0.890	0.774
Temkin	A_T (dm^3/g)	27.48	79.76	3.19
	B_T (J/mol)	6.42	2.72	25.99
	R^2	0.807	0.919	0.752

Table 3 The comparison of experimental sorption capacities of BEW, HBEW and UBEW to some sorbents for malachite green sorption

Adsorbents	Dye	Adsorption Capacity, q_e (mg/g)	References
Ginger Waste	Malachite Green	84.03 at 30 degrees C, 163.9 at 40 degrees C, 188.6 at 50 degrees C	Ahmad and Kumar (2010)
Neem Sawdust	Malachite Green	4.354	Khattri and Singh (2009)
Chemically Cross-Linked Chitosan Beads	Four Reactive Dyes (RB2, RR2, RY2, RY86)	ranges from 1911 to 2498	Chiou *et al.* (2004)
Synthesized hydroxyapatite (Hyd) and Fe-hydroxyapatite (Fe-Hyd) composite	Methylene Blue	2.90 - 5.64	Çiftçi (2016)
Aspergillus Flavus Mediated Synthesis Of Silver Nano Particles	Malachite Green	44.21	Muthu *et al.* (2016)
Organically Modified Hydroxyapatite	Malachite Green	188.18	El-Zahhar and Awwad (2016)
Pumice Powder	Methylene Blue	0.362	Çiftçi and Meriç (2016)
Limonia Acidissima (Wood Apple) Shell	Malachite Green	80.645	Sartape *et al.* (2017)
Cu Nanowires Loaded On Activated Carbon	Malachite Green	434.8	Ghaedi *et al.* (2015)
Industrial Waste Shells Of Egg	Methylene Blue, MB and Congo Red, CR	94.9 and 49.5	Abdel-Khalek *et al. (*2017)
Modification of Boron Enrichment Process Waste	Methylene Blue	107.0, 160.7 and 145.3	Oden and Kucukcongar (2018)
The Almond Gum	Malachite Green	172.41 at 303.16 K, 181.81 at 313.16 K, 196.07 at 323.16 K	Bouaziz *et al. (*2017)
Rice Bran-Based Composites	Malachite Green	143.17	Bhatti *et al.* (2017)

Table 3 Continued

Adsorbents	Dye	Adsorption Capacity, q_e (mg/g)	References
Powdered Tourmaline	The Diazo Direct Red 23	153	Liu *et al.* (2018)
Biochars	Methylene Blue and Methyl Orange	234.57 and 306.13	Çağlar *et al.* (2018)
Coir Dust, Saw Dust, Rice Husk, Tea Waste	Cibacron blue	31, 12, 9, 8	Amarasinghe *et al.* (2007)
Power Plant And Agricultural Waste	Chrysoidine Y	7.27×10^{-5}, 3.35×10^{-5}	Mittal *et al.* (2010)
Mesoporous Carbon CMK-3	Methyl Orange	294.1	Mohammadi *et al.* (2011)
Fe_3O_4 nanoparticles	Methylene blue and Safranin-O	89.2–91.9	Ghaedi *et al.* (2015)
Modified (with H_3PO_4) Water Nut Carbon	Congo Red and Malachite Green	38.8 and 46.27	Ahmad and Mondal (2010)
Refused Tea Waste	Acid Yellow 36	71.97	Wijetunga and Gunasekara (2017)
Modified And Raw Boron Enrichment Process Waste	Malachite Green	147.05, 434.78 and 192.30	In this study

adsorbed particles are distributed between liquid and solid phases (Bouaziz *et al.* 2017). Over the years, a wide variety of equilibrium isotherm models (Langmuir, Freundlich, Temkin isotherm) have beeen used for different fundamental approaches (Malek and Farooq 1996). The Langmuir adsorption model assumes that adsorption occurs in specific homogeneous adsorption sites within the adsorbent and intermolecular forces, and decreases rapidly as it moves away from the adsorption surface (Bhatti *et al.* 2017). Freundlich isotherm is the oldest known relationship that defines non-ideal and reversible adsorption, not limited to monolayer formation. The distribution of this empirical model adsorption temperature and the distribution of affinities (affinity, interest, etc.) on the heterogeneous surface can be applied to uneven multi-layer adsorption (Freundlich 1906, Adamson and Gast 1997, Foo and Hameed 2010). The provision isotherm includes a computation factor that clearly takes into account the adsorbent-adsorbate interactions. By ignoring extremely low and high concentration values, the model assumes that all molecules in the layer have a heat of adsorption (the function of temperature) and will be reduced linearly instead of logarithmic (Tempkin and Pyzhev 1940, Foo and Hameed 2010). Calculated constants relating to the models are calculated using Figs. 4-6 and given in Table 2. The adsorption equilibrium data showed a good fit to the Langmuir isotherm model as compared to the Freundlich and Tempkin isotherm model. According to the data given in the Table 2, the amount of R^2 related to the Langmuir model is more than the other linear coefficients.

In this study, Malachite Green (MG) dye removal from synthetic wastewaters by adsorption process using raw boron enrichment waste (BEW) and it's modifications (with acid and ultrasound) were aimed. The adsorption capacity of different adsorbents is given in Table 3.

This example studies show that there are many adsorbents deals with the removal of dye efficiency. But this present study has got high adsorption capacity than the other study for the removal of MG from aqueous systems.

3.6 Adsorption thermodynamics

Adsorption studies have focused on the adsorption thermodynamics to describe the adsorbent's

Table 4 Thermodynamic parameters for the adsorption of malachite green onto BEW, HBEW and UBEW

Adsorbent	T (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol·K)
BEW	298	-20.319	82.760	0.345
	308	-23.778		
	318	-27.237		
HBEW	298	-53.382	212.040	0.890
	308	-62.288		
	318	-71.195		
UBEW	298	-31.201	74.551	0.354
	308	-34.749		
	318	-38.298		

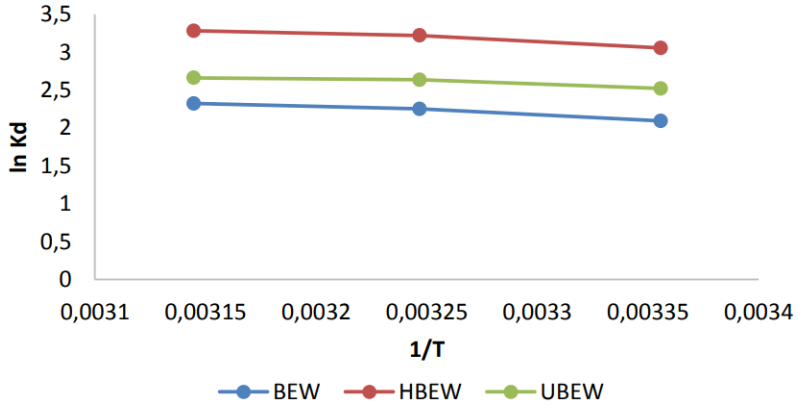


Fig. 3 Thermodynamic plot for malachite green dye adsorption on waste materials (shaking speed:200 rpm, temperature: 298 Kelvin, dye concentration: 50 mg/ dm^3, pH: 5-6, 10 and 8, dosage 500, 200, 375 mg/dm^3, contact time 40, 20, 30 minutes for BEW, HBEW and UBEW, respectively

adsorbate dependence. These parameters reflect the feasibility and spontaneousnature of the process. To determine the adsorption thermodynamic; ln K_d and 1/T relations of equilibrium data at different temperature (298, 308 and 318 K) were investigated (Fig. 3). The results of the experiments were given in Table 4. These parameters including Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were calculated using Eqs. (7) and (8). The respective values of (ΔG°) at 298, 308, and 318 K were found as negative (in kJ/mol), which indicates the spontaneous adsorption process of malachite green.

The positive value of ΔH° indicates that the sorption process of MG is endothermic, whereas the positive value of ΔS° indicates that the adsorption occurs due to the energy redistribution between MG and waste materials. Also, the positive ΔS° value reflects the affinity of adsorbent material towards MG (Bouaziz *et al.* 2017).

Thermodynamic study indicates the spontaneous and endothermic nature of the sorption process due to negative values of (ΔG°) and positive value of (ΔH°), respectively. Finally it is concluded that, the three adsorbents can be an economical and effective alternative to the dye removal from the aqueous solution.

3.7 Adsorption kinetics

The kinetic parameters, which are helpful for the prediction of adsorption rate, give important information for designing and modeling the adsorption processes. The kinetic models such as, pseudo-first-order, pseudo-second-order and intra-particle-diffusion model were applied to interpret the experimental results. The adsorption rate constant was determined in Fig. 4 and the values are given in Table 5. The correlation coefficient (R^2) value was found the highest in the so-called second order model. Data of the so-called second-order model data and other kinetic models

Table 5 Values of rate constants of pseudo-first order, pseudo-second order reaction and intra particle diffusion at different adsorbent for the removal of malachite green by adsorption on waste materials

	Pseudo-first-order			Pseudo-second-order			Intra-particle diffusion		
25 ^{0}C (298 K)	k_1 (1/min)	R^2	qe (mg/g)	k_2 (min.g/mg)	R^2	qe (mg/g)	k_{int} (mg/g.min$^{1/2}$)	R^2	C
BEW	0.0028	0.755	59.347	0.0005	0.967	78.740	7.028	0.863	2.959
HBEW	0.0040	0.367	23.768	0.0038	0.999	204.081	6.724	0.519	149.6
UBEW	0.0029	0.579	28.873	0.042	0.999	111.111	4.537	0.662	73.96

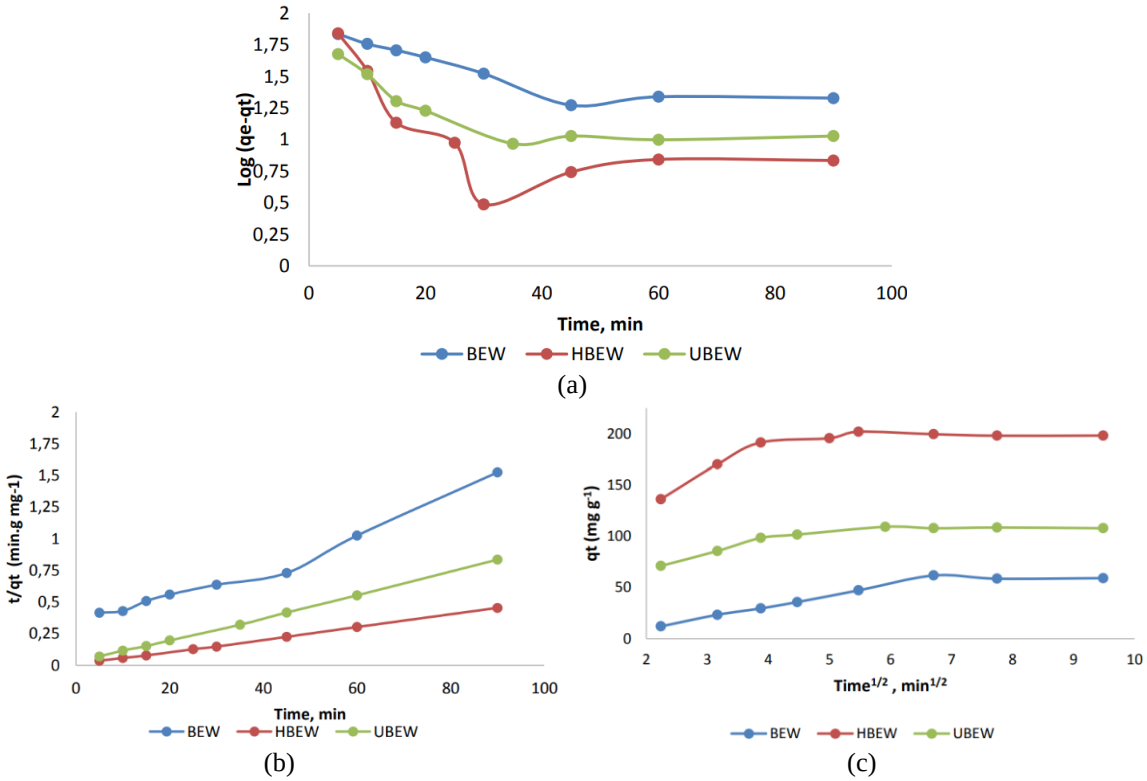


Fig. 4 Pseudo-first-order (a), Pseudo-second-order (b) and Intra-particle diffusion (c) plots for Malachite green dye adsorption on composites (shaking speed:200 rpm, temperature: 298 Kelvin, dye concentration: 50 mg/ dm^3, pH: 5-6, 10 and 8, dosage 500, 200, 375 mg/dm^3, contact time 40, 20, 30 minutes for BEW, HBEW and UBEW, respectively

were calculated and shown in Table 5. The highest R^2 indicates kinetic models where the adsorption data fit. The adsorption kinetics followed pseudo-second-order kinetic equation for sorption of MG onto wastes.

4. Conclusions

Boron enrichment waste and adsorbents obtained from waste by chemical and physical modification were proved to be very successful at dye removal from wastewater. It is a great success to make treatment by using a waste material which is an environmental threat. So that the environment was preserved by removing wastewater pollutant through a waste material. The removal of Malachite Green was found to be 81%, 82% and 84% for boron enrichment waste (BEW), modified boron enrichment waste with HCl (HBEW) and modified boron enrichment waste with ultrasound (UBEW) adsorbents with initial dye concentration 50 mg/dm^3 at 5-6, 10 and 8 pH values, 500, 200, 375 mg/dm^3 at adsorbent dosages, in 40, 20, 30 minute contact time respectively by shaking at 200 rpm at 298 K. Thermodynamic study demonstrates the spontaneous and endothermic nature of sorption process due to negative values of free energy change and positive value of enthalpy change, respectively. The maximum adsorption capacities were equal to about 147,05 mg/g, 434,78 mg/g and 192,30 mg/g for BEW, HBEW and UBEW adsorbents at 200 rpm values at 298 K, respectively.

On the whole, this study showed that boron enrichment waste, acid and ultrasound-modified boron enrichment waste served as good alternative adsorbents in dye removal from wastewater. In addition, the waste materials are freely available because they are discharged into fields by enrichment plants. At the same time, through this process, waste materials gain economic value. And what is more, waste materials used as adsorbents reduce environmental pollution, and provide dye removal from wastewater.

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References

Abdel-Khalek, M.A., Abdel Rahman, M.K. and Francis, A.A. (2017), "Exploring the adsorption behavior of cationic and anionic dyes on industrial waste shells of egg", *J. Environ. Chem. Eng.*, **5**(1), 319-327. https://doi.org/10.1016/j.jece.2016.11.043.

Abussaud, B., Asmaly, H.A., Saleh, T.A., Gupta, V.K. and Atieh, M.A. (2016), "Sorption of phenol from waters on activated carbon impregnated with iron oxide, aluminum oxide and titanium oxide", *J. Mol. Liq.*, **213**, 351-359. https://doi.org/10.1016/j.molliq.2015.08.044.

Adamson, A.W. and Gast, A.P. (1997), *Physical Chemistry of Surfaces*, Wiley, New York, U.S.A.

Ahmad, A.L., Harris, W.A. and Ooi, B.S. (2002), "Removal of dye from wastewater of textile industry using membrane technology", *Jurnal Teknologi*, **36**(1), 31-44. https://doi.org/10.11113/jt.v36.581.

Ahmad, R. and Kumar, R. (2010), "Adsorption studies of hazardous malachite green onto treated ginger waste", *J. Environ. Manage.*, **91**(4), 1032-1038. https://doi.org/10.1016/j.jenvman.2009.12.016.

Ahmad, R. and Mondal, P.K. (2010), "Adsorption studies of hazardous malachite green onto treated ginger waste", *Sep. Sci. Technol.*, **45**(3), 394-403. https://doi.org/10.1016/j.jenvman.2009.12.016.

Ali Khan, M., Khan, M. and Zafar, S. (2017), "Removal of different anionic dyes from aqueous solution by anion exchange membrane", *Membr. Water Treat.*, **8**(3), 259-277. https://doi.org/10.12989/mwt.2017.8.3.259.

Alizadeh, R. and Zeidi, A. (2017), "Adsorption of methylene blue from an aqueous dyeing solution by use of santa barbara amorphous-15 nanostructure: Kinetic and isotherm studies", *Adv. Environ. Res.*, **6**(2), 113-125. https://doi.org/10.12989/aer.2017.6.2.113.

Amarasinghe, B.M.W.P.K., Jayasinghe, P.A. and Gunesekara, M.Y. (2007), "Adsorption of cibacron blue dye from aqueous solutions onto HCL treated waste biomass", *Eng. J. Inst. Eng.*, **40**(3), 7-15.

Bhatti, H.N., Jabeen, A., Iqbal, M., Noreen, S. and Naseem, Z. (2017), "Adsorptive behavior of rice bran-based composites for malachite green dye: Isotherm, kinetic and thermodynamic studies", *J. Mol. Liq.*, **237**, 322-333. https://doi.org/10.1016/j.molliq.2017.04.033.

Bouaziz, F., Koubaa, M., Kallel, F., Ghorbel, R.E. and Chaabouni, S.E. (2017), "Adsorptive removal of malachite green from aqueous solutions by almond gum: Kinetic study and equilibrium isotherms", *Int. J. Biol. Macromol.*, **105**, 56-65. https://doi.org/10.1016/j.ijbiomac.2017.06.106.

Buthelezi, S., Olaniran, A. and Pillay, B. (2012), "Textile dye removal from wastewater effluents using bioflocculants produced by indigenous bacterial isolates", *Molecules*, **17**(12),14260. https://doi.org/10.3390/molecules171214260.

Chiou, M.S., Ho, P.Y. and Li, H.Y. (2004), "Adsorption of anionic dyes in acid solutions using chemically cross-linked chitosan beads", *Dyes Pigm.*, **60**(1), 69-84. https://doi.org/10.1016/S0143-7208(03)00140-2.

Çağlar, E., Donar, Y.O., Sınağ, A., Biroğul, İ., Bilge, S., Aydincak, K. and Pliekhov, O. (2018), "Adsorption of anionic and cationic dyes on biochars, produced by hydrothermal carbonization of waste biomass: Effect of su", *Turk. J. Chem.*, **42**(1), 86-99.

Çiftçi, D.İ. (2016), "Enhancement of Methylene Blue dye adsorption by Fe-Hydroxyapatite composite", *Adv. Environ. Res.*, **5**(4), 225-235. https://doi.org/10.12989/aer.2016.5.4.225.

Çiftçi, D.İ. and Meriç, S. (2016), "Optimization of methylene blue adsorption by pumice powder", *Adv. Environ. Res.*, **5**(1), 37-50. https://doi.org/10.12989/aer.2016.5.1.037.

Dubinin, M.M. (1965), "Modern state of the theory of volume filling of micropore adsorbents during adsorption of gases and steams on carbon adsorbents", *Zh. Fiz. Khim.*, **39**(6), 1305-1317.

Elsharkawy, R.G. (2017), "Incorporation of copper/melamine complexes in silica surface and their sorption activity of organic dye", *Iran J. Chemistry Chem. Eng.*, **36**(5), 99-114.

El-Zahhar, A.A. and Awwad, N.S. (2016), "Removal of malachite green dye from aqueous solutions using organically modified hydroxyapatite", *J. Environ. Chem. Eng.*, **4**(1), 633-638. https://doi.org/10.1016/j.jece.2015.12.014.

Evliyaogullari, N.E., Oden, M.K. and Kucukcongar, S. (2017), "The removal of chromium from aqueous solutions using an industrial waste material", *Int. J. Ecosyst. Ecol. Sci.*, **7**(4), 671-676.

Foo, K.Y. and Hameed, B.H. (2010), "Insights into the modeling of adsorption isotherm systems", *Chem. Eng. J.*, **156**(1), 2-10. https://doi.org/10.1016/j.cej.2009.09.013.

Freundlich, H.M.F. (1906), "Over the adsorption in solution", *J. Phys. Chem.*, **57**, 385-471.

Gadekar, M.R. and Ahammed, M.M. (2016), "Coagulation/flocculation process for dye removal using water treatment residuals: Modelling through artificial neural networks", *Desalin. Water Treat.*, **57**(55), 26392-26400. https://doi.org/10.1080/19443994.2016.1165150.

Ghaedi, M., Hajjati, S., Mahmudi, Z., Tyagi, I., Agarwal, S., Maity, A. and Gupta, V.K. (2015), "Modeling of competitive ultrasonic assisted removal of the dyes–Methylene blue and Safranin-O using Fe3O4 nanoparticles", *Chem. Eng. J.*, **268**, 28-37. https://doi.org/10.1016/j.cej.2014.12.090.

Ghaedi, M., Shojaeipour, E., Ghaedi, A.M. and Sahraei, R. (2015), "Isotherm and kinetics study of malachite green adsorption onto copper nanowires loaded on activated carbon: Artificial neural network modeling and genetic algorithm optimization", *Spectrochim. Acta Part A*, **142**, 135-149.

https://doi.org/10.1016/j.saa.2015.01.086.
Gupta, V.K., Jain, R., Nayak, A., Agarwal, S. and Shrivastava, M. (2011), "Removal of the hazardous dye—Tartrazine by photodegradation on titanium dioxide surface", *Mater. Sci. Eng. C*, **31**(5), 1062-1067. https://doi.org/10.1016/j.msec.2011.03.006.
Gupta, V.K., Pathania, D., Agarwal, S. and Sharma, S. (2012), "De-coloration of hazardous dye from water system using chemically modified Ficus carica adsorbent", *J. Mol. Liq.*, **174**, 86-94. https://doi.org/10.1016/j.molliq.2012.07.017.
Indu, M., Gupta, A. and Sahoo, C. (2014), "Electrochemical oxidation of methylene blue using lead acid battery anode", *APCBEE Procedia*, **9**, 70-74. https://doi.org/10.1016/j.apcbee.2014.01.013.
Jirankova, H., Mrazek, J., Dolecek, P. and Cakl, J. (2010), "Organic dye removal by combined adsorption—membrane separation process", *Desalin. Water Treat.*, **20**(1-3), 96-101. https://doi.org/10.5004/dwt.2010.1170.
Khattri, S.D. and Singh, M.K. (2009), "Removal of malachite green from dye wastewater using neem sawdust by adsorption", *J. Hazard. Mater.*, **167**(1), 1089-1094. https://doi.org/10.1016/j.jhazmat.2009.01.101.
Kushwaha, A.K., Gupta, N. and Chattopadhyaya, M.C. (2014), "Removal of cationic methylene blue and malachite green dyes from aqueous solution by waste materials of Daucus carota", *J. Saudi Chem. Soc.*, **18**(3), 200-207. https://doi.org/10.1016/j.jscs.2011.06.011.
Lafi, R., Mabrouk, W. and Hafiane, A. (2019), "Removal of Methylene blue from saline solutions by adsorption and electrodialysis", *Membr. Water Treat.*, **10**(2), 139-148. https://doi.org/10.12989/mwt.2019.10.2.139.
Liu, N., Wang, H., Weng, C.H. and Hwang, C.C. (2018), "Adsorption characteristics of Direct Red 23 azo dye onto powdered tourmaline", *Arab. J. Chem.*, **11**(8), 1281-1291. https://doi.org/10.1016/j.arabjc.2016.04.010.
Malek, A. and Farooq, S. (1996), "Comparison of isotherm models for hydrocarbon adsorption on activated carbon", *AIChE J.*, **42**(11), 3191-3201. https://doi.org/10.1002/aic.690421120.
Mittal, A., Mittal, J., Malviya, A. and Gupta, V.K. (2010), "Removal and recovery of Chrysoidine Y from aqueous solutions by waste materials", *J. Colloid Interface Sci.*, **344**(2), 497-507. https://doi.org/10.1016/j.jcis.2010.01.007.
Mohammadi, N., Khani, H., Gupta, V.K., Amereh E. and Agarwal, S. (2011), "Adsorption process of methyl orange dye onto mesoporous carbon material–kinetic and thermodynamic studies", *J. Colloid Interface Sci.*, **362**(2), 457-462. https://doi.org/10.1016/j.jcis.2011.06.067.
Oden, M.K. and Kucukcongar, S. (2018), "Acid and ultrasound assisted modification of boron enrichment process waste and using for methylene blue removal from aqueous solutions", *Global Nest J.*, **20**(2), 234-242.
Oden, M.K. and Sari-Erkan, H. (2018), "Treatment of metal plating wastewater using iron electrode by electrocoagulation process: Optimization and process performance", *Process Saf. Environ. Protect.*, **119**, 207-217. https://doi.org/10.1016/j.psep.2018.08.001.
Oei, B.C., Ibrahim, S., Wang, S. and Ang, H.M. (2009), "Surfactant modified barley straw for removal of acid and reactive dyes from aqueous solution", *Bioresour. Technol.*, **100**(18), 4292-4295. https://doi.org/10.1016/j.biortech.2009.03.063.
Özdemir, C., Öden, M.K., Şahinkaya S. and Kalipçi, E. (2011), "Color removal from synthetic textile wastewater by sono-fenton process", *Clean-Soil Air Water*, **39**(1), 60-67. https://doi.org/10.1002/clen.201000263.
Pandian, A.M.K., Karthikeyan, C. and Rajasimman, M. (2016), "Isotherm and kinetic studies on nano-sorption of malachite green onto Aspergillus flavus mediated synthesis of silver nano particles", *Environ. Nanotechnol. Monit. Manage.*, **6**, 139-151. https://doi.org/10.1016/j.enmm.2016.10.001.
Radushkevich, L.V. (1949), "Potential theory of sorption and structure of carbons", *Zh. Fiz. Khim.*, **23**, 1410-1420.
Rizzi, V., D'Agostino, F., Fini, P., Semeraro, P. and Cosma, P.(2017), "An interesting environmental friendly cleanup: The excellent potential of olive pomace for disperse blue adsorption/desorption from

wastewater", *Dyes Pigm*., **140**, 480-490. https://doi.org/10.1016/j.dyepig.2017.01.069.
Sartape, A. S., Mandhare, A.M., Jadhav, V.V., Raut, P.D., Anuse, M.A. and Kolekar, S.S. (2017), "Removal of malachite green dye from aqueous solution with adsorption technique using Limonia acidissima (wood apple) shell as low cost adsorbent", *Arab. J. Chem.*, **10**, S3229-S3238. https://doi.org/10.1016/j.arabjc.2013.12.019.
Sharma, A., Verma, M. and Haritash, A.K. (2016), "Degradation of toxic azo dye (AO7) using Fenton's process", *Adv. Environ. Res*., **5**(3), 189-200. http://dx.doi.org/10.12989/aer.2016.5.3.189.
Tempkin, M.I. and Pyzhev, V. (1940), "Kinetics of ammonia synthesis on promoted iron catalyst", *Acta Phys. Chim.*, **12**, 327-356.
Weber, W.J. and Morris, J.C. (1963), "Kinetics of adsorption on carbon from solution", *J. Sanit. Eng. Div. Am. Soc. Civ. Eng*., **89**, 31-60.
Wijetunga, S. and Gunasekara, C.D.F.A. (2017), "Evaluation of refused tea waste activated carbon for color removal: Equilibrium and kinetic studies", *Adv. Environ. Res*., **6**(1),1-14. https://doi.org/10.12989/aer.2017.6.1.001.

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