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Friendly-Natural (Clay-Biochar) Composite for the Removal of Methylene Blue from Aqueous Phase

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Abstract

Developing a new adsorbent, kaolin clay-biochar (KC-BC) composite, to eliminate methylene blue (MB), a highly applied and hazardous dye from wastewater, was the main target of this research work. The composite was prepared by blending kaolin clay(KC) with date seeds(DS) at a mass ratio of 1:1 KC:DS, followed by carbonization at 500 °C for 1h. This composite was characterized by pH_{pzc}, BET-specific surface area, XRD, SEM, and EDX to identify the morphological and chemical characteristics of the composite. The BET-surface area of the composite was 33.10 m^2/g, while its mean pore volume amounted to 13.45nm, suggesting its mesoporosity. This composite was implemented in batch adsorption of MB from an aqueous phase. The best removal of MB (99.42 %) by the as-created composite using 0.15 g of the composite at 40 °C for 1h at a pH of 10. The reusability of the exhausted composite was also investigated.

Introduction

Global industrialization processes have caused water contamination to become a serious environmental and economic issue [1]. Organic dyes, which are harmful pollutants, are widely dispersed into the environment by the textile, paper and pulp, tannery, and paint industries [2]. Dyes are very toxic, carcinogenic, mutagenic, non-biodegradable, and can result in major water contamination [3]. A thiazine cationic dye was identified as methylene blue (MB) (3,7-bis(Dimethylamine)-phenothiazin-5-iumchloride). Figure 1 is frequently used for biological staining in addition to coloring paper, cottons, hair, silk, and wools. Furthermore, methemoglobinemia and urinary tract infections are treated with MB injection [4,5].

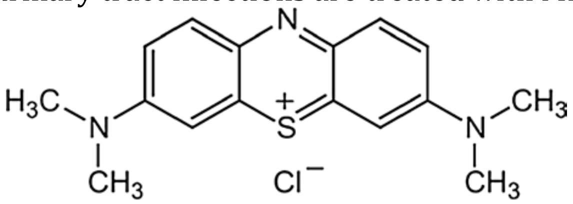

Fig. 1: *Chemical structure of methylene blue.*

When consumed by humans, MB can have negative health effects, such as cancer, shortness of breath, high blood pressure, nausea, and other allergic reactions [6]. The complex aromatic molecular structure of MB, like that of the majority of dyes, renders it resistant to light, heat, and oxidizing chemicals. MB dye must therefore be removed from effluent prior to it is discharged because even a small amount of dye in water is dangerous and extremely noticeable [1]. The scientific community has therefore concentrated its research on creating efficient color removal procedures. Recently, the adsorption approach for removing dyes from solutions utilizing various adsorbents has garnered much attention [7]. When considering initial cost, convenience of use, therapeutic efficacy, flexibility due and simplicity of design, adsorption has been proven to be superior to alternative methods for reusing water, and it can range up to 99.9% in terms of removal efficiency. Additionally, adsorption doesn't produce dangerous chemicals [5-7]. According to the United States Environmental Protection Agency (USEPA), adsorption is one of the most effective and best methods for treating wastewater [8]. MB dye has been removed from aqua solution using a variety of adsorbents, many of which are overly accessible, such as waste biomass materials [9,10] and clay minerals [11,12], which also serve as affordable adsorbents. Recently, attempts to combine these two kinds of adsorbents to create a novel class of clay-biomass composites [13,14] or clay-biochar composites have been adopted to exploit the beneficial properties of both of these materials[15]. These include adding new structural and functional properties superior to those of the individual low-cost adsorbents [16]. Methylene blue is considered a net water pollutant, and there is research that used cobalt oxide and another used activated carbon to absorb methylene blue[17,18]

This work adopted the development of a novel clay-biochar composite to be used in water purification. The composite was synthesized using kaolin clay with date seeds as local raw materials via the slow carbonization. After identification, the as-prepared composite was tested in eliminating MB dye from its aqueous phase.

Materials and Methods

Raw Materials

The natural kaolin clay (KC) was brought from the Zawite region (north of Iraq). After collection, stones and other foreign particles were removed from the clay. The date seeds (DS) outstrip from the date fruit, which is an agricultural product available in abundance in Iraq. The DS was washed thoroughly with tap water to remove dirt attached to its surface, sun-light dried for a day, and crushed by an industrial electric grinder, then sifted to obtain a 75- mesh particle size.

Chemical used in this work were Methylene blue, (MB); ($C_{16}H_{18}ClN_3S$, molecular weight, 319.9 g/mol, Fluka, 99.5%), hydrochloric acid (HCl, Scharlau, 36%), and sodium hydroxide (NaOH, Scharlau, 98%), They were of analytical grade and utilized as received. The solutions of these chemicals were dissolved using deionized water (DW) .

Synthesis Of KC-Biochar Composite

The KC and DS were mixed at a mass ratio of 1:1. The KC was dispersed in DS, followed by the addition of the dried DS. The mixture was mixed by stirring on a magnetic stirrer for 2 h to obtain a homogeneous mixture, which was then oven-dried at 105°C until entire drying. The dried blend was then carbonized at 500°C for 1h in a muffle tube furnace under a limited oxygen environment to produce a KC-biochar composite. The resulting dark product was washed several times with distilled water to remove ash and soluble impurities, followed by drying in an oven at 105°C until dryness. Lastly, it was stored in an airtight plastic container for subsequent adsorption tests.

Characterization of Kc-Biochar Composite

Brunauer-Emmett-Teller (BET) surface area analyser (BELSORP MINI II, Japan, surface area and porosimetry analyser) was implemented to determine the specific surface area of the composite and pore size distribution. The morphological features of the composite were observed by field-emission scanning electron microscopy (FMSEM, TESCAN MIRA FESEM, Czech Republic). At the same time, the elementary composition were determined using energy dispersive x-ray spectroscopy (EDX, IE 300x, Oxford, UK). The structure and crystallinity of the adsorbent were determined by X-ray diffraction (XRD) analysis of the samples was recorded on a Malvern Panalytical X-ray diffractometer, UK x-ray diffractometer. The point of zero charge (pHpzc) of the prepared composite was detected by pH meter, while the titration approach was also used to look at all the acidic and basic groups on the surface of the composite.

Batch Adsorption Studies

Batch adsorption experiments were conducted to evaluate the efficiency of the as-created composite in removing MB dye from the aqueous solution. A stock solution of MB (500 mg L^{-1}) was prepared by dissolving an appropriate amount of MB dye in a 1L of DW. The dye solutions with different concentrations (as required for our experiments) were made by suitable dilution from the stock solutions in DW. The effect of various parameters on the adsorption of MB was studied, including the initial pH (2–10), initial concentration of MB (20-200 mg/L), adsorbent dose (0.05–0.3 g), adsorption temperature (10-60°C), and the contact time (5-180 min). The tests were accomplished via agitating a mixture of 50 cm^3 MB solution (100 mg/L) with the proper amount of the composite on a thermostatic shaker at 150 rpm at room temperature (23 ± 3°C) for a certain period. The pH of the MB solution was adjusted by adding 0.1M NaOH or 0.1M HCl. After equilibrium, the suspension was separated by centrifuge at 3000 rpm for 10 min. The residual concentration of MB was determined directly by spectrophotometric method at wavelengths of 663 nm (λ_{max} of MB)as illustrated in Figure 2(a), depending on the prepared calibration curve and straight line equation shown in Figure2(b) . The absorbance of MB was measured by a UV- VIS spectrophotometer (PD-3000 UV , APEL, Japan).

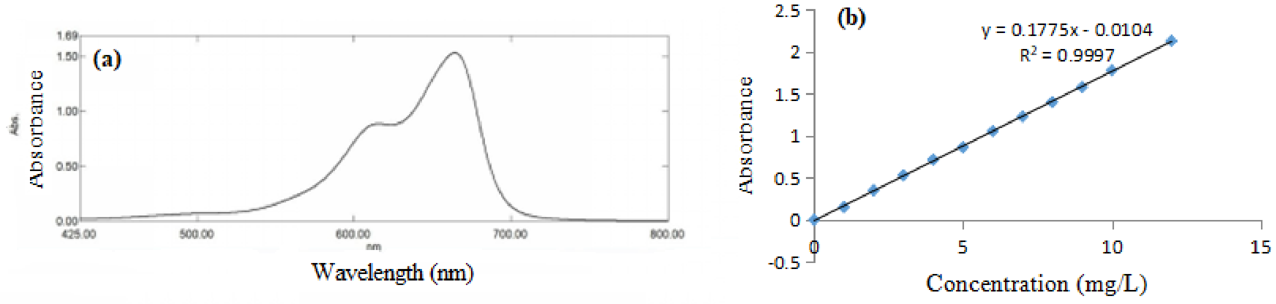

Fig. 2*:* *(a)Adsorption Spectrum of MB; (b) Calibration curve of MB dye*

The percentage removal of MB was determined using Eq. 1, while Eq. 2 was utilized to determine the composite's adsorption capacity. [1,19]:

$$R(\%) = \frac{(C_0 - C_e)}{C_0} X\ 100 \ldots\ldots\ldots (1)$$

$$q_e = \frac{(C_o - C_e)\ V}{W} \ldots\ldots\ldots (2)$$

Where C_0 (mg/L) and C_e (mg/L) are the initial and equilibrium concentrations of methylene blue, respectively, q_e (mg/g) is the adsorptive capacity for MB dye, V(L) refers to the volume of solution, and m (g) denotes the weight of the dried adsorbent used in the experiment.

Reusability of the Composite

To determine the possibility of reusing the composite after adsorption of MB dye at optimum condition of separation, several experiments were conducted, as follows:

1. The spent composite was treated with ethanol (90%) in a Soxhlet extractor, followed by filtration, drying at 105 °C, and reusing under the optimum conditions.
2. Activate ethanol-treated sample at 500°C for 30 min.
3. Thermal activation of the spent composite at 500°C for 30 min.

The reusability test was repeated twice

Results and Discussion

Characteristics of KC-BC Composite

As per the N_2 adsorption-desorption isotherm; Figure3(a), it was found that the as-synthesized composite showed a distinctive type II isotherm with H3 hysteresis loops. This loop occurs due to the capillary condensation of N_2 in mesoporous, macro pores, or both. This finding confirmed the occurrence of slit-like narrow pores created by the accretion of silicate particles in the composite adsorbent. The BET surface area of the as-created composite amounted to 33.10 m^2/g, while its mean pore diameter was 13.45 nm, assuring its mesoporous structure. Also, the BJH surface area of the composite was above BET surface area, which also confirmed the mesoporous structure of the created composite. Figure 3 the texture and chemical features of the asp-prepared composite.

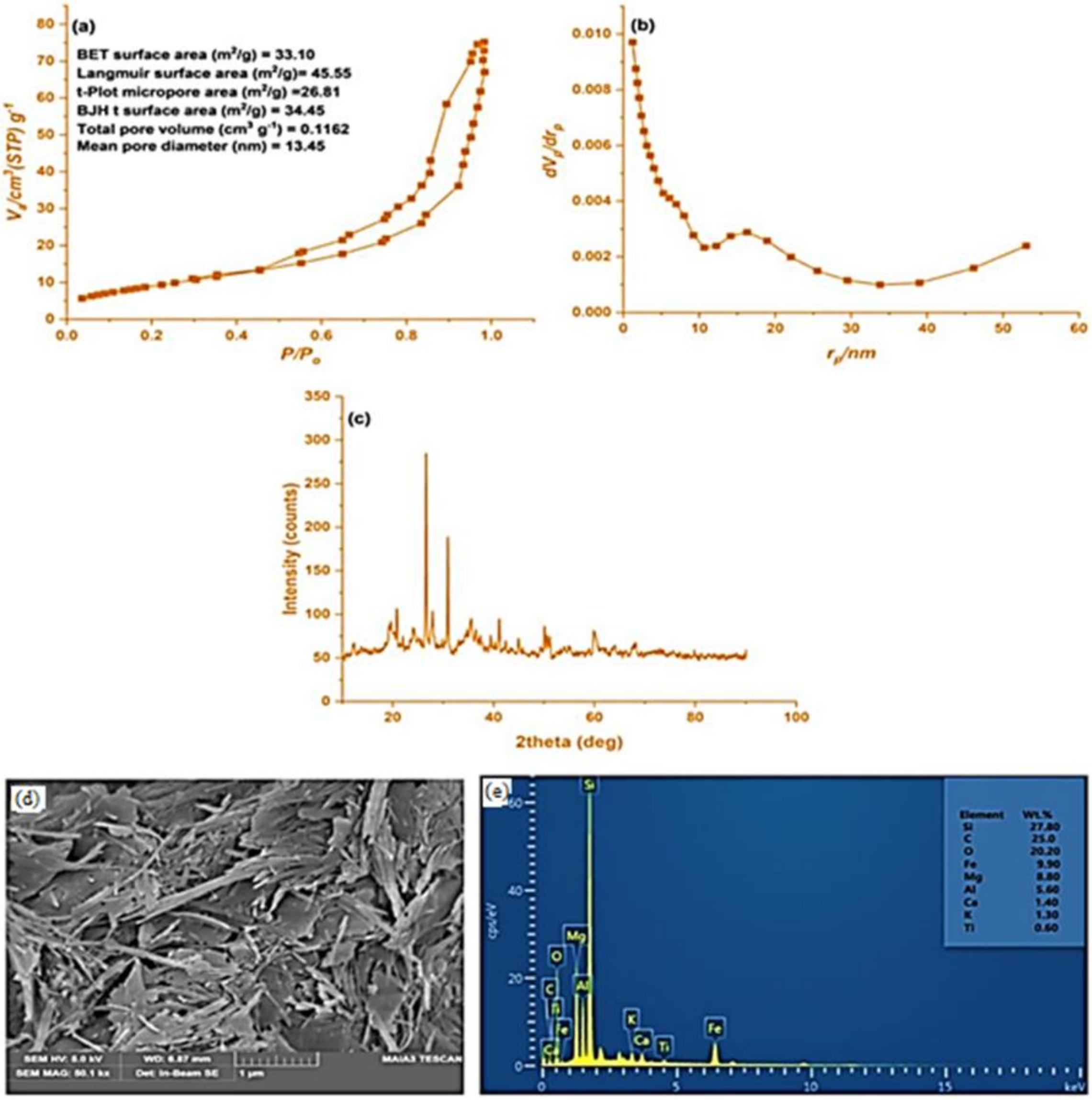

Fig. 3*: (a) N_2 adsorption-desorption isotherms, (b) pore size distribution, (c) XRD pattern, (d) FESEM image, and (e) EDX of the KC-BC composite.*

The FESEM images of the as-created composite at different magnifications was determined to inspect its surface morphology. It is obvious from Figure 3 (d), which presents the FESEM image of the composite, that its surface contained pores with varied sizes and shapes. The occurrence of these pores could be attributed to the creation of char as a result of the carbonization of the parent DS. Also, the presence of these pores ensures that the as-synthesized composite can adsorb pollutants of various molecular sizes. It can also be seen from the FESEM of the composite the presence of flaky structures over the composite surface, which belongs to clay minerals. However, these flakes did not entirely cover the composite surface. The EDX was utilized to determine the chemical composition of the as-prepared composite, as shown in figure 3(e). The EDX spectrum of the composite indicated to the occurrence of multiple high peaks, which belong to various metals in the prepared composite, including O, Si, Fe, Mg, Al, P, and K. These metals are the essential constituents of the clay. From the other side, C was also seen in the EDX spectrum, which is originated by the decomposition of the DS upon the carbonization process. The XRD pattern of the as-synthesized composite is shown in Figure 3(c), which exhibited multiple diffraction peaks at 2θ between 20° to 90°. The XRD pattern indicated that the peak of quartz was highly intense and well-promoted aggregate of kaolinite are found. It can be seen from the XRD patterns_of the produced composite that it showed multiple diffraction peaks at different positions. The presence of carbon in the as-prepared composite could be affirmed as a result of the diffraction peaks at 2θ=22° and 2θ=42.1°, which respectively belong to(001) and (100). The presence of these peaks in the obtained composite indicates the amorphous structure of carbon. The other diffraction peaks which belong to quartz and kaolin in the prepared composite are these peaks located at 2θ=19.27°, 2θ=20.81°, 2θ=26.58°, 2θ=27.89° and 2θ=35.63°, these peaks represent the phase (004), (020), (101), (101), (112) Also the presence of these phases ensure the presence of kaolin in the as-prepared composite.

The XRD outcomes are compatible with the SEM-EDX results, which showed that clay constituents were incorporated onto the biochar matrix.

Effect of Parameters on MB Adsorption by Composite

The solution pH has a significant impact on the adsorption process. The chemistry of the pollutants' solution, the competition with other ions in the sorption medium, and the activity of binding sites in adsorbents are all influenced by the solution pH [20]. Figure 4a shows the impact of the initial pH on the removal of MB. The elimination effectiveness of MB increased as pH increased, reaching its maxima at pH=10. This may be explained by the fact that the number of hydroxyl groups on the adsorbent's surface rises at higher pH levels. This increases the amount of negative charges and strengthens the attraction between the dye and the adsorbent surface [21]. Thus, it can be concluded that the removal of MB dyes is pH dependent and a basic medium is the best for cationic dye removal.

The influence of the initial MB concentration between 20 and 100 mg. L^{-1} was investigated. According to figure 4b, with increasing initial MB concentration, its adsorption capacity increased by a certain mass of the composite. As per literature, increasing the initial adsorbate concentration is required to slow down the amount of mass transfer impedance between the composite particles and the MB particles in the solution, leading to enhancing the adsorptive capacity of the composite to MB molecules[22].

The relationship between the adsorbent dose and the removal efficiency of MB by the as-prepared KC-BC composite is illustrated in Figure 4c, which exhibited an increase in the R% of MB when the composite dose increased from 0.05 g to 0.15 g. At the low dose of the adsorbent, the number of particles or active sites ready for adsorbing MB species will not be enough. With increasing the composite dose, the number of effective positions for adsorption will increase, causing a better removal of MB[23]. Beyond 0.15 g, no further removal of MB was noticed due to the absence of MB species in the solution as an outcome of the adsorption by the composite.

The temperature's effect on the MB removal % by the KC-BC composite (Figure 4d) indicated to an increase in the adsorption removal of MB as temperature raised from 10 °C to 40 °C. This finding suggests that upon raising the temperature, collisions among the composite particles with MB species will increase, leading to better removal of the dye from the solution. Also, as the adsorption of MB by the aforesaid composite increased with temperature, it can be said that the adsorption is endothermic. As the temperature rose above 40 °C, a decrease in the R% of MB was observed. These phenomena may primarily result from the raised temperature increasing the kinetic energy of MB species beyond the composite's surface's capacity to attract them, increasing the desorption rate.

The adsorption of MB using the aforementioned composite was examined over a range of time ranged from 5 to 180 min, with keeping other factors at their optimum values. Figure 4e showed an improvement in the R% of MB with extending time from 5 min to 120 min so that the maximum removal of MB was maximum at 120 min. Beyond this period, no further adsorption was observed due to the absence of sufficient empty pores for adsorption of MB species.

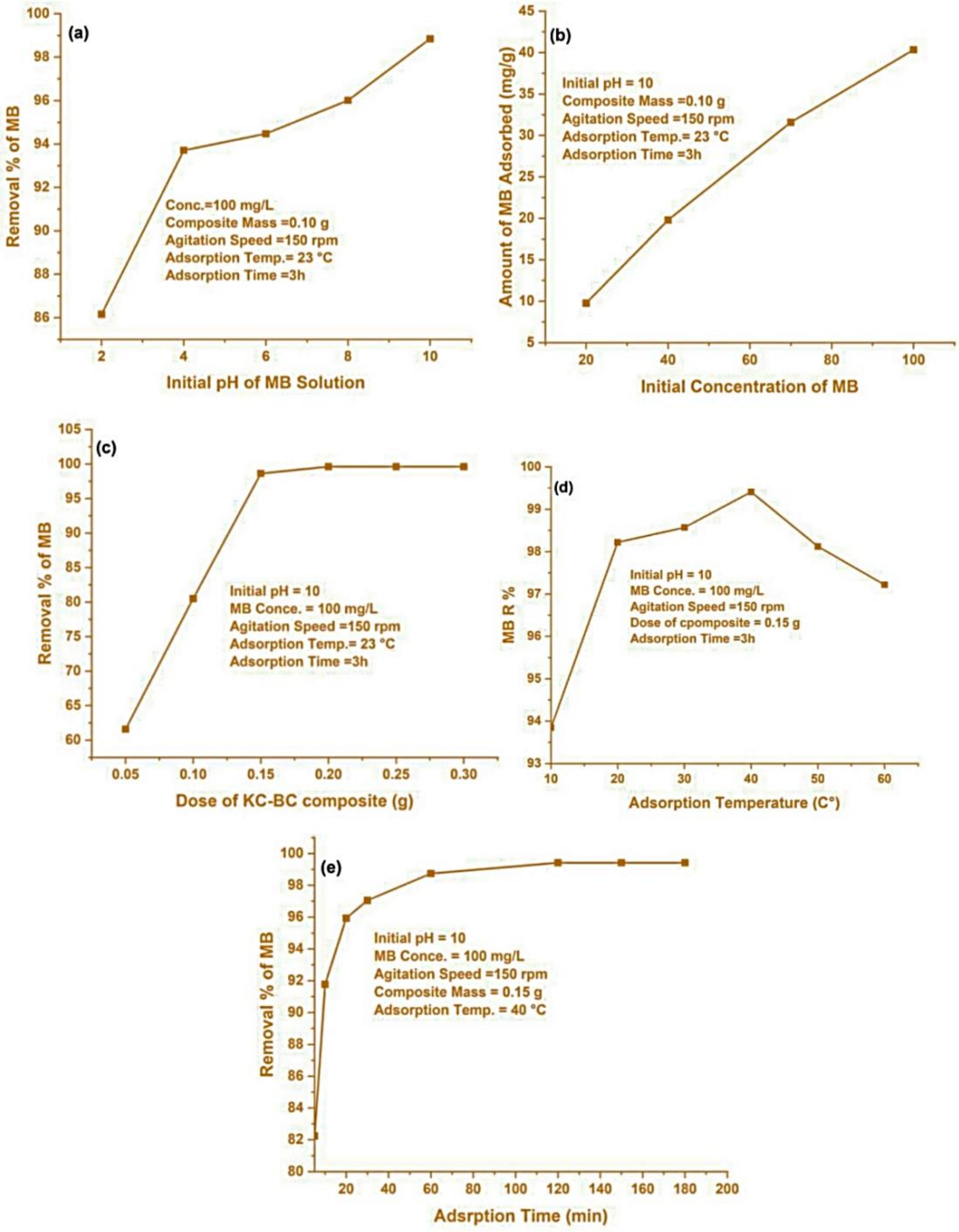

Fig. 4: *Effect of Parameters on MB Adsorption by Composite, (a) Initial pH, (b) Initial Concentration of MB, (c)Dose of KC-BC composite, (d) Adsorption Temperature, and (e) Adsorption Time.*

Isothermal and Kinetics Studies

Isotherm models can be used to clarify the kind of MB molecules interaction with the surface of the adsorbent [24]. As an outcome, the adsorption findings of MB by AC were analyzed employing the Langmuir and Freundlich isotherm models, whose linear expressions are shown in Eq.(3) and (4), respectively

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \ldots\ldots\ldots (3)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \ldots\ldots..(4)$$

where Ce represents the equilibrium mass balance of MB (mg/L), q_e refers to the capability (mg/g) of MB adsorptive, and K_L denotes the Langmuir constant. The Freundlich constants, KF and n, are associated with the adsorption ability and intensity of Freundlich. The monolayer coverage of the adsorbate on a homogeneous adsorbent's surfaces is provided by the Langmuir isotherm of adsorption, which also shows that no further adsorption occurs at those locations [25]. The separation factor (RL) is an important attribute of the Langmuir isotherm, and Eq.(5) was employed in calculating it.

$$R_L = \frac{1}{1 + C_0 K_L} \qquad (5)$$

This factor indicates how well an adsorbent can adsorb the adsorbate in particular. The preferred adsorption takes place when the R_L value is between $0 < R_L < 1$. A preferable adsorption of MB by the said composite was affirmed due to the value of RL, which was $0 < R_L < 1$. The Freundlich equation is a numerical formula that is able to express an adsorbent's surface heterogeneity[25]. This model also accounts for the fact that, for a given adsorbent, the amount of adsorbate absorbed increases with an increase in adsorbate concentration. For the adsorption to be preferable as per this model, the n's value must be > 1. As the value of n for MB adsorption by the as-created composite was above 1, the value of n was more than 1, its adsorption is favourable. According to the results tabulated in Table 1, the Langmuir model reflected the MB adsorption by the stated BC – KC composite better than Freundlich model. This finding was reached because the Langmuir model had a larger R^2 value than the Freundlich model, suggesting that a monolayer coverage of MB onto the composite was involved. It also implies that the influential5 distribution locations on the BC-KC composite surface is uniform[26]. The linear plots of the examined adsorption isotherms are shown in Figure.5.

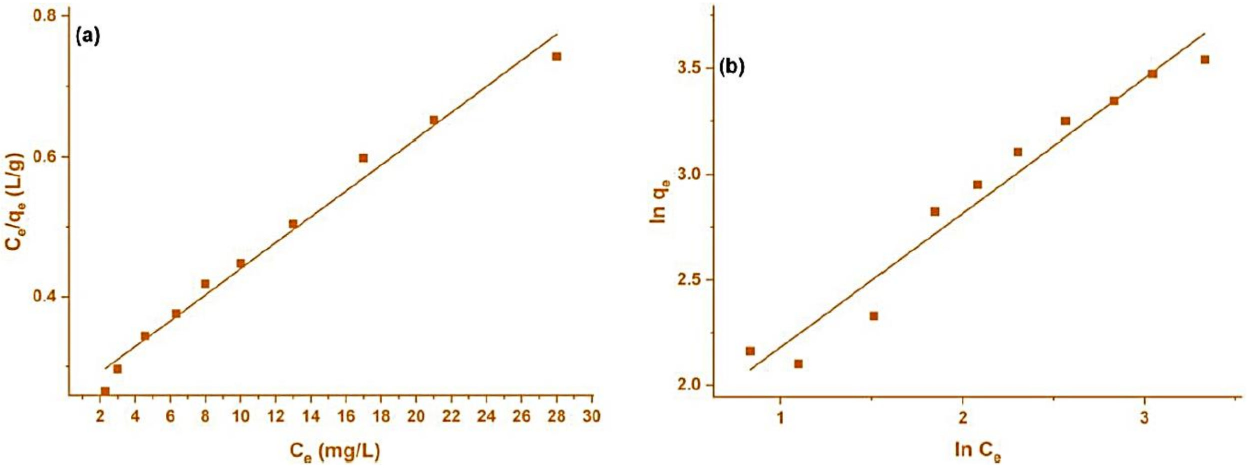

Fig. 5: *Adsorption isotherm (a) Langmuir (b) Frendlich models for MB dye adsorption by the BC-KC composites.*

Table 1: Constants of the Langmuir and Freundlich models for MB adsorption by the BC-KC composite.

Langmuir constants				Freundlich constants		
R^2	q_m (mg/g)	K_L	R_L	R^2	n (mg/g)	K_F
0.9843	55.55	0.0707	0.1247	0.9588	1.54	0.6368

In addition to the adsorption isotherms, numerous kinetic models have been applied for clarifying the adsorption of MB by previously created BC-KC composite[27]. The most widely utilized kinetic models, known as pseudo-1st-order and pseudo-2nd-order, were employed to explain the obtained BC-KC composite's MB adsorption. These models' linear formulas are shown in Eqs. (6) and (7), respectively:

$$\ln(q_e - q_t) = \ln(q_e) - k.t \dots\dots.(6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \dots\dots..(7)$$

Where q_t and qe (mg/g) denote respectively the quantity of MB adsorbed at equilibrium and t (minute), while k (minute) and k_2 (g/(mg.min^{-1}) signify the pseudo-1st-order and pseudo-2nd-order rate constants respectively. In addition to these models, the intra-particle diffusion model, which its linear form is given in Ed.(8), was employed to identify the diffusion controlled adsorption process.

$$q_t = k_{id} t^{1/2} + C \dots..(8)$$

Where, $t^{1/2}$ represents the square root of t, while C is constant (mg/g) refers to the thickness of the boundary layer, while k_{id} expresses intra-particle diffusion rate(mg/g $t^{0.5}$). This model assists also in identifying the process included the adsorption of dye by the composite, as well as determining the rate-controlling stages impacting MB adsorption kinetics [26].

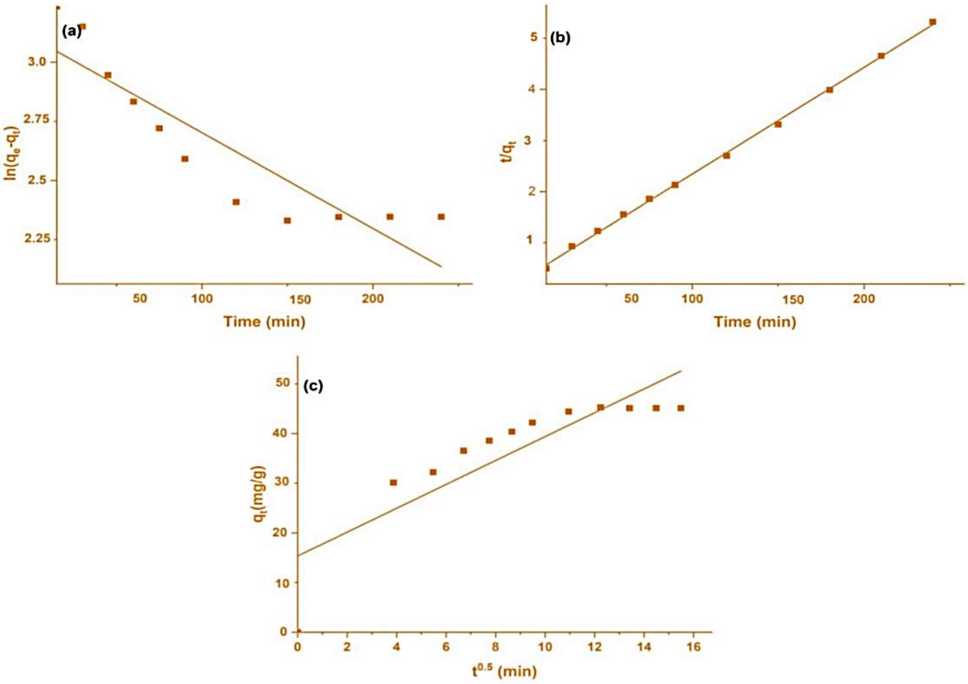

Fig. 6: *The adsorption kinetics fits for MB adsorption on composites DS-Kc . (a) pseudo first-order model, (b) pseudo -second-order model . (c) intra particle diffusion model of MB on BM-KC composite.*

Table 2 shows the R^2 values for the kinetics models in addition to constant values. According to the results offered in the pre-referred table, the pseudo-1st-order model's R2 was significantly lower than the pseudo-2nd-order model's, which was close to unity. Furthermore, q_e value of the pseudo-1st-order model was significantly below the value observed experimentally. In contrast, the q_e for the pseudo-2nd-order model was reasonable and extremely near to that achieved in an experiment. According to all of these findings, the pseudo-2nd-order model is more convenient than the other models to describe the adsorption kinetics of MB elimination by the BC-KC composite, demonstrating that chemisorption chemical process is included in the elimination of MB species from aqua media. The MB adsorption by the BC-KC composite was not represented by an origin in the intra-particle diffusion plot, revealing that there are several rate-controlling phases besides diffusion in MB adsorption by the BC-KC composite. The linear plots of the investigated kinetic models are depicted in Figure 6.

Table 2: The Psedue-1st-order and Psedue-2nd-order constants for MB adsorption by BC-KC composite.

Psedue-1st-order			Psedue-2nd-order			Intra-particle diffusion		
R^2	q_e (mg/g)	k_1	R^2	q_e (mg/g)	k_2	R^2	C	K_{id}
0.8085	1.30	0.0040	0.9989	47.89	0.0017	0.7469	15.37	2.40

Reusability of Composites

One of the most important feature of an adsorbent is its reusability as a result of its importance on the application at the industrial scale[28]. As such, the spent composite was regenerated and reused for many cycles. For this purpose, different approaches of regeneration were adopted. The first, the spent adsorbent was treated with ethanol, dried, and then applied to remove MB from its aqueous solution under typical conditions. The R% of MB by this method reached 69.75 %. So, to enhance the efficiency of this approach, after treating the spent composite with ethanol and then dried, it was thermally activated at 500 °C for 30 min. The use of this sample exhibited a removal efficiency of 99.249%. In the second method of regeneration, the spent composite was thermally activated at 500 °C for 30 min, and then reused for the same purpose. The R% of MB by this method reached 99.45 % in the 1st cycle, while it amounted to 99.15 % in the 2nd cycle. These findings show that the type of regeneration method, besides its conditions, has a great impact on the regeneration of spent adsorbent.

Comparison of KC-BC composite with other sorbents

Bioaccumulation of dyes in aqueous ecosystems has resulted in dyes resistance to decompose. MB is among the most significant dyes contaminating water resources. Table (3) compares the adsorption capacity of the KC-BC composite with other investigations to highlight the capability of the prepared KC-BC for MB removal.

In comparison with other sorbents, KC-BC composite represented good adsorption capacity; besides the synthesized composite is green, don’t required chemicals, cost-beneficial, and available.

More importantly, KC-BC composite separated easily due to its composite nature from the solution when the adsorption process ended. Considering all these, suggesting KC-BC composite as an effective adsorbent for MB removal seems rational**.**

Table 3: Comparing the generated composite's adsorption capacity in the current study to the literature on the elimination of MB.

Adsorbent	Adsorption conditions	Adsorption capacity (mg/g)	References
Kaolinite clay-pumpkin seed cake composite	pH 9.98 dose 1.56 g/L 55 min	119.7	[13]
ZnO/biochar (Bamboo stakes) nanocomposites	MB 160mg/g, catalyst dosage 25%,UV light 225 min	160	[28]
Clay biochar composites	Co 20 ppm, pH 5.7 22±0.5° C	7.90	[29]
Iron Oxide Magnetic Nanoparticles Coated with Sugarcane Bagasse	Co 10ppm Dose 0.6 g pH 7.0 60min	37.45	[30]
Sludge- rice husk biochar composites	Co 100 ppm, dose 1g, pH 6.48 , 25±0.5° C, 360 min	14.493	[31]
IKC-DS composite	Co 100 ppm, dose 0.15g, pH 10, 40° C, 120 min	55.55	Present work

Conclusion

To solve the ubiquitous water pollution challenges, this research focus on the use of natural clay and locally available biomass sources as cheap and available precursors for producing a novel adsorbent. A novel KC-BC was synthesized from the said raw materials and then applied in removing MB dye from its aqueous media. The results affirmed that the prepared can be recommended as a new adsorbent for eliminating organic dyes from wastewaters at moderate conditions.

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مركب طبيعي (طيني- فحم حيوي) لإزالة أزرق الميثيلين من الطور المائي

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الخلاصة:

كان الهدف الرئيسي للبحث الحالي هو تطوير مركب جديد ممتز، وهو طين الكاولين والفحم الحيوي للتخلص من أزرق الميثيلين والتي تعد صبغة متعددة التطبيق وخطرة متواجدة في مياه الصرف الصحي وذلك عن طريق مزج طين الكاولين مع بذور التمر بنسبة 1:1تليها الكربنة عند 500 درجة مئوية لمدة ساعة واحدة . تم تمييز المركب الناتج بواسطة تقنيات مختلفة لتحديد الخصائص المورفولوجية والكيميائية للمركب كانت مساحة السطح للمركب 33.1 م^{2}/غم في حين بلغ متوسط حجم المسام 13.45 نانوميتر مما يشير إلى مسامية المسامية. تم استخدام المركب المحضر في امتزاز صبغة ازرق المثيلين من المحلول المائي وبلغت نسبة الاستعادة 99.42% عند استخدام 0,15 غم من المركب المحضر وبدرجة 40 مئوية وكانت افضل دالة حامضية 10 .تم التحقق من امكانية اعادة استخدام المركب .

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