Acta Polytechnica **59**(2):192–202, 2019
doi:10.14311/AP.2019.59.0192

ADSORPTION OF CATIONIC DYE FROM AQUEOUS SOLUTION USING COMPOSITE CHICKEN EGGSHELL - ANTHILL CLAY: OPTIMIZATION OF ADSORBENT PREPARATION CONDITIONS

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Abstract. A composite adsorbent was prepared from anthill and eggshell mixture, using an incipient wetness impregnation method and it was used for an adsorption of cationic dye (methylene blue, MB) from an aqueous solution. The effects of three preparation parameters including calcination temperature, calcination time and mixing ratio of eggshell to anthill on the MB uptake were investigated using the central composite design (CCD) of response surface methodology (RSM). A quadratic model was developed to predict the response with a high accuracy. The optimal adsorbent sample was characterized by scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy and X-ray fluorescence (XRF) spectroscopy. The obtained results revealed that the calcination temperature significantly affected the MB adsorption. The optimum MB uptake of 23.87 mg/g was achieved under the optimum conditions including a calcination temperature of 823.45 °C, calcination time of 3.54 h and eggshell/anthill mixing ratio of 1.89:1. A detailed characterization of an optimal adsorbent sample confirmed the presence of pores, active functional groups and various molecular adsorption sites on its surface. Equilibrium adsorption isotherms and kinetics were also studied and it was revealed that the isotherms and kinetics data fitted well to the Freundlich model and pseudo-second-order kinetics model, respectively.

Keywords: Anthill, adsorption, central composite design, eggshell, methylene blue.

1. Introduction

The generation of wastewater containing dye by textile industry has become an issue as its release into the environment usually leads to water pollution. Generally, these effluents contain a significant amount of basic dyes that are harmful to human beings and aquatic species. For example, they give colour to surface water, which alters the availability and toxicity of heavy metals to aquatic life [1]. In the last decade, most researchers are searching for appropriate treatments in order to remove these harmful pollutants and to achieve a complete degradation of effluent containing dyes [2]. In general, treatment of industrial effluents, which contain dyes, is being achieved by the Fenton-biological method, ultrafiltration, ion exchange membrane, chemical precipitation, electrochemical degradation, photocatalytic process and adsorption [3–8]. Among these treatment methods, adsorption process is found to be efficient, because most dyes are difficult to breakdown biologically, hence can easily be removed by porous solid material called adsorbent [1]. Researches have proven that adsorbents, such as alumina, silica gel, commercial activated carbon and molecular sieves, are effective for the removal of dyes from wastewater [9, 10]. However, these adsorbents are expensive, thus making the search for alternative adsorbents necessary. Such alternatives could be sourced from agricultural waste/biomass [11, 12], naturally occurring materials [13], microorganism [14] and industrial waste [15].

In the present study, the aim is to prepare a composite adsorbent from an anthill clay and chicken eggshells, optimize the preparation process condition and apply to methylene blue (MB) adsorption. The MB is chosen among the available dyes because of its visibility even in small quantity. An anthill is a form of clay, which is formed at the entrances of ant colonies [16]. It has numerous industrial usefulness, including ceramic, cement, bricks, and sand casting making [17] and catalyst synthesis [18]. Chicken eggshells are agricultural waste, which poses a solid waste disposal menace. Eggs are commonly a consumable product worldwide because of its nutritional values [19]. However, over 90% by weight of a dried eggshell is calcium carbonate ($CaCO_3$), and therefore, it is possible to synthesize calcium oxide (CaO) based adsorbent from waste eggshells. Several researchers have synthesized CaO based adsorbents from different birds' eggshells for the removal of MB from an aqueous solution [20, 21]. Meanwhile, the adsorption site in an activated eggshell adsorbent had been determined to be only CaO [22], which might not be sufficient enough to completely remove the adsorbate. This is substantiated by Tsai et al. [20], who determined the adsorption capacity of an eggshell adsorbent for MB removal to be relatively low (0.8 mg/g). To the best of my knowledge, no study has been conducted on the optimization of preparation conditions of a composite adsorbent from eggshells and anthill clay for MB dye adsorption using the design of an experiment.

The use of a suitable statistical design of experiment in determining the influence of operational parameters is necessary. However, among the various optimization and statistical tools contained in design expert software, response surface methodology (RSM) has been regarded as the most powerful tool because it could identify and quantify interactions between variables [22]. It has been widely employed in numerous chemical engineering operations, such as catalysis, coagulation, photocatalytic degradation, adsorption and biodiesel synthesis [2, 9, 23, 24]. The application of statistical experimental design techniques in the development of the adsorption process can result in a reduced process variability coupled with the requirement of less resources (time, raw materials and experimental work) [10]. Number of experimental runs required is dependent on the type of the design chosen: central composite design (CCD) or Box-Behnken designs [24, 25]. The difference between these two forms of the RSM design is the number of runs required and combinations of the levels [10]. In the case of the CCD, almost as much information is provided as a multilevel factorial, which requires very few experiments compared to a full factorial. Therefore, in this present study, the central composite design (CCD) has been employed for the optimization of the preparation condition of a composite eggshell anthill clay (CEAC) adsorbent. The variables considered were calcination temperature, calcination time and mixing ratio of eggshell to anthill clay. Also, the optimal CEAC adsorbent sample was characterized by using various characterization techniques, such as scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy and X-ray florescence (XRF). In addition, adsorption isotherms and kinetics parameters were evaluated in order to understand the adsorption mechanisms of MB dye onto CEAC.

2. Material and methods

2.1. Material

The chicken eggshells were collected from the cafeteria of postgraduate students, Afe Babalola University, (ABUAD), Ado-Ekiti, Nigeria. While the anthill situated behind Fidelity Bank, ABUAD, Ado-Ekiti, Nigeria was harvested. The cationic dye used as adsorbate was methylene blue (MB), which was collected from Department of Chemistry, ABUAD, Ado-Ekiti, Nigeria. MB's molecular formula and weight are $C_{16}H_{18}N_3CIS$ and 319.85 g/mol respectively. A 1000 mg/L stock solution of MB was prepared by dissolving 1.00 g of MB dye in 1000 mL of de-ionized water. Various solutions of needed initial MB concentrations (25, 50, 100, 150, 200, 250 and 300 mg/L) were obtained by diluting the stock solution with the required amount of de-ionized water.

2.2. Preparation of composite eggshell-anthill clay (CEAC) adsorbent

The waste eggshells were carefully washed to remove the white membrane and impurities from it and was, thereafter, heated up at 110 °C in an oven overnight in order to remove residual moisture. The dried eggshells were ground with the aid of a mechanical grinder and then kept in a covered plastic container. The anthill was crushed into a powder, and thereafter kept in a covered plastic container. Both powders' particles were sieved to obtain a particle size of 125 – 300 μm. The screened eggshell and anthill powders were mixed in different proportions of anthill to eggshells according to the data points suggested by the central composite design (Table 1). An adequate amount of distilled water was added to the mixtures contained in a beaker to form a suspension and stirred for 2 h on a hot plate to achieve a homogenous mixture. The mixtures were then filtered and the residue was placed in an oven to remove any excess water at a temperature of 125 °C for 2 h. The twenty different proportions of dried mixed anthill-eggshell powders were thus calcined in a muffle furnace at a different temperature in a range between 700 and 900 °C, and different corresponding time in a range between 1 and 4 h with a heating rate of 10 °C/min.

2.3. Design of experiment

In order to evaluate the effect of adsorbent preparation process parameters on the MB removal uptake, three main factors were considered: calcination temperature, x_1 °C, calcination time, x_2 h and mixing ratio of eggshells to anthill, x_3. A total of twenty experiments were conducted in this work, $2^3 = 8$ factorial points, 6 axial points and 6 replicates at the centre point. The experimental ranges and levels of the adsorbent preparation variables for the MB removal are given in Table 1. The extreme values of those variables considered were chosen based on results obtained from a preliminary experiment. The coded values were denoted by -1 (low level), 0 (center point), +1 (high level) and $\pm\alpha$ (distance from the centre point, which can be inside or outside the range).

The MB uptake, a response, was used to develop a mathematical model that correlates it to the adsorbent preparation process parameters by the second-order polynomial equation expressed in Eq. 1. However, the response was determined via an adsorption of MB onto prepared composite adsorbents.

$$Y = a_0 + a_1x_1 + a_2x_2 + a_3x_3 + a_{12}x_1x_2 + a_{13}x_1x_3 + a_{23}x_2x_3 + a_{11}x_1^2 + a_{22}x_2^2 + a_{33}x_3^2 \quad (1)$$

2.4. Batch equilibrium studies

Batch mode adsorption experiments were performed in twenty sets of 250 mL conical flasks in which 100 mL of the MB solution with an initial concentration of

Variables	Description	Level				
		$-\alpha$	-1	0	1	$+\alpha$
x_1	Calcination temperature (°C)	668.4	700	800	900	931.6
x_2	Calcination time (h)	0.5	1	2.5	4	4.5
x_3	Mixing ratio of eggshell to anthill clay	0.5	1	2.5	4	4.5

Table 1. Levels of the composite adsorbent preparation variables chosen for this study.

50 mg/L was charged into each flask and 0.2 g of each of the prepared composite adsorbent was also added to each flask. The flask and its contents were agitated in a thermostatic water bath shaker (SearchTech Instrument) operated at 30 °C and 150 rpm until an equilibrium was reached. The residual MB concentration was analysed on a double beam UV-vis spectrophotometer (UV- 1920 Jenway, UK) at a maximum absorbance wavelength of 660 nm. The uptake of the MB was thus calculated by using Equation 2.

$$q_e = \frac{(C_0 - C_e)V}{w} \tag{2}$$

In order to evaluate the adsorption mechanisms of MB dye onto the composite adsorbent, batch adsorption experiments were further conducted at different concentrations of MB dye (25 – 300 mg/L) using an optimal composite eggshell-anthill clay (CEAC) sample as an adsorbent at the same operating parameters employed above. The un-adsorbed MB concentration was also analysed on the same double beam UV-vis spectrophotometer at a maximum absorbance wavelength of 660 nm and the MB dye adsorbed was also determined using the same eq. 2.

2.5. Batch kinetic experiment

The procedure employed in conducting the kinetic experiment was similar to that of the equilibrium study. The experiment was conducted by taking samples from the aqueous solutions at a pre-set time interval of every 10 min and the concentration of the residual MB dye concentrations were similarly determined. The kinetic experiment was carried out by considering the MB dye concentration of 50 mg/L using an optimal CEAC sample as an adsorbent at the same operating parameters employed in section 2.4. The dye uptake at a time t, q_t was thus calculated as follows.

$$q_t = \frac{(C_0 - C_t)V}{w} \tag{3}$$

2.6. Characterization of the prepared composite adsorbent

The properties of the composite adsorbent prepared under optimum conditions was determined by using scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy and X-ray fluorescence (XRF) techniques. The SEM image of the optimal composite adsorbent was viewed through a microscope (SEM, JEOL-JSM 7600F) in order to examine its surface morphology, while the FTIR spectrophotometer (IR Affinity-1S, Shimadzu, Japan) was employed to determine the surface functional groups of the prepared adsorbent and the IR spectra of the sample studied were collected in the range of 4000-500 cm^{-1}. The chemical composition of the as-prepared CEAC adsorbent as well as the raw anthill and raw eggshell samples were determined by the XRF analysis.

2.7. Adsorption isotherms

The experimental results were analysed using two-parameter isotherm models (Langmuir and Freundlich isotherms). The essence of the adsorption isotherm is to correlate the bulk concentration of the MB dye to the equilibrium amount of the MB dye adsorbed at the interface [26]. The Langmuir model assumes a monolayer, homogenous adsorption site and thus, saturation is attained, beyond which no further attachment of the adsorbate on the adsorbent takes place. The nonlinear form of the Langmuir model is given by Eq. 4.

$$q_e = \frac{q_{max} b C_e}{(1 + bC_e)} \tag{4}$$

Another important feature of the Langmuir isotherm model is the separation factor (R_L), which determines the nature of the isotherm shape. It can either be favourable ($0 < R_L < 1$), unfavourable adsorption ($R_L > 1$), linear ($R_L = 1$) or irreversible adsorption ($R_L = 0$). The dimensionless parameter is given by Eq. 5.

$$R_L = \frac{1}{(1 + bC_0)} \tag{5}$$

The Freundlich model assumes multilayer adsorption on heterogeneous surface and it is expressed in it nonlinear form as follows:

$$q_e = k_f C_e^{1/n} \tag{6}$$

2.8. Adsorption kinetics

In the present study, two different adsorption kinetic models, namely pseudo-first-order, and pseudo-second-order were applied to evaluate the extent of the utilization of the adsorption capacity with respect to a contact time between the MB dye (adsorbate) and the CEAC (adsorbent). The linearized forms of the pseudo-first-order [27], and pseudo-second-order [28] models are expressed in Eqs. 7 and 8, respectively as follows:

$$\log(q_e - q_t) = \log(q_e) - \left(\frac{k_1}{2.303}\right) t \qquad (7)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \qquad (8)$$

3. Results and discussion

3.1. Central composite design (CCD) model and analysis

The three-factor CCD matrix, as generated by the Design-Expert software (Trial version 7.0.0), and the experimental data obtained in the batch adsorption runs are presented in Table 2. According to the results obtained, an empirical model that correlates the dependent to independent variables was obtained and given by the Equation 9. Equation 9 represents the empirical model in terms of coded values.

$$\begin{aligned} Y = 24.43 + 2.04x_1 + 0.86x_2 + 0.95x_3 - \\ - 2.21x_1x_2 - 0.52x_1x_3 - 0.25x_2x_3 - \\ - 3.13x_1^2 - 0.12x_2^2 - 0.003x_3^2 \end{aligned} \qquad (9)$$

The amounts of the MB adsorbed by various samples of the CEAC have been predicted by Eq. 2 and presented in Table 2. There was a cordial agreement between the predicted and experimental values of the MB uptake. The correlation between the actual and predicted responses was evaluated by a correlation coefficient (R^2) and the value obtained ($R^2 = 0.9409$) implies that the predicted values agreed excellently well with the experimental values. This indicates that only 94.09% of the total variations for the MB uptake are described by the model, while only about 5.91% of the variation is not explained by the model. The standard deviation was also used to measure the goodness of a fit. According to Tan et al. [9], the smaller the standard deviation is, the more accurate the dependent variable (response) is predicted by the model. The standard deviation for the developed model was found to be 1.07 and this indicates that the predicted values for the MB uptake matched the experimental values reasonably well.

The analysis of variance (ANOVA) is also a measure of the goodness of a fit. It is required to test the significance and adequency of the model [10]. ANOVA usually shows whether the variation from the developed model is significant or not when comapred with the one associated with the residual error [22]. This comparison is done by F-value, which is the ratio of the model mean square to the residual error. Accoding to Giwa et al. [10], the experimental result is said to be well predicted by the model, if the F-value obtained is greater that the tabualted value of the F-distribution. However, the F-value obtained herein is 17.69 indicating the adequency of the model fits. More so, x_1, x_2, x_3, x_1x_2, and x_1^2 are regarded as significant model terms, because their values of "$prob > F$" are less than 0.05. Based on this result, the three independent variables studied had significant effects on the MB dye uptake. However, the calcination temperature (x_1) had the most significant effect on the response due to its F-value, which was discovered to be 41.71 (Table 3).

Fig. 1 shows the effect of the calcination temperature and calcination time on the MB dye uptake (mg/g) for the mixing ratio of eggshells to anthill clay of 2.5:1. As it can be seen from Fig. 1, the MB dye uptake increased with the increasing calcination temperature and calcination time. The reason for this observation is because both variables interact and were found to have synergistic effects on the adsorption capacity of the prepared composite adsorbent. As widely reported in literature, a high calcination temperature and calcination time enhanced pore creation and enlargement [9, 18]. Thus, it indicates a good possibility for the adsorption of MB [9]. This phenomenon is further affirmed by the fact that the interaction of the calcination temperature with time has the most influential effect on the MB adsorbed as indicated by the highest F-value in the ANOVA (Table 3) compared to other interaction terms.

3.2. Optimization of CEAC preparation process variables

The optimum CEAC preparation conditions were established to be the calcination temperature of 823.45 °C, calcination time of 3.54 h and the mixing ratio of eggshells to anthill clay of 1.89:1, which resulted in a 23.87 mg/g of MB uptake. However, the predicted MB dye uptake was calculated based on the empirical model developed by the design expert software and was found to be 24.93 mg/g. Thus, the experimental value is in a good agreement with the predicted value with a relatively slight error between the two responses, which was only 4.44%.

3.3. Characterization of CEAC adsorbent prepared under optimum conditions

The SEM image shown in Fig. 2A revealed the surface morphology of the CEAC sample prepared under optimum conditions. It was observed that the surface of the adsorbent is rough, irregular and possesses pores of different sizes, which enhance the adsorption of the MB dye. After the adsorption of dyes, the morphology of the adsorbent changes and the pores initially present on its surface have been blocked by the dye molecules (Fig. 2B).

Fig. 3 shows the FTIR spectrum of the CEAC sample prepared under the optimum conditions. In the spectrum, a number of absorption bands are displayed indicating that several functional groups are present

Run No.	Composite adsorbent preparation variables			MB uptake, Y (mg/g)	
	Calcination temperature x_1 (°C)	Calcination time x_2 (h)	Mixing proportion of eggshell to anthill x_3	Predicted	Experimental
1	0 (800)	0 (2.5)	$+\alpha$ (4.5)	25.63	24.51
2	$+\alpha$ (931.6)	0 (2.5)	0 (2.5)	21.69	21.71
3	+1 (900)	-1 (1)	-1 (1)	23.85	23.72
4	$-\alpha$ (668.4)	0 (2.5)	0 (2.5)	16.32	15.67
5	-1 (700)	+1 (4)	+1 (4)	23.40	23.80
6	0 (800)	0 (2.5)	$-\alpha$ (0.5)	23.12	23.61
7	-1 (700)	-1 (1)	+1 (4)	17.76	18.37
8	-1 (700)	+1 (4)	-1 (1)	20.95	21.97
9	0 (800)	$-\alpha$ (0.5)	0 (2.5)	23.08	24.18
10	+1 (900)	+1 (4)	+1 (4)	22.02	23.35
11	+1 (900)	-1 (1)	+1 (4)	25.21	24.46
12	0 (800)	$+\alpha$ (4.5)	0 (2.5)	25.35	23.62
13	-1 (700)	-1 (1)	-1 (1)	14.31	13.25
14	+1 (900)	+1 (4)	-1 (1)	21.67	21.33
15	0 (800)	0 (2.5)	0 (2.5)	24.43	24.38
16	0 (800)	0 (2.5)	0 (2.5)	24.43	24.48
17	0 (800)	0 (2.5)	0 (2.5)	24.43	24.65
18	0 (800)	0 (2.5)	0 (2.5)	24.43	24.60
19	0 (800)	0 (2.5)	0 (2.5)	24.43	24.76
20	0 (800)	0 (2.5)	0 (2.5)	24.43	24.49
$R^2 = 0.9409$; $Adj - R^2 = 0.8877$; $st.dev = 1.07$					

Table 2. Experimental design matrix and responses.

Source	Sum of squares	Degree of freedom	Mean square	F-value	Prob > F
Model	182.68	9	20.30	17.69	< 0.0001
x_1	47.84	1	47.84	41.71	< 0.0001
x_2	8.57	1	8.57	7.47	0.0211
x_3	10.35	1	10.35	9.03	0.0132
x_1x_2	38.94	1	38.94	33.95	0.0002
x_1x_3	2.19	1	2.19	1.91	0.1967
x_2x_3	0.51	1	0.51	0.44	0.5220
x_1^2	68.27	1	68.27	59.51	< 0.0001
x_2^2	0.10	1	0.10	0.091	0.7696
x_3^2	$6.17 \cdot 10^{-3}$	1	$6.17 \cdot 10^{-3}$	$5.379 \cdot 10^{-3}$	0.9430
Residual	11.47	10	1.15	-	-

Table 3. Analysis of variance (ANOVA) for response surface quadratic model for MB dye adsorption.

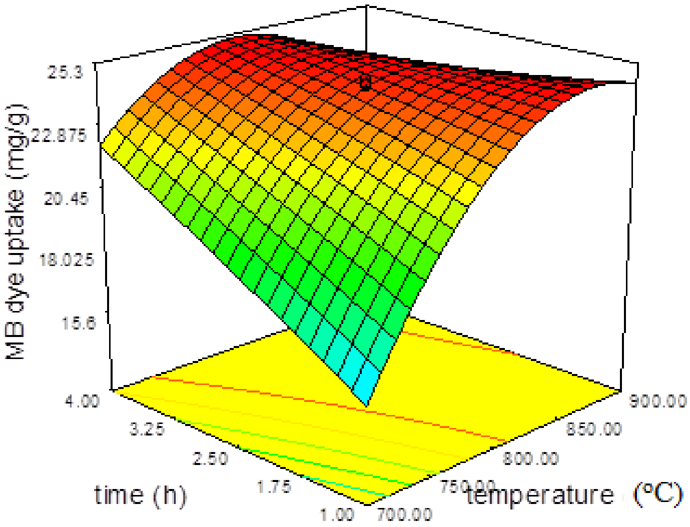

Figure 1. The response surface plot of MB uptake (mg/g) as the function of calcination temperature and calcination time at fixed 2.5:1 mixing ratio of eggshell to anthill clay.

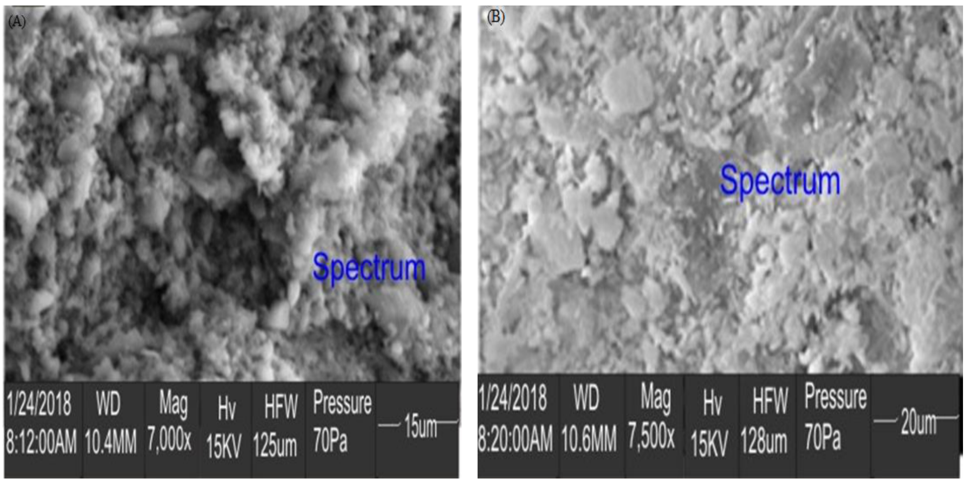

Figure 2. SEM images of CEAC adsorbent (A) before adsorption and (B) after adsorption.

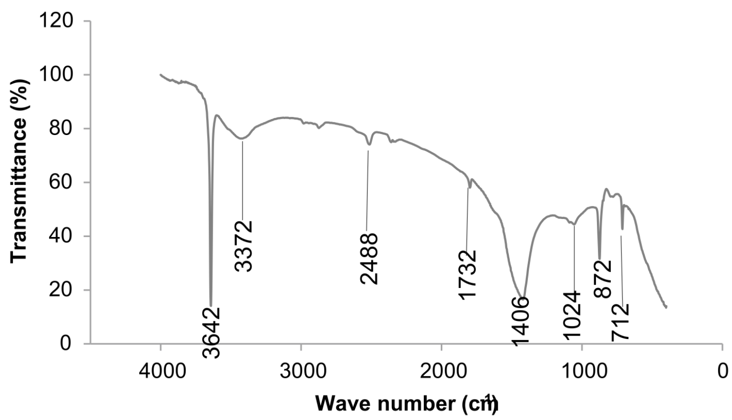

Figure 3. FTIR spectrum of CEAC adsorbent prepared under optimum conditions.

on the adsorbent surface. The sharp and broad absorption bands at 3642 cm^{-1} and 3372 cm^{-1} respectively are assignable to a hydroxyl bond from the adsorbed moisture. The absorption bands observed at 2488 cm^{-1} and 1732 cm^{-1} are attributed to S-H stretching and C=O stretching respectively. While the band at 1024 cm^{-1} is due to the P-O-C antisymmetric stretching. The optimal CEAC adsorbent also shows another set of bands at 1406 cm^{-1}, 872 cm^{-1} and 712 cm^{-1} which can be respectively attributed to the in-plane-OH bending, the CH out-of-plane deformation and OH out-of-plane deformation. The high adsorption capacity of the optimal CEAC in the adsorption of dye from an aqueous solution may be due to the presence of the surface functional groups, among which carboxylic (C-O and C=O) and hydroxyl (OH) groups play the main role.

Table 4 depicts the chemical compositions of a raw anthill, raw eggshell and optimal CEAC adsorbent, which were determined by the XRF analysis. The major composition in the anthill sample were determined to be silica (SiO_2), alumina (Al_2O_3) and zirconia (ZrO_2), while the main mineral composition in eggshells was found to be calcium oxide (CaO). The high LOI in the raw anthill and eggshell samples is due to the presence of organic matters and moisture content [20]. However, CaO constitutes the larger amount in an optimal CEAC sample, followed by SiO_2. It was observed that the calcination at 823.45 °C for 3.54 h was able to transform the mixed eggshell-anthill clay into a synergetic mixed oxide structure. Thus, the result obtained indicates that not only CaO plays a significant role in the CEAC performance but also the other metal oxides (SiO_2, Al_2O_3, ZrO_2 and Fe_2O_3) contained in the optimal CEAC sample can determine the form of the molecular adsorption sites and their level of capacity. The presence of SiO_2 in the composite adsorbent plays a key role in the adsorption [29]. SiO_2 is known as an inorganic adsorbent and could adsorb either positive or negative contaminant depending on the pH of the solution [30]. Its surface contains silinol (OH group), which can act as the centre of a molecular adsorption during their specific interaction with adsorbates [31]. Other mineral oxides, such as Al_2O_3, Fe_2O_3 and ZrO_2, also exhibit the phenomenon of electrostatic interaction [30, 32, 33]. This indicates that the maximum dye adsorption capacity of the CEAC can be attributed to the electrostatic interaction of the adsorbate with the surface CaO, SiO_2, Al_2O_3, ZrO_2 sites. This observation could be the reason why the CEAC adsorbent had an improved performance in the adsorption of the MB dye compared to the adsorbent prepared only from eggshells, which has a single adsorption site (CaO).

3.4. Adsorption isotherm

The nonlinear plots of Langmuir and Freundlich models, amount of the MB dye adsorbed per unit mass of CEAC, q_e (mg/g) versus equilibrium concentration (C_e) at fixed temperature of 30 °C are depicted in Fig. 4. The values of parameters contained in Langmuir (q_{max} and b) and Freundlich (k_F and n) models were all determined from the plots and are presented in Table 5 with their correlation coefficients (R^2). The best model was selected based on the R^2 value and it was found out that Freundlich model provided the best fit with the experimental data. This indicates that the CEAC adsorbent surface is dominated by the multilayer and heterogeneous active sites. The value of R_L (0.2717), as indicated in Table 5, is less than 1, which suggests a favourable adsorption process. This is confirmed by the magnitude of the Freundlich exponent n (3.24) which also indicates a favourable adsorption condition, because n is greater than 1.

A comparison of the adsorption capacities of the CEAC and other various adsorbents for the MB uptake from an aqueous environment are presented in Table 6. The CEAC is found to possess a relatively large adsorption capacity of 43.46 mg/g and this implies that the adsorbent is highly effective for the treatment of water and wastewater containing dye. It can be concluded that the value of q_{max} agrees excellently well with those reported by the previous researchers [28, 39], indicating that the MB dye could be effectively adsorbed on the CEAC synthesized in this work. In addition, the aim to investigate the performance of the CEAC in the adsorption of the MB from aqueous solution was successful as the uptake capacity of the CEAC (43.46 mg/g) is far greater than the value (0.8 mg/g) reported for the eggshells by Tsai et al. [20]. This result indicates that the anthill clay played a significant role in improving the adsorption properties of the prepared adsorbent.

3.5. Adsorption kinetics

The kinetics parameters for the MB dye adsorption by the CEAC were determined from the combined plots of $\log(q_e - q_t)$ against t (pseudo-first-order kinetics) and t/q_t against t (pseudo-second-order kinetics) shown in Fig. 5. The magnitudes of the kinetics parameters are presented in Table 7. The results reveal that the calculated q_e (cal) value does not match with experimental q_e (exp) value at an adsorbate concentration of 50 mg/L with low R^2 value (0.9861). Therefore, the adsorption of the MB dye onto the CEAC cannot be best predicted by a pseudo-first-order kinetics model. However, the high R^2 value (0.9989) and cordial agreement between the calculated and experimental q_e values of pseudo-second-order kinetics model compared to the pseudo-first-order kinetics as can be seen in Table 7 indicate that MB dye adsorption onto CEAC can be well predicted by the pseudo-second-order kinetics model.

4. Conclusion

The process conditions for the preparation of the CEAC adsorbent developed for the MB adsorption from an aqueous solution were optimized. The effect

	Chemical composition		
Compound	Raw anthill	Raw eggshell	Optimal CEAC
SiO_2	63.51	0.79	9.83
Al_2O_3	16.21	0.12	2.62
Fe_2O_3	4.33	2.68	1.52
ZrO_2	6.83	-	1.15
MgO	-	1.78	0.14
CaO	1.22	86.74	81.57
K_2O	2.11	0.09	0.73
P_2O_5	-	1.21	0.58
TiO_2	1.08	-	-
SO_3	0.02	0.12	0.08
LOI	4.69	6.47	1.78

Table 4. Chemical composition analysis of raw anthill, raw eggshell and optimal CEAC adsorbent.

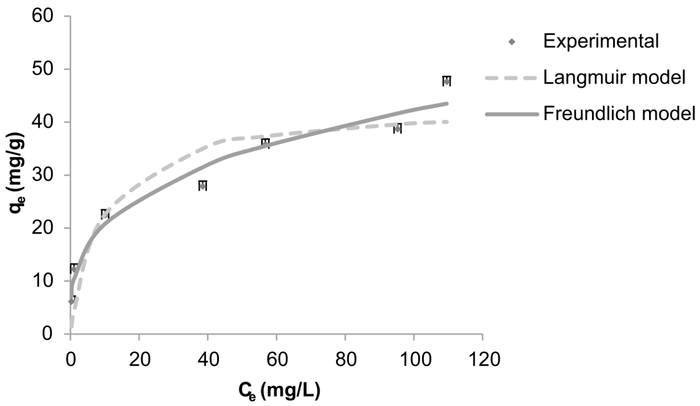

Figure 4. Two-parameter isotherm models for adsorption of MB dye onto CEAC at 30 °C.

Isotherm	Value
Langmuir	
q_{max} (mg/g)	43.46
b (L/mg)	0.1072
R^2	0.9068
R_L	0.2717
Freundlich	
k_F (mg/g(L/mg)$^{1/n}$)	10.19
n	3.24
R^2	0.9652

Table 5. Two-parameter isotherm constants and correlation coefficients for adsorption of MB dye on CEAC.

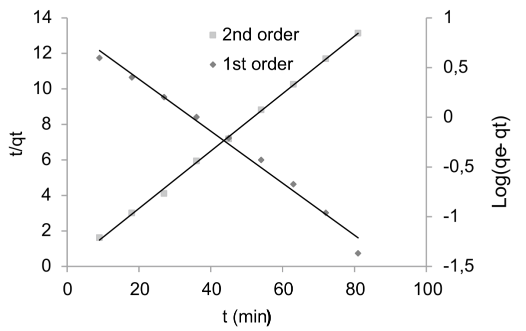

Figure 5. Pseudo-first-order and Pseudo-second-order kinetics for adsorption of MB dye onto CEAC.

of operating parameters on the adsorption of the MB was evaluated by the central composite design. The optimum values of the calcination temperature, calcination time and mixing ratio of eggshells to anthill clay, 823.45 °C, 3.54 h and 1.89:1 respectively, resulted in a 23.87 mg/g of the MB uptake. A high correlation coefficient ($R^2 = 0.9409$) exhibited by an analysis of variance indicated a satisfactory adjustment of the model developed with the experimental data. The result of the equilibrium adsorption isotherm analysis revealed that the isotherm data fitted well to the Freundlich model. The kinetic data analysis showed that the pseudo-second-order model provided the best fit with the experimental data suggesting a chemisorption process.

Adsorbent	Maximum adsorption capacity (mg/g)	Operating temperature (°C)	Reference
Eggshell	0.80	25	[20]
Eggshell membrane	0.24	25	[20]
Acrylic polymer/bentonite composite	36.60	30-70	[33]
Crushed brick	96.61	20	[34]
Rice husk	40.58	25	[35]
Wheat shells	16.56	30	[36]
Orange peel	18.60	30	[37]
Raw orange tree sawdust	39.68	20	[38]
Alkali-treated orange tree sawdust	78.74	20	[38]
CEAC	43.46	30	Present study

Table 6. Comparison of monolayer adsorption capacities of different adsorbents for MB dye adsorption.

Kinetic model	Value of parameter
Pseudo-first-order	
q_e (exp) (mg/g)	6.1720
q_e (cal) (mg/g)	2.4773
k_1 (min^{-1})	0.0603
R^2	0.9861
Pseudo-second-order	
q_e (cal) (mg/g)	6.1805
k_2 ($\text{gmg}^{-1}\text{min}^{-1}$)	0.8555
R^2	0.9989

Table 7. Kinetic parameters of MB dye adsorption on CEAC.

List of symbols

Y response variable of MB uptake [mg/g]
x_1 calcination temperature [°C]
x_2 calcination time [h]
x_3 mixing ratio of eggshells to anthill clay
a_{is} regression coefficients for linear terms
a_{ik} regression coefficients for quadratic terms
C_o initial concentration of MB dye in aqueous solution [mg/L]
C_e equilibrium concentration of MB dye in aqueous solution [mg/L]
C_t liquid-phase concentration of MB at time t [mg/L]
V volume of the MB dye solution [L]
w weight of adsorbent used [g]
q_e amount of MB dye adsorbed at equilibrium [mg/g]
q_{max} maximum adsorption capacity [mg/g]
b Langmuir equilibrium constant [L/mg]
R_L Separation factor
k_F Freundlich equilibrium constant [$\text{mg/g(L/mg)}^{1/n}$]
n adsorption intensity
q_t amount of MB dye adsorbed at time t [mg/g]
k_1 pseudo-first-order rate constant [1/min]
k_2 pseudo-second-order rate constant [g/(mg min)]

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