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Utilization of Macadamia seed husks as a low-cost sorbent for removing cationic dye (basic blue 3 dye) from aqueous solution

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ABSTRACT

This study examined the possibility of using Macadamia Seed Husks (MSH) as a low-cost sorbent for removal of recalcitrant Basic Blue 3 Dye (BB3). Batch adsorption experiments were performed to evaluate the capability of MSH in the removal of BB3 under varied experimental conditions. The percentage BB3 dye uptake surged with an increase in interaction time, MSH dosage, initial BB3 dye concentration, temperature and pH but significantly dropped with rise in particles size. The sorption equilibrium was attained within 40 min with adsorption efficacy of up to 99.8% at optimum pH 12. Experimental data obeyed the pseudo second order kinetic model with high regression coefficients ($R^2 > 0.9970$) depicting domination of chemisorption. Freundlich adsorption isotherms gave a good fit to the experimental data with high regression coefficient values ($R^2 = 0.9991$) suggesting multiple layer adsorption. The result proves that MSH can be a suitable and efficient alternative in the removal of synthetic dyes from industrial effluents.

1. Introduction

The increased demand for textile products across the world has fueled rise in consumption of toxic synthetic dyes by textile industries to color products resulting in severe aquatic pollution. Polluted wastewater is among the environmental challenges facing the modern world and impacting negatively on the population. Acidic and basic recalcitrant dyes present in industrial effluents have played a major role in causing this hazard. Presently, there are over 1.0×10^5 types of industrially prepared dyes [1]. Up to 7.0×10^5 loads of dyes are manufactured annually around the globe with 2.0×10^5 tons getting to water streams through disposal of untreated effluents [2]. It is estimated that about 15% of synthetic dyes spent in textile and other industries are released into the environment, aggravating grave aquatic pollution [3]. Aromatic structures of synthetic dyes makes them stable to heat, light, oxidation, chemical and biological degradation [4-6]. Moreover, their color is clearly visible even at very low concentration thus, affecting transmission of light and oxygen negatively affecting photosynthesis [7,8].

Azo dyes like Basic Blue 3 (Fig. 1) are toxic carcinogenic, mutagenic and hazardous. Basic blue 3 is majorly applied in the textile industries for direct printing acrylic carpet, dying wool, acrylic blended fabric and silk [9]. Poor dyeing procedure, low fixation, incomplete dye exhaustion, wastage, and poor fastness results in discharge of extremely colored wastewater that badly pollute aquatic environment. Direct exposure to the dye may cause skin and eye irritation/damage, acute toxicity upon inhalation, gut irritations, genetic mutations and cancer [10]. Due to these effects, effluent treatment prior disposal is mandatory.

Many wastewater treatment approaches comprising physical, chemical and biological treatment have been practiced with variable success. These technologies face many limitations like high cost, low performance, long operation time and production of high quantities of sludge [11]. Adsorption has been acclaimed as the best technique in effluent treatment owing to its, simplicity, ease of application, cost-effective, highly efficient, less operation time and possibility of recycling dye and adsorbent regeneration [12]. Activated carbon have been the main adsorbent for many industries but its high cost and loss during regeneration has restricted its use [13]. This has moved many researchers to search for freely available and biodegradable adsorbents such as macadamia seed husks [2], *Eichhornia crassipes* roots [14], cabbage waste [15], coffee husks [16], rambutan (*Nephelium lappaceum*) peel

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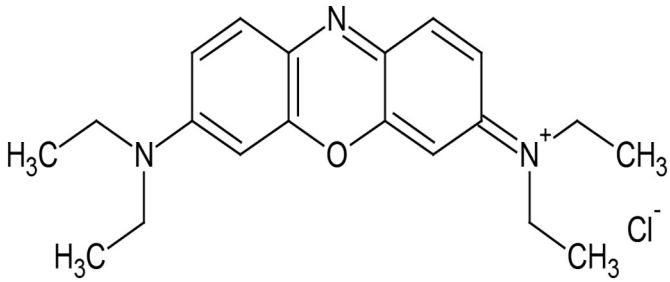

Fig. 1. Structure of Basic Blue 3 dye.

[17], rejected tea [18], garlic peel [19], grass waste [20], *Rhizophora mucronata* stem-barks [21], wheat husk [22] and saw dust [23].

Macadamia nut farming has risen after capturing the attention of many famers in the Eastern parts of Africa due to the ability of the nuts to sell at higher prices compared to other cash crops like coffee and tea [24]. Macadamia nuts are utilized in making highly nutritious cooking oil, alternative oil in diesel engine and whole or cracked nut food ingredient in making biscuits, ice cream and cake [25]. The upsurge has greatly elevated the quantity of disposable macadamia seed husks causing environmental pollution through filling landfills which cause low hygiene and pollution. Unutilized husks take very long to decompose providing breeding ground for disease causing pathogen like mosquitos, rodents and snakes. Currently, the macadamia nut husks are disposed by burning in open field causing air pollution. The biggest challenges facing macadamia nut processing factory in Kenya is developing an environmental green technique to handle these residual wastes. An innovation to develop substitute technology of utilizing these wastes in solving environmental problems is valuable given its plentiful supply. The present study evaluates the potential of utilizing MSH as cost effective biosorbent in the removal of BB3 from aqueous solution. The effectiveness of MSH in the removal of BB3 was explored and factors affecting dye removal optimized.

2. Material and methods

2.1. Adsorbate and adsorbent preparation

Macadamia seed husks were collected from the dumping ground of Jungle macadamia nut processing factory in Thika town, Kenya. Dust, soil particles and other dirt were removed by washing the husks extensively using tap water before sun drying. The dry MSH was mechanically pulverized into a powder and cleaned thoroughly using double distilled water. The clean powder was sun dried and sieved using standard sieves obtaining different particle sizes ranging from 150 to 300; 300–600; 600–1180; 1180–2360 and 2360–4750 μm. Analytical grade, basic blue 3 dye ($C_{20}H_{26}ClN_3O$; molecular weight; 359.9 g) supplied by Sigma Aldrich Nairobi, Kenya was used in this research. A stock solution was made by dissolving 0.5 g of BB3 powder in 1 L of double distilled water. Working solutions for sorption experiments were attained through proper dilution of the stock solution.

2.2. Adsorption experiments

Batch adsorption studies were executed in a series of 100 mL Erlenmeyer flasks containing 50 mL BB3 dye solution of different concentration on KJ-201BD mechanical shaker agitating at 140 p.m. for 120 min. Contact time was evaluated using 0.4 g MSH solid sorbent of 300–600 μm particle size in 50 mL solution of concentration 12.2362 mg/L at 25 °C and pH 12. The effect of MSH dose was investigated using 0.1, 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2 g in separate flasks at 25 °C. Particle size effect on BB3 adsorption process was examined using 0.4 g of different particle sizes in 50 mL BB3 solution of concentration 12.2362 mg/L at 25 °C. Initial BB3 solution concentration effect was studied by varying the concentration from 2.6992–12.2362 mg/L while temperature was evaluated at diverse temperatures ranging from 25 to 70 °C. The influence of pH was investigated at the range of 3–12. 0.01 NaOH and 0.01 HCl were used to vary the pH. BB3 dye solutions of known concentration were carefully prepared and their absorbance measured to create a standard curve for calibration purposes. All experimentations were performed in triplicates and the mean value reported. After every 10 min, aliquots were drawn from the mother solution filtered into rectangular cuvettes and the absorbance measurements taken at BB3 maximum wavelength (654 nm) against double distilled water as blank solution using (HALO RB- 10) UV – Vis spectrophotometer supplied from Dynamica scientific Ltd. - United kingdom. The solution was returned into the reaction mixture immediately after measurement to avoid changes in volume. The quantity of BB3 adsorbed onto MSH at equilibrium Q_e and at time t, Q_t (mg/g) was calculated using Eqs. (1) and (2).

$$Q_e = \left(\frac{C_{o-C_e}}{W}\right) \mathrm{V} \tag{1}$$

$$Q_t = \left(\frac{C_{o-C_t}}{W}\right) \mathrm{V} \tag{2}$$

where C_o, C_e and C_t are the original, equilibrium and time t BB3 solution concentration (mg/L) respectively. V is the volume of BB3 solution (L) while W the quantity of MSH adsorbent used (g). The following equation was applied for calculating the percentage BB3 dye uptake from the initial solution.

$$\%\text{BB3 dye uptake} = \left(\frac{C_{o-C_e}}{C_o}\right) \text{x } 100 \tag{3}$$

Sorption kinetics and isotherms of dye uptake was investigated using variable BB3 dye concentration at 70 °C and pH 12, using 0.40 g of MSH powder of particle size 150–300 μm mixing with 50 mL BB3 dye solution at 140 rpm. Aliquots of 3.0 mL were drawn at 10-min time intervals and the remaining CV dye concentration determined.

3. Results and discussion

3.1. Effect of contact time

Time of contact in adsorption is significant in evaluating the efficacy of the sorbent which help in industrial valuation of the cost effectiveness of sorption technique in effluent treatment. Fig. 2a. illustrates the impact of interaction time on the sorption of BB3 dye on MSH for a phase of 120 min. From the plot, it's apparent that the rate of BB3 dye removal was swift as the process begun and slowed down after attaining equilibrium at around 70th minute. For instance, 0.7 of the total 1.4 mg/g was adsorbed during the first 10 min. After equilibrium, further agitation of the reaction mixture resulted to negligible increase in the dye uptake. The high dye uptake during the early phases of the process can be explained by presence of many unoccupied binding sites on the MSH sorbent outer surface. The ability of MSH to adsorb BB3 dye molecules declined with lapsing time since most of the active binding spaces had been used and the remaining sites became tough to occupy owing the forces of repulsion between BB3 molecules on the MSH sorbent solid surface and the bulk aqueous phase. Comparable results have been noted on the adsorption of crystal violet using coffee husks [13] and BB3 dye on nano scale zero valent iron [26].

3.2. Effect of adsorbent particle size

Efficacy of sorption process relies greatly on the surface area available. Large surface area corresponds to a higher number of binding sites therefore better sorption ability of the adsorbent. Impact of particle size was examined using diverse particle sizes in the range of 150 to 4750 μm and the outcome shown in Fig. 2b. Dye uptake declined from 99.8% to 62.7% as MSH particle size increased from (150–300) to (2360–4750) μm. The higher adsorption rate of the smaller particles can be ascribed to their larger

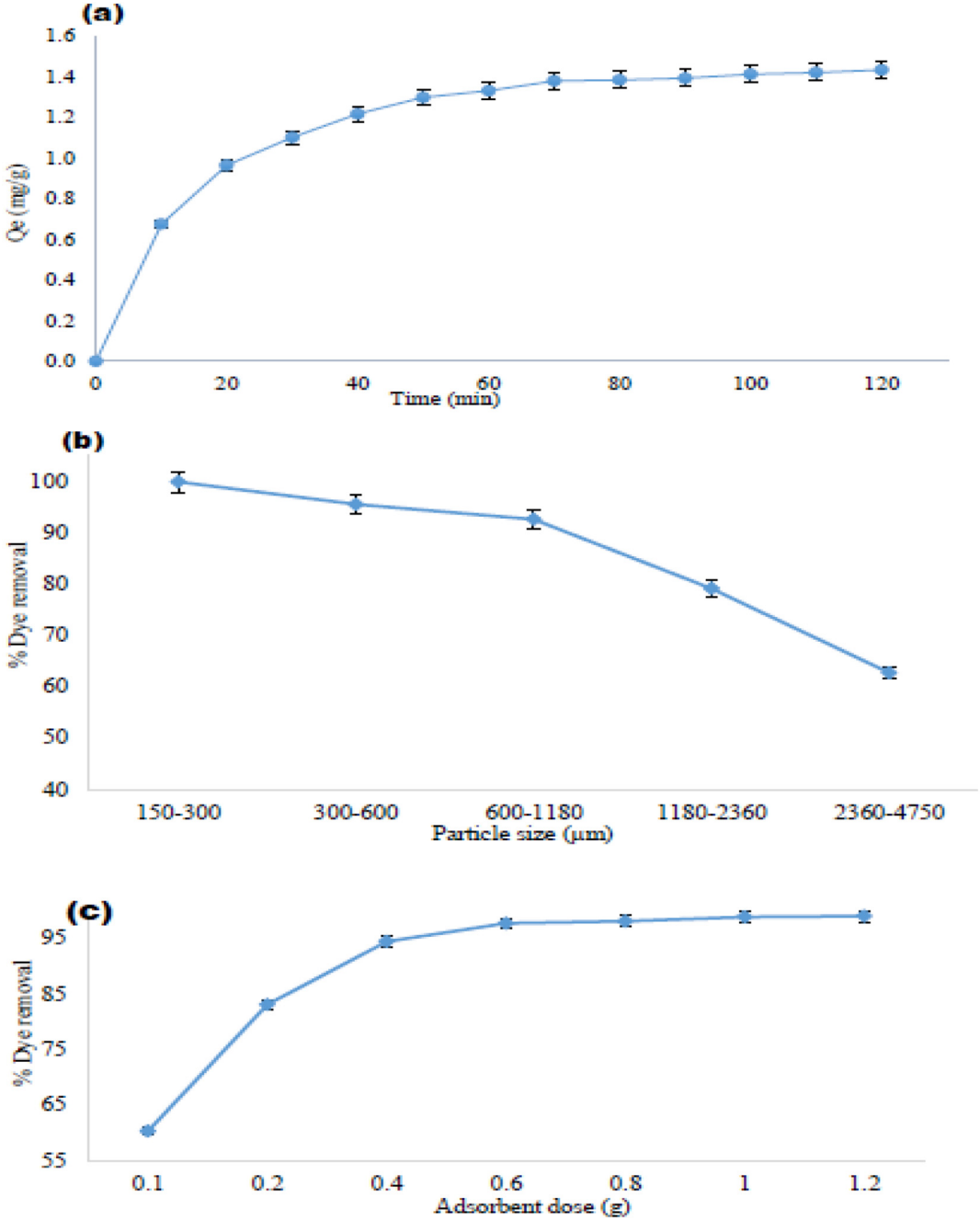

Fig. 2. (a) Effect of time of contact on basic blue 3 dye biosorption; (b) Effect of MSH particle size on basic blue 3 dye adsorption; (c) Effect of MSH dose on basic blue 3 dye sorption. Conditions: (Basic blue 3: 12.2362 mg/L, MSH 0.1–1.2 g/50 mL, particle size; 300–600 µm, pH 12; at 25 °C).

external surface area which increases the number of available sorption sites. Additionally, smaller particles move faster in solution giving higher opportunity of adsorbate – adsorbent collision in comparison to bigger particles. The outcomes are in line with correlated studies on the sorption of methylene blue dye on peas shells [27] and *Eichhoria crassipes* [12].

3.3. Effect of adsorbent dose

The mass of sorbent employed in adsorption is essential in determining the most effective adsorbate – adsorbent ratio in aqueous solution for cost effectiveness. The influence of various MSH biomass dose on BB3 removal at initial dye concentration 12.2362 mg/L was evaluated and the results shown in Fig. 2c. The percentage BB3 removal was found to increase from 60.4% to 99.0% as the mass of MSH dose was raised from 0.1 to 1.2 g. This outcome can be accredited to an increase in the MSH surface area and adsorption sites as the quantity of MSH were increased resulting to more adsorbate – adsorbent interaction. Similar findings were recorded on the biosorption of BB3 dye on polyaniline/magnetite (Fe_3O_4) composites [28] and methylene blue dye on *Metroxylon spp.* [29].

3.4. Effect of initial BB3 dye concentration

The impact of initial dye concentrations on the removal of BB3 dye was studied using 0.4 g MSH at 25 °C and the outcomes presented in Fig. 3a. At equilibrium, the amount of dye removed increased with the increase of initial BB3 concentration. For instance, the quantity of BB3 adsorbed increased from 0.3447 to 1.5223 mg/g as the initial BB3 concentration was raised from 2.6992 to 12.2362 mg/L. The above outcome can be accredited

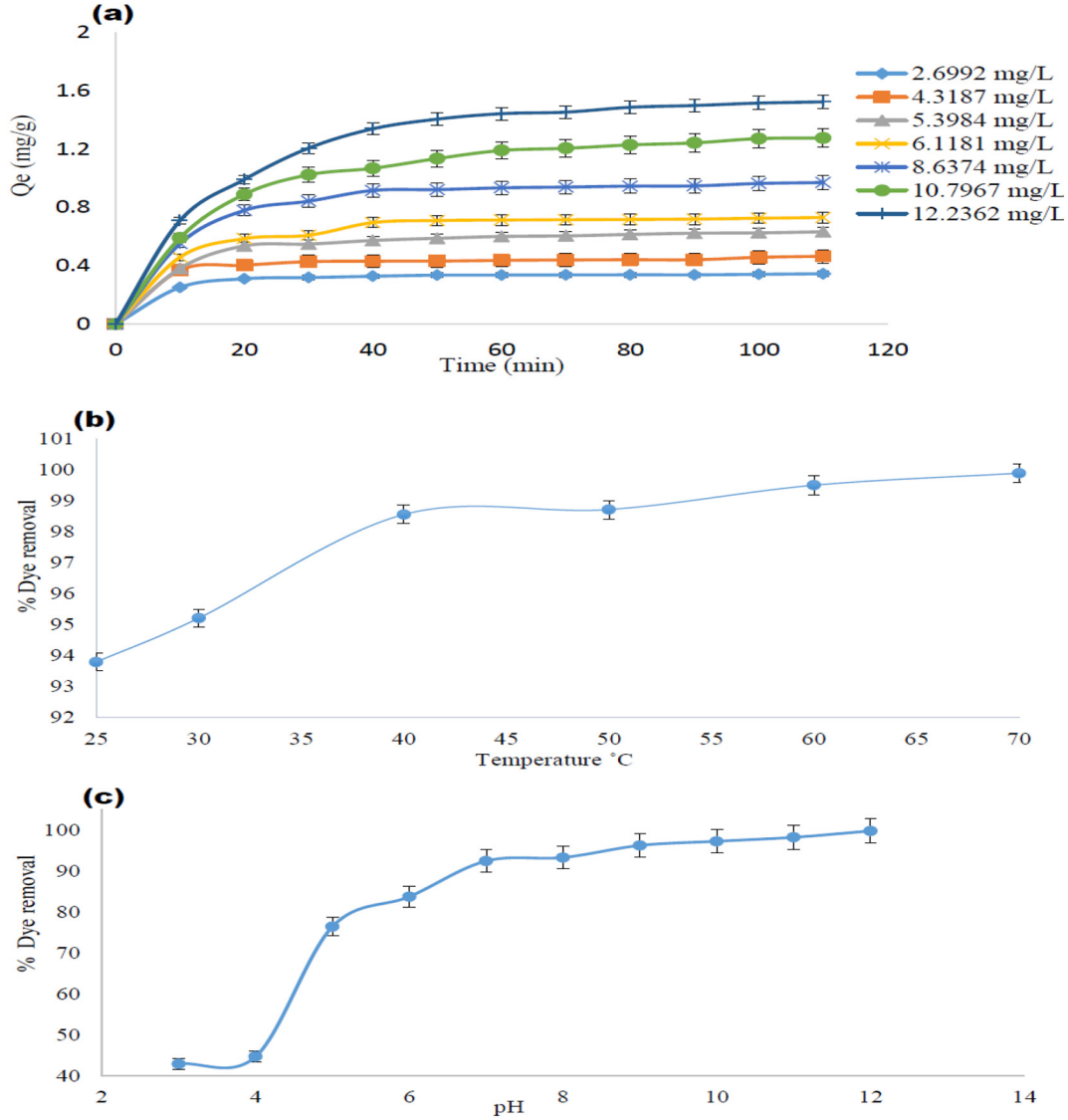

Fig. 3. (a) Effect of initial dye concentration on basic blue 3 dye sorption; (b) Effect of temperature on basic blue 3 dye removal; (c) Effect of pH on basic blue 3 dye removal. Conditions: (Basic blue 3: 2.6992–12.2362 mg/L, MSH 0.4 g/50 mL, particle size; 300–600 μm, pH 2–12; at 25–70 °C).

to an upsurge in the driving force of the concentration gradient overcoming the mass transfer resistances on the adsorbate molecules between the bulk solution and solid phase leading to an increasing equilibrium sorption until saturation is attained [14]. Additionally, increasing the initial adsorbate concentration increases the number of collisions (interaction) between the adsorbate and adsorbent enhancing the sorption process. However, sorption efficacy reduced with increase in the initial BB3 concentration as a result of saturation of the active sorption sites on the MSH surface. These results are comparable with outcomes obtained on the adsorption of artificial dyes from solution [13,30].

3.5. Effect of temperature on BB3 adsorption

Temperature plays a crucial part in the sorption method because it reduces the viscosity of the aqueous solution and increases the speed of adsorbate diffusion over the exterior layer and in the interior pores of the adsorbent material [15]. The impact of various temperatures on BB3 dye removal was examined and the results displayed on Fig. 3b. From the display, it's evident that a rise in temperature increased the dye uptake elucidating an endothermic process. As the temperature increased from 25 to 70 °C the percentage BB3 uptake rose from 93.8% to 99.9% at equilibrium. The upsurge in BB3 dye uptake with rise in temperature can be attributed to a surge in mobility/reduced viscosity of BB3 molecules increasing their interaction with the active adsorptive sites on the MSH surface. These can further be attributed to stronger intermolecular forces between the active binding spaces on the MSH surface and the BB3 dye particles than those between the solvent and dye particles. There is also a likelihood of opening the MSH internal pores increasing the sites of adsorption the dye hence higher adsorption at higher temperatures. Related findings were obtained in the sorption of BB3 dye on ternary polymer nanocomposite [31] and methylene blue dye on *Calotropic proceral* leaf powder [32] where the sorption process was also endothermic.

3.6. Effect of pH on BB3 adsorption

pH controls the magnitude of ionization of the dye molecules and affects surface charge on the sorbent material in adsorption [33]. Fig. 3c displays the results of BB3 dye removal in pH 3–12. From the graph, it's clear that adsorption took place in both acidic and basic conditions. However, there was an upsurge in BB3 removal as the pH was increased. For example, the percentage of BB3 removed increased 42.9% at pH 3 to 99.8% at pH 12. pH 12 was recorded as the optimum pH for BB3 removal. The higher sorption rates at higher pH could be accredited to the reduction of H^+ ions concentration on the MSH surface and higher electrostatic forces of

attraction between the active sorption sites and the positive BB3 dye molecules at basic conditions. As well, higher rate of sorption at basic conditions have been recorded on the removal of BB3 dye from solution using sulfuric acid- activated montmorillonite mineral [34], quartenized sugar cane bagasse [35] and methylene blue dye on prickly (peel) bark of cactus fruit [36].

3.7. Sorption kinetics

An economically viable adsorbent material for large scale industrial effluents treatment should have high rate of adsorbate uptake for efficiency. To explain the rate governing steps for BB3 dye on MSH, the data obtained experimentally was evaluated using the pseudo first order and the pseudo second order kinetic models. The linearized form of the pseudo first order kinetic model [37] is given below.

$$\text{In}\,(q_e - q_t) = \text{In}\,q_e - K_1\,\text{t} \tag{4}$$

where, q_e and q_t are the amount of BB3 adsorbed at equilibrium and at time t, (mg/g) correspondingly. K_1 (g/mgmin) is the first order sorption rate constant. The values of K_1 and $q_{e.cal}$ were obtained from the gradient and intercept of plotting ln (q_e-q_t) against the time t of Eq. (4), presented in Fig. 4a. The pseudo first order gave high regression coefficient ($R^2 > 0.8409$) values as in Table 1. However the calculated $q_{e.cal}$ hugely deviated from experimental $q_{e.exp}$ depicting that the pseudo first order model was not applicable for explaining BB3 sorption process on MSH.

The same data was also subjected to the second order kinetic model [38] given in Eq. (5).

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

where, K_2 is the pseudo-second order sorption rate constant (g/mg min). q_e and q_t are the quantities (mg/g) of BB3 dye adsorbed at equilibrium and at specific time t while t is the time (min). Plots of $\frac{t}{q_t}$ versus the time t (Fig. 4b) gave linear correlations for all the BB3 concentrations tested. The constants q_e and K_2 for the various concentrations were tabulated from the gradient and intercept of the plots and the values recorded in Table 1. The plots gave very high (close to a unit) regression coefficient values ($R^2 > 0.997$). As well, the corresponding calculated $q_{e.cal}$ and experimental

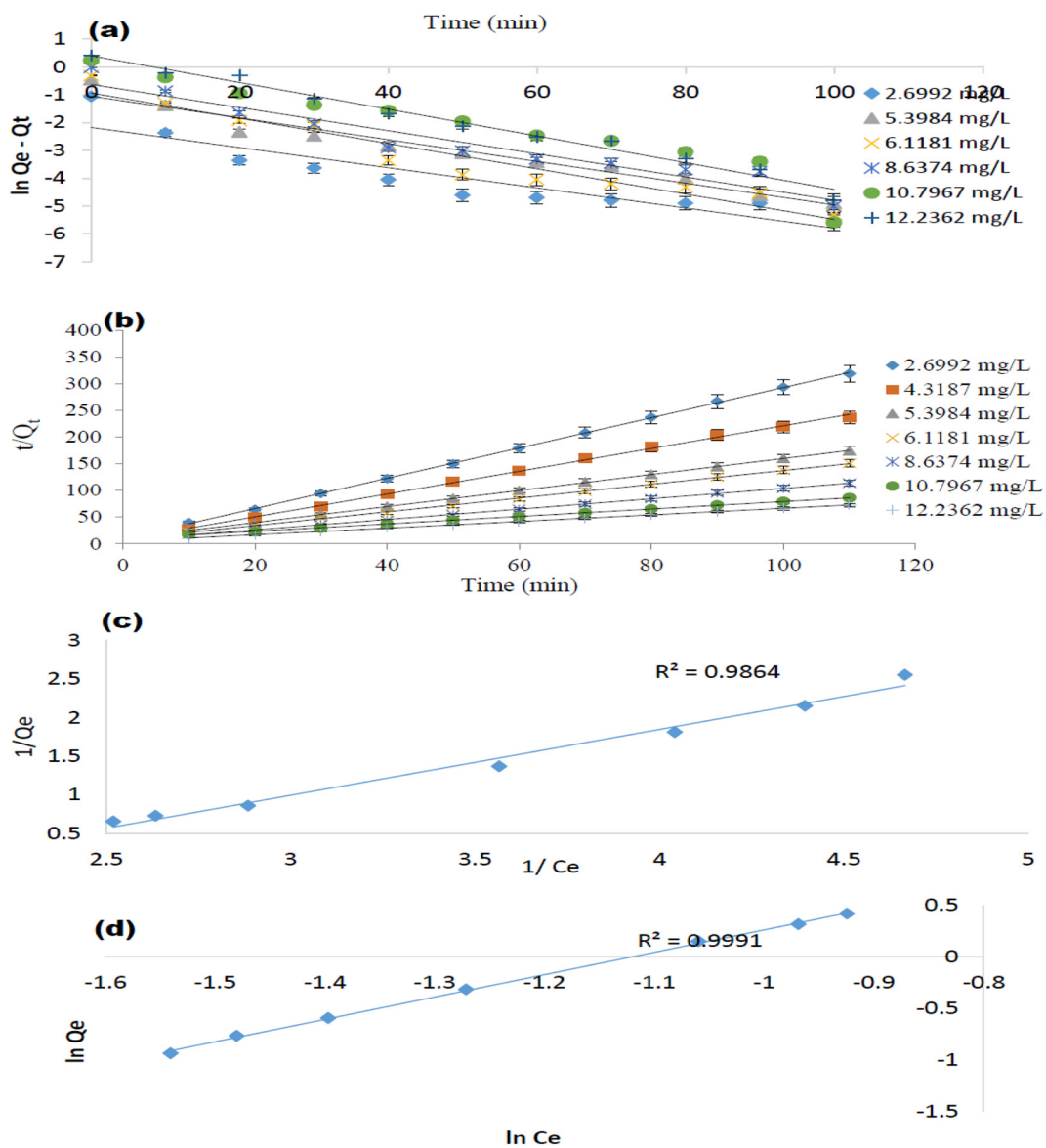

Fig. 4. (a) Pseudo-first order kinetics plot for the adsorption of basic blue 3 dye;. (b) Pseudo-second order kinetics plot for the sorption of basic blue 3 dye; (c) Langmuir adsorption isotherm and (d) Freundlich adsorption isotherm for basic blue 3 dye sorption.

Table 1
Sorption kinetics values of BB3 dye sorption on MSH.

C_e (mg/L)	$q_{e.exp}$ (mg/g)	Pseudo first order			Pseudo second order		
		$q_{e.cal}$ (mg/g)	K_1 min^{-1}	R^2	$q_{e.cal}$(mg/g) (g/mgmin)	K_2	R^2
2.6992	0.3447	8.339	0.0362	0.8409	0.3527	0.8666	0.9970
4.3187	0.4646	6.637	0.0379	0.9311	0.4686	0.5866	0.9983
5.3984	0.6324	2.877	0.0391	0.9542	0.6666	0.2301	0.9970
6.1181	0.7323	2.562	0.0454	0.9223	0.7734	0.2105	0.9989
8.6374	0.9697	1.867	0.0417	0.9289	1.0286	0.1453	0.9991
10.796	1.2747	1.239	0.0465	0.9166	1.4280	0.0894	0.9995
12.236	1.5223	1.489	0.0480	0.9822	1.6121	0.0543	0.9995

$q_{e.exp}$ (mg/g) values were very close making the second order kinetic model the most efficient for explaining the adsorption of BB3 on MSH. These results illustrated that the overall rate of BB3 sorption on MSH was greatly influenced by contact time and concentration of the BB3 solution. Similarly, suggesting domination of chemical sorption comprising valency forces through exchange or sharing of electrons between the BB3 sorbate molecules and MSH adsorbent particles. The small deviation between the $q_{e.exp}$ and $q_{e.cal}$ values was possibly owed to boundary layer effect during the sorption process [2]. These output is in agreement with results documented in the removal of remazol black B dye using alluvial soils [39], BB3 dye on both *Sphagnum magellanicum* peat [40] and ternary polymer nanocomposite [41] and methylene blue dye on activated carbon [42].

3.8. Sorption isotherms

Adsorption isotherms are central in explaining adsorbate – adsorbent interactions at equilibrium. Langmuir and Freundlich isotherm models were employed to evaluate the practicality of the sorption method in the removal of BB3 from solution using MSH. The Langmuir isotherm model assumes all active adsorption spaces are equivalent in energy and their ability to adsorb an adsorbate molecule does not influenced by the bordering sites being occupied or vacant. Moreover, it suggests saturation of the sorbent surface by a single layer. Eq. (6) gives the integral formula of the of the Langmuir model [43].

$$\frac{C_e}{Q_e} = \frac{1}{Q_{Max}b} + \frac{1}{Q_{Max}}C_e \tag{6}$$

where, Q_e is the amount of BB3 adsorbed on the solid sorbent at equilibrium (mg/g), Q_{max} the maximum single layer capacity (mg/g), C_e the adsorbate concentration at equilibrium (mg/L) and b the Langmuir free energy constant (L/mg).

The separation factor (equilibrium parameter) R_L articulated by Eq. (7) [44,45] was used to analyze the fundamental features of the Langmuir isotherm.

$$R_L = \frac{1}{1 + \mathrm{b}\ (\mathrm{C\ o})} \tag{7}$$

where C_o (mg/g), is the initial BB3 concentration and b (L/mg), is the Langmuir constant related to the affinity of the binding sites. The value of R_L is an indicator of the shape of the isotherm as either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). Q_{max} and b were obtained from the slope and intercept respectively of the linear correlation given by plotting $\frac{1}{Q_e}$ as a function of $\frac{1}{C_e}$ (Fig. 4c). Single layer sorption was attained with a high regression coefficient, $R^2 = 0.9864$, maximum BB3 adsorbed $Q_{max} = 1.4$ mg/g, Langmuir free energy constant b = 1.8327 L/mg and the separation factor $R_L = 0.0427$ fitting the favorable conditions ($0 < R_L < 1$). The Langmuir sorption model was therefore apposite for describing the adsorption of BB3 on MSH.

The Freundlich isotherm model, effective for multiple layer sorption on a heterogeneous sorbent surface [12], was similarly applied to analyze the experimentally acquired data. Eq. (8) expresses the linear formula of the Freundlich model [46].

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{8}$$

where; Q_e is quantity of BB3 adsorbed on MSH at equilibrium (mg/g), C_e the adsorbate concentration in the solution at equilibrium (mg/L), K_f the Freundlich constant indicating the sorption ability of the adsorbent and n the Freundlich constant signifying the intensity of the adsorption process. Values of $n > 1$ represent favorable multi-layer sorption. Plotting ln Q_e vs ln C_e (Fig. 4d) gave a linear relationship. The parameters K_f and n were calculated from the intercept and gradient of the plot. The data fitted satisfactorily in the Freundlich model giving higher correlation coefficient, $R^2 = 0.9991$, sorption capability, $K_f = 11.4501$ and adsorption intensity of $n = 0.4599$ making it efficient for describing the adsorption of BB3 on MSH. Factoring the high correlation coefficients R^2, and favorable fit for both Langmuir and Freundlich isotherms, it can be reasoned that both single and multiple layer sorption i.e. chemisorption and physiosorption, happened during the process. Similar outcomes have been recorded in the removal of BB3 dye and reactive orange 16 by quartinized sugar cane bagasse [35], Congo red dye on cabbage powder [15] and crystal violet on coffee husks [16].

4. Conclusion

The study found that MSH is definitely realistic, cost effective adsorbent for biosorption of basic blue 3 dye from aqueous solution with over 99.9% efficiency. Based on the outcomes of this study, MSH is an economical, easily available adsorbent for BB3 dye removal at optimum conditions. The time of contact, sorbent dose, MSH particle size, initial BB3 concentration, temperature and aqueous solution initial pH had a great impact on the adsorption process. The percentage rate of BB3 uptake increased with increase in contact time, MSH dosage, initial concentration, temperature, pH and declined with increasing size of the MSH particles. Optimum BB3 dye removal was realized after 70 min of contact time, using 300–600 μm particle size, 0.4 g MSH dose, 70 °C temperature and pH 12. The process was found to attain equilibrium after around 40 min of agitation. The rate controlling steps conformed to the pseudo second order kinetics model giving high regression coefficients values ($R^2 > 0.997$) depicting domination of chemisorption. The experimental data fitted both the Langmuir and Freundlich sorption isotherms with high regression coefficients values ($R^2 = 0.9864$) and ($R^2 = 0.9991$) respectively. This confirmed occurrence of both chemisorption and physiosorption during the adsorption of BB3 by MSH. Consequently, it can be resolved that, MSH can be applied as an economically sustainable, locally available, biodegradable and highly efficient alternate of activated carbon in the removal of BB3 dye from effluents by adsorption technique.

Credit author statement

Mutunga M Felista: Investigation, acquisition of data and Writing- Original draft preparation Funding acquisition

Wycliffe C. Wanyonyi: Conceptualization, Methodology, Software, Data curation, Supervision, Writing- Reviewing, and Editing, Software, Validation, Funding acquisition, Resources, Formal analysis, Visualization and final approval of the version to be published

Ongera Gilbert: substantial contribution to conception, Supervision and Visualization,

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