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Equilibrium, Isotherms and Kinetics Studies of Removal of Methylene Blue on Montmorillonite-Silica Nanocomposite

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Abstract: Montmorillonite-silica nanocompsite synthesized from locally available materials obtained from rice husk and montmorillonite clay is used as an adsorbent in the removal of methylene blue dye from aqueous solution. Batch adsorption method was employed in this study where the influential parameters studied were adsorbent dose, initial concentration and contact time at the optimum conditions; 0.5g, 3 mg and 20 minutes respectively at room temperature. The maximum percentage removal obtained from the adsorption processes was 99.30%. The isotherms results obtained for Langmuir isotherm was R^2 = 0.7656 and Freudlich; R^2 = 0.1568. From the above, it is obvious and certain that the Langmuir isotherm best fit the adsorption process carried out in this study. The R_L =0.982 indicates that the adsorption process was favourable since the value is close to one and the maximum adsorption capacity obtained was found to be q_{max} = 58.82 using the Langmuir isotherm. The kinetic study was employed using the pseudo-first order and the pseudo-second order kinetics. The obtained results show that the pseudo-second order best fit the adsorption process with the correlation factor R^2 = 0.9018. Form the above results, montmorillonite-silica nanocomposite, can be used as cost effective adsorbent in the adsorptive removal of methylene blue dye from aqueous solution.

Keywords: Methylene Blue, Adsoption, Kinetics, Isotherms and Montmorillonite-Silica Nanocomposite

1. Introduction

Methylene blue dye is a cationic dye also known as basic dye which is used in different industries for the purpose of producing different products, [1] The methylene blue has a molecular formula as; $C_{16}H_{18}ClN_3S.3H_2O$ with a molecular weight of 319.852g/mol, [2]. Dyes are widely utilized in different industries such as leather, food stuff, plastics, paper, textile, cosmetic to color products, [3, 4] The used of these dyes in various industries has resulted in the production of dye effluents being mostly discharged into the environment (land or rivers) without any treatment because the conventional treatment methods are not effective, [5] The discharge of these effluents into the environments results in hazardous health problems as most of these dyes have carcinogenic effects. The presence of dye in the water body inhibits penetration of sunlight there by retarding the growth of aquatic plants, [5]. Because dye cannot be decomposed easily, ground-waters are also affected by these pollutants because of leaching from the soil. Conventional methods of dyes treatment includes; electrochemical method, Coagulation and flocculation, Chemical oxidation, Liquid-liquid extraction, Ozonation, membrane filtration, Biological treatment, and Adsorption. But adsorption has been shown to be an effective way for removing organic matter from aqueous solutions in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substances, [5, 6]. Thus, montmorillonite clay has been reported as cost effective adsorbent for adsorption of methylene blue, [7]. Nanocomposite is a multiphase material where one of the phases has one, two, or three dimensions of less than 100 nano-meters (nm) or structures having nano-scale repeat distances between the different phases that make up the material, [8, 9 10]. There are several applications of nanocomposite in different areas such electronics, medicine, environment and water purifications. The aim of this research is to explore the absorption potentials of montmorillonite-silica nanocomposite for removal of methylene blue dye.

2. Materials and Methods

2.1. Preparation of Solution / Reagents

M H_2SO_4: A 5.3ml of concentrated sulphuric acid was pipetted and poured into 30ml distilled water in a 100ml volumetric flask and diluted with distilled water to the mark.

1MHCl: A measuring cylinder was used to measure 30.9ml of concentrated HCl. It was then transferred into a 100 ml volumetric flask and diluted to the mark with distilled water.

2.5M NaOH: An accurately weighed 100g of sodium hydroxide was placedin 1000 ml volumetric flask, distilled water was added up to the mark.

1000mg/L Methylene blue stock solution: One grammemethylene blue was weighed and placed in 100 ml volumetric flask. Distilled water was added and mixture thoroughly shaken until the methylene blue dissolved. It was then made up to the mark with distilled water.

2.2. Sample Collection and Preparation

Both montmorillonite clay and rice husk samples were collected at Talasse, Balanga Local Government Area of Gombe state, Nigeria. The 1000g rice husk was washed thoroughly with tap water for about six times and rewashed with distilled water three times to remove the adhesive dirt. It was dried overnight and subsequently oven dried at 95°C and kept for further ashing.

The clay (1000g) was washed several times with tap water, and rewashed further with distilled water for four times. The washed sample was air dried and then oven dried for four hours at 110°C. The clay was grinded and sieved using a 250µm sieve. A weighed of 250g of the powdered clay was refluxed with 500 ml of 1M HCl for 1 hour at 120°C. It was then washed with distilled water five times to remove the acid. The clay was then dried in an oven at 105°C for six hours until a constant weight was obtained. It was then grinded and kept for further synthesis of the montmorillonite –silcanano composite, [11, 12].

2.3. Preparation of Rice Husk Ash

Rice husk ash was prepared according to [4]. A 500g portion of dried rice husk was refluxed with 1000ml hydrochloric acid for 1 hour at 95°C to remove some metallic impurities. After completion, it was washed thoroughly with distilled water five times, dried in an oven for five hours at 110°C. The treated rice husk was calcined in a muffle furnace for 7 hours at 650°C. The white rice husk ash was obtained and kept for further preparations.

2.4. Synthesis of Montmorillonite-Silca Nanocmposite

A 20g of white rice husk ash (WRHA) was refluxed with 2.5M NaOH solution for 1 hour with constant stirring at 200°C and then filtered, where a clear sodium silicate solution was obtained. A weighed amount of 80g of acidified clay was added into 200ml solution of the sodium silicate obtained with constant stirring. It was then precipitated with 1M H_2SO_4 drop wise and measuring the pH until it is equal to 8.9, it was then kept for 24 hours and then washed five times with distilled water until the pH was observed to be 7. It was then oven dried for five hours, grinded and sieved with a 250µ sieve, [13, 14, 15].

2.5. Adsorption Studies

All the experiments in these studies were carried out in 500ml conical flask both containing 200ml methylene blue. After adding the amount of adsorbent, the flasks were agitated using magnetic stirrer while studying the parameters such as; the effect of adsorbent dose, initial concentration and contact time

After the adsorption process, the flash content was filtered using whattman filter paper. The filtrate obtained was analyzed using UV/Visible spectrophotometer (Model JENWAY 6300) at the wavelength of 666 nm. The adsorption percentage of the adsorbate at equilibrium qe (mg/g) and qt (mg/g) at time t, were calculated according to the following equation;

$$\text{Adsorbate removal \%} = \frac{(Co-Ce)x\,100}{Co}$$

$$q_e = \frac{(Co-Ce)xV}{Co}$$

$$q_t = \frac{(Co-Ce)xV}{m} \quad (1)$$

3. Result and Discussion

3.1. Effect of Adsorbent Dose

The effect of adsorbent dose for methylene blue dye is shown in Table 1 and Figure 1, the percentage removal increases with decreases in the adsorbent dose and this may be probably due to the adsorption sites remaining unsaturated during the adsorption process. Therefore, it can be suggested that a more economics designed way of the removal of dyes from effluent can be achieved by the use of a small amount of absorbent as observed from the experiment above with the percentage removal of 91.60% at an adsorbent dose of 0.5g.

Table 1. *Methylene blue effect of adsorbent dose.*

Ads dose (g)	ABS	Co (mg/L)	Ce (mg/L)	Co-Ce (mg/L)	%Removal	q_e (mg/g)	Log qe	Log Ce	Ce/qe (mg/L)
0.5	0.051	3	0.265	2.735	91.16	109.4	2.039	- 0.576	0.0024
1.0	0.074	3	0.385	2.615	87.16	52.30	1.718	- 0.415	0.0074
1.5	0.159	3	0.828	2.172	72.40	28.96	1.461	- 0.082	0.0285
2.0	0.448	3	2.333	0.667	22.23	06.27	0.824	0.368	0.349
2.5	0.437	3	2.276	0.724	24.13	05.76	0.762	0.357	0.3951

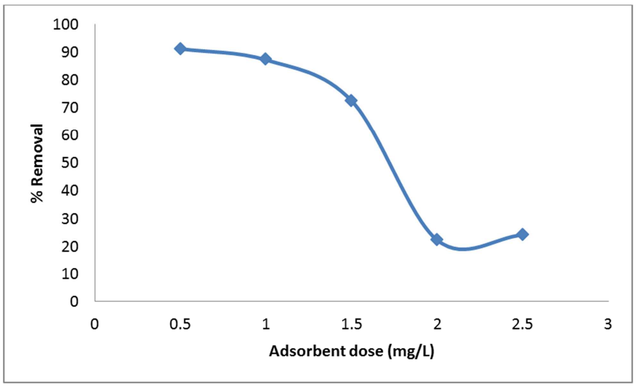

Figure 1. *Methylene blue adsorbent dose graph at adsorbent dose of 0.5, 1.0, 1.5, 2.0, and 2.5g, adsorbate conc. of 3mg/L, and contact time of 60 (min).*

3.2. Effect of Initial Concentration of Adsorbates

The adsorption of methylene blue dye on montmorillonite-silica nanocomposite was studied at different initial concentrations from 1mg/L to 5mg/L. The results of the study is represented in Table 2 and Figure, it was observed that there was increase in percentage removal from 1mg/L to 3mg/L which beyond this concentration, the percentage removal increases very slightly. The percentage removal of the methylene blue was found to be 97.80% at initial concentration of 3mg/L which shows a good interaction of the adsorbates with the binding sites of the adsorbent at lower concentration and at higher concentration, the decrease in percentage removal may be due, insufficient adsorption sites in the adsorbent to accommodate all the dye ions in the solution, [16]. Hence, the optimum concentration for methylene blue was 3mg/L.

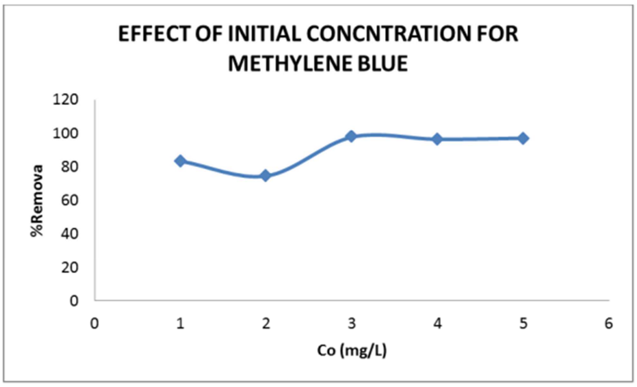

Figure 2. *Methylene blue effect of initial concentration graph at adsorbent dose of 0.5g, contact time 60min, concentration of 1, 2, 3, 4 and 5mg/L.*

Table 2. *Effect of initial concentration for methylene blue.*

Ads dose (g)	ABS	Co (mg/L)	Ce (mg/L)	Co-Ce (mg/L)	%Removal	q_e (mg/g)	Log q_e	Log Ce	Ce/q_e (mg/L)
0.5	0.032	1	0.167	0.833	83.30	33.32	1.523	-0.772	0.0050
0.5	0.098	2	0.510	1.490	74.50	59.60	1.775	-0.292	0.0085
0.5	0.014	3	0.073	2.927	97.57	117.08	2.068	-1.137	0.0006
0.5	0.029	4	0.151	3.849	96.23	153.76	2.186	-0.821	0.0009
0.5	0.30	5	0.156	4.844	96.88	193.76	2.287	-0.806	0.0008

3.3. Effect of Contact Time

As seen from the experimental results (Table 3 and Figure 3) obtained from the batch adsorption process of the methylene blue, the percentage removal of the dye increases rapidly with the increase of the contact from 10 minutes to 20 minutes. And then decreases at a significant narrow range from 30 minutes to 40 minutes from which it increases rapidly at 50 minutes. Then at 60 minutes, it decreases to the lowest percentage removal and this look so abnormal to account for. Thus, the optimum contact time was found to be 20 minutes with the percentage removal of 99.30%.

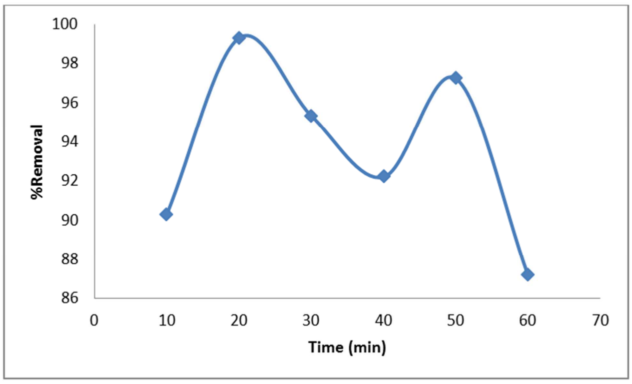

Figure 3. *Effect of contact time graph for methylene blue at varied time of 10, 20, 30, 40, 50 and 60min, adsorbate conc. of 3mg/L and adsorbent dose of 0.5g.*

Table 3. *Effect of contact time for methylene blue.*

Time (min)	Adsorbent dose (g)	Co (mg/L)	Ce (mg/L)	Co-Ce (mg/L)	% Removal	q_e (mg/g)	Log q_e	Log Ce	Ce/q_e (mg/L)
10	0.5	3	0.291	2.709	90.30	108.36	2.034	-0.536	0.0026
20	0.5	3	0.021	2.979	99.30	119.16	2.076	-1.677	0.0001
30	0.5	3	0.140	2.860	95.33	114.40	2.058	-0.853	0.0012
40	0.5	3	0.234	2.760	92.20	110.40	2.042	-0.631	0.0021
50	0.5	3	0.083	2.917	97.23	116.68	2.066	-1.080	0.0007
60	0.5	3	0.385	2.615	87.16	104.60	2.019	-0.414	0.0037

3.4. Adsorption Isotherm Study

The experiment data studied in this adsorption process were analysed using only two models namely: Langmuir isotherm model and Freudlich isotherm model.

3.4.1. Langmuir Isotherm

For the Langmuir adsorption isotherms: This describes quantitatively the formation of a monolayer adsorbate on the outer surface of the absorbent, and after that no further adsorption takes place. Thereby, the Langmuir represents the equilibrium distribution of metal ions between the solid and liquid phase, the Langmuir isotherm is valid for monolayer adsorption on to a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. For liquid adsorbates however, the Langmuir isotherm is usually expressed as follows;

$$q_e = \frac{(q_{max}C_e)}{(K_l + C_e)} \tag{2}$$

For correlation purposes, the equation is rearranged as follows;

$$\frac{C_e}{q_e} = \frac{1}{K_l q_{max}} + \frac{1}{q_{max}} . C_e \tag{3}$$

Where

C_e = the equilibrium concentration of adsorbate (mg/L).

q_e = Is the equilibrium value of adsorbate adsorbed per unit weight of adsorbent (mg/g).

q_{max} =Is the maximum amount of adsorption corresponding to monomolecular layer coverage (mg/g).

K_l = Is the Langmuir constant and is related to measure of affinity of the adsorbent (l/mg).

A linearized plot of $\frac{Ce}{qe}$ against Ce yields a straight line graph which has an intercept and slope which correspond to $\frac{1}{K_l q_{max}}$ and $\frac{1}{q_{max}}$respectively, from which the q_{max} and K_l can be calculated.

To confirm the favourability of an adsorption process to Langmuir isotherm, the essential features of the isotherm can be expressed in terms of a dimensionless constant known as the separation factor or equation parameter R_L, which can be calculated by the following equation;

$$R_l = \frac{1}{K_l q_{max}} \tag{4}$$

Where, C_o is the initial concentration.

The value of R_l indicates whether the isotherm is irreversible (R_l=0), favourable (0<R_l<1), linear (R_l=l), or unfavourable (R_l>1).

As shown in Table 4, the maximum adsorption capacity was found to be 58.82 mg/g and the R^2 values was obtained to be 0.77 which indicates fitness of the experimental data. The R_L was found to be 0.982 which shows that the adsorption process was favourable. These finding is in line with the one reported by, [16].

Table 4. *Langmuir Isotherm Data.*

DYE	ISOTHERM	CONSTANT	VALUES
Methylene Blue	Langmuir	q_{max}	58.82
		R^2	0.7657
		K_L	0.00062 (L/mg)
		R_L	0.982

3.4.2. Freudlich Isotherm

The Freundlich isotherm is an empirical equation employed to describe heterogeneous system, it assumes that the adsorption energy of a solution or ion binding to a side on an adsorbent depends on whether or not the adjacent sites are already occupied.

The Freundlich equation is written as;

$$\text{Log qe} = \text{LogK} + 1/\text{nlogCe} \tag{5}$$

Where qe and Ce are the equilibrium adsorption capacity of the adsorbent and the equilibrium concentration in the aqueous solution respectively.

K and n are the Freundlich constants related to adsorption capacity. And the plot of Log qe against Log Ce gives the Freundlich isotherm graph. And the parameters; n and K were also obtained from the slopes and intercept of the graph. From Table 4, R^2 value obtained was 0.1568 which indicate lack of fitness of the experimental data.

Table 5. *Freudlich Isotherm table.*

DYE	ISOTHERM	CONSTANT	VALUE
Methylene blue	Freundlich	R^2	0.1568
		K	2.436 (mg/mg)
		n	0.604

3.5. Kinetic Adsorption Study

The Pseudo-first order and the Pseudo-second order kinetics are the only kinetics studied for this experimental adsorption process.

The Pseudo-first order equation is represented as follows:

$$\log(qe - qt) = logqe - \frac{K1t}{2.303} \quad (6)$$

Where, K_1 is the Lagergren rate constant of adsorption (1/min).

The plot of log (q_e-q_t) against t, gives linear relationship from which q_e and K_1 are determined from the intercept and slope of the plot respectively.

The pseudo-second order equation can be represented by the following linear form.

$$\frac{t}{q_e} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

Where, K_2 is the second order rate constant of adsorption (g/mg min). The values of K_2 and q_e are determined from the intercept of the plot of t/q_t againt t.

Table 6. *Kinetic Adsorption Parameters (Pseudo First Order).*

Dye	Parameters	Time (min)					
		10	20	30	40	50	60
Methylene Blue	Removal (%)	90.30	99.30	95.33	92.20	97.23	87.16
	K_1 (1/min)	0.04	0.02	0.006	0.005	0.003	0.002
	q_e (mg/g)	108.36	119.16	114.40	110.40	116.68	104.60
	R^2	0.589					

Table 7. *Kinetic Adsorption Parameters (Pseudo Second Order).*

Dye	Parameters	Time (min)					
		10	20	30	40	50	60
Methylene Blue	Removal (%)	90.30	99.30	95.33	92.20	97.23	87.16
	K_2 (g/mg min)	0.0002	0.0008	0.0007	0.0006	0.0005	0.0003
	q_e (mg/g).	108.36	119.16	114.40	110.40	116.68	104.60
	R^2	0.90					

From the above kinetics adsorption, it can be deduced that pseudo second order kinetic fitted to the experimental data with R^2 value of 0.9 than pseudo first order which have R^2 value of 0.589. Pseudo second fitted the experimental data according to [17, 18].

3.6. Conclusion

The adsorption process of the dye, methylene blue using montmorilonite silica nano composite was investigated. From the experimental data, the highest percentage removal of the dye was 99.30% at initial concentration of 3mg/l, contact time of 20minutes, and an adsorbent dose of 0.5g. The adsorption process of methylene blue dye was favoured by the Langmuir Isotherm greater than the Freudlich Isotherm with R^2 values of 0.7656 and 0.1568 respectively. Also the R_L value of 0.982 obtained from Langmuir isotherm indicated the favourability of the adsorption process. The kinetic model that fits the adsorption process of methylene blue was observed to be the pseudo second order kinetics with an R^2 value of 0.9.

From the above results, it can be seen and observed that montmorilonite silica nanocomposite obtained from montmorilonite clay and Rice husk ash can be used as a cost effective adsorbent in the removal of methylene blue dye.

References

[1] Weng C. H, and Pan Y. F (2007). Adsorption of a cationic dye (methylene blue) onto spent activated clay. *Journal of Hazarous material* 144; 355-362.

[2] Olusegun Sodinde and Ugba Eboreme (2013). Adsorption of textile waste containing methylene blue and congo red using activated carbon produced from coconut shell. *International journal of computational engineering and management*, 16 (5), 2230-7893.

[3] Demirbas A (2009) Agricultural based activated carbon for the removal of dyes from aqueous solution: *A Review Journal of Hazard matter* 162: 1-9.

[4] Mohammad A. R., Ruhul A. SM. and Shafiqul A. A. M. (2012). Removal of Methylene Blue from Waste Water Using Activated Carbon Prepared from Rice Husk, *Dhaka University Journal of Science,* 60 (2): 185-189.

[5] Sen T. K. and Dawood (2014). Review on Dye Removal from Its Aqueous Solution into Alternative Cost Effective and Non-Conventional Adsorbents. *Journal of Chemical and Process Engineering*, 1: 1-11

[6] Mulugeta M, Lelisa B (2014). Removal of Methylene Blue (Mb) Dye from Aqueous Solution by Bioadsorption onto Untreated *Partheniumhystrophorous* Weed. *Modern Chemistry and applications*, 2 (4), 2-5.

[7] Almeida CA, Debacher NA, Downs AJ, Cottet L, Mello CA (2009). Removal of methylene blue from colored effluents by adsorption onmontmorillonite clay. *Journal of Colloid Interface Science.* 332: 46-53.

[8] Barka N, Assabbane A, Nounah A, Laanab L, Ichouy (2009). Removal of textiledyes from aqueous solution By natural phosphate as a new adsorbent desalination 235; 264-275.

[9] Mansoori. T, Rohani. B, A. Ahmad. P, Z. and Eshaghi (2008). Environmental application of nanotechnology. *Annual review of nano research*, 2 (2): 1-73.

[10] Mishra A. K. (2015). Nanocomposites in wastewater treatment. Pan Stanford Publishing Pte.Ltd, Singapore, 1.

[11] Atassi Y., Hussan – Aldeen. K, and Muhammad T. (2013). Preparation of clay base on superabsorbent polymer composite (acrylate-co-acrylate) with bentonite via microwave radiation. *Research & Reviews in polymers*, 4 (4): 145-150.

[12] Qian Z., Hu G., Zhang S. and Yang M. (2008). Preparation and Characterization of Montmorillonite-Silica Nanocomposites: A Sol-Gel Approach to Modifying Clay Surfaces, *Physica B*, 403 (18): 3231-3238.

[13] Awizar D. A., Othman N. K., Jalar A., and Daud A. R. (2013). Nanosilicate Extraction from Rice Husk Ash as Green Corrosion Inhibitor. *International Journal of Electrochemical Science,* 8 (2013) 1759–1769.

[14] Hafez M. A. and Hassona M. E., (2015). Poly M-Aminophenol/montmorillonitenano-composite for adsorption of Lead from authentic water sample and spiked water river nail water. *International journal of Engineering Research and General Science,* 3 (2): 2091-2730.

[15] Sadek O. M., Safenaz M. R. and, Reemk, A. (2013). Preparation and characterization of silica and clay silica core shell nanoparticles using sol gel method; *advances in Nanoparticles*, 2: 165-178.

[16] Wei W., Yang L., Zhong W. H., Li S. Y., Cui J. and Wei Z. G. (2015). Fast removal of methylene blue from aqueous solution by adsorption onto poorly crystalline hydroxyapatite nanoparticles, *Digest Journal of Nanomaterial and Biostructures*, 10 (4), 1343-1363.

[17] Zohre S., Ataallah S. G. and Mehdi A. (2010). Experimental study of methylene blue adsorption from aqueous solutions onto carbon nano tubes, *International Journal of Water Resources and Environmental Engineering*, 2 (2), 016-028.

[18] Chang J., Jianchao M., Qingliang M., Duoduo Z., Nannan Q., Mengxiao H., and Hongzhu M. (2015). Adsorption of methylene blue onto Fe_3O_4/activated montmorillonite nanocomposite, *Applied Clay Science*, 119, 132–140.