REMOVAL OF METHYL ORANGE DYE FROM AQUEOUS SOLUTION BY ADSORPTION ON HCL AND NH_4 OH TREATED RICE HUSKS

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Abstract

Rice husk, one of the agricultural waste products commonly available in Nigeria in large quantity was used as a sorbent material to remove methyl orange from synthesized aqueous solution. The rice husk treated with HCl was found to be far more effective in removing methyl orange from aqueous solution as compared with that treated with NH4OH. Adsorption capacity increased with initial concentration and time, but decrease with increase pH and sorbent dosage using HCl treated husk. Adsorption using NH4OH treated husk decreased with increase in the afore mentioned parameters. Freundlich and Langmuir isotherm equations were used to establish the levels of adsorption. Adsorption using NH4OH treated husk did not fit into both Langmuir and Freunlich models, invariably due to poor adsorption. Fruendlich isotherm reveals n=1.52 and k=21 using HCl treated husk. Adsorption using NH4OH treated husk was not also consistent with Freundlich isotherm for the same reason as stated above. Conclusively, HCl treated rice husk can be used to bioremediate methyl orange dye polluted water bodies as an alternative to more costly adsorbent.

Keywords: Methyl Orange, Adsorption, Rice husk, Hydrochloric acid, Ammonium hydroxide.

Introduction

Industrial effluents are major culprits in environmental pollution and this has especially been of serious concern in developing countries. Our environment has to be protected from this continuous pollution, because most of these azo dyes and their degradation products such as aromatic amines are very carcinogenic (Wena *et al.*, 2018). Apart from textile industries, paper, cosmetic, plastic, rubber and leather industries synthesize dyes (Moghaddam *et al.*, 2009). These industries release partly treated effluents with dyes into our water bodies, ultimately leading to eutrophication and perturbation of aquatic life(Qiu *et al., 2*009). In addition dye waste water discharge into our water bodies are unacceptable for human consumption (Gao *et al*., 2007). It is therefore necessary to remove all the dyes from industrial effluent.

Different treatment methods are described in literature by different researchers for waste water that contains dyes; they include membrane filtration, electro-coagulation, electrochemical destruction, ion exchange, irradiation, advanced ozonation, precipitation and adsorption involving the use of activated carbon (Gemea *et al*., 2003; Lopez-Grimau,2006) and also adsorption using modified agricultural wastes. Reports have shown that activated carbon has been effective and it can be obtained from carbonaceous material such as coconut shell, wood, nut shell, rice husk. But commercially activated carbon is very expensive and its generation and reuse makes it more costly. Its use also accompanied with combustion at high temperature makes it not to be environmentally friendly.

Consequently, many researchers have studied the feasibility of agricultural waste substances for the removal of various dyes and pollutants from wastewater (Kayode and Olugbenga 2015).

Milling of rice crop produces rice husk as agricultural waste material with little or no commercial and economical value. Rice husk is commonly used as a low value energy resource; burned in fields, or discarded, adding to the problems of pollution in our environment (Chen *et al*., 2011). Rice husk primarily consist of ash old organic matter, containing cellulose, hemicellulose and lignin (Liou and Wu 2009). It has a content of about 20% which makes it viable as feed stock for the production of silica based materials that can be used in separation, adsorption, catalysis and thermal insulation (Lin *et al*., 2013).

The researcher has decided to use HCl and NH_4OH treated rice husks to adsorb synthetic dye (methyl orange) from aqueous solution, since this is cheap and environmentally friendly.It serves as a way of alleviating the problem of rice husk disposal.

Materials and Method

Materials

Apparatus
Measuring Cylinder
Volumetric flask

Reagents

Hydrogen Chloride or Hydrochloric acid
Ammonium hydroxide solution (NH_4OH)
Sodium hydroxide solution (NaOH)
Methyl Orange
Distilled water.

Collection and Pretreatment

Rice husk was obtained from a local mill at Ekpoma Edo State and was washed with ordinary water several times and rinsed twice with distilled water. The clean rice husk was dried under the sun towards the tail end of harmattan for one week. The dried husk was sieved to 250-500nm size and was used without further purification.

Methods

The husk was divided into two parts a part was treated with HCl and the other with NH_4OH as follow**:**100g each of rice husk was soaked in 0.6M HCl and NH_4OH for 2h at 20^0C. The slurries were dried over night at 50^0C, and thereafterwas heated to 120^0C. The product was washed repeatedly with distilled water (200ml per g husks) to remove any HCl and NH_4OH, left. This was followed by oven drying overnight at 100^0C.

Preparation of Dye Solution

Methyl orange was used without further purification. Astock solution of the dye was prepared by dissolving 1g of dye in 1000cm^3 of distilled water. The experimental solution were prepared by diluting definite volume of stock solution to get the desired concentration. The maximum wavelength of methyl orange was measured at 464nm. The concentrations during experiment were determined from a standard calibration curve.

Adsorption Studies

Equilibrium adsorption isotherm for the 0.6M HCl and 0.6M NH_4OH treated rice husks were investigated at agitation rate of 150rpm at room temperature for 5,10, 15 20 and 25 ppm initial dyes concentrations into each concentration in a 250cm^3 Erlenmeyer flask,10g/dm^3 of adsorbent was added. The contents were mixed thoroughly for 2 hours, then small amounts were withdrawn and centrifuged at 4000revolution per minutes for 5 mins. The supernatants were analyzed for dye content. Each of the experiments was carried out in duplicate; the relative deviation was less than 5%

The adsorption performance of each sample was studied by evaluating the adsorption capacity of methyl orange from this formula $[(C_0 - C) \div C_0] \times 100$………. 1

Where $C_0$is the initial concentration of methyl orange

C is the solution concentration after adsorption at a particular time.

Effect of time on the dye removal at various predetermined intervals was performed by shaking the reaction mixture, Centrifuging and then analyzing for dye content at the end of each contact time 30, 60, 90, 120 and150 minutes

Sorbent concentration of 100-500g/dm^3 in a dye solution of 10mg/dm^3 in each 250cm^3 Erlenmeyer flask was investigated for effect of the sorbent dosage.

pH effect on adsorption was investigated from pH 3 – pH 11., and effect of doses of adsorbent was also investigated.

Kinetics of adsorption were determined by analyzing adsorption uptake of the dye concentration from aqueous solution at different time intervals.

Thus the amount of dye adsorbed onto the rice husk qe (mg/g) was calculated according to the following mass balance equation.

$qe = (C_0 - C_e)V \div W$……… 2

where C_0= the initial concentration (mg/dm^3)

C_e= equilibrium concentration mg/l of the dye

V= volume of the solution (dm^3)

W= weight (g) of the rice husk used

Results and Discussion

Effect of Initial Concentration

The effect of initial concentration on the removal efficiency of rice husk was investigated using different initial concentrations of methyl orange. These concentrations of methyl orange ranged from 5ppmto 25ppm. A fixed mass was added to each. The quantity adsorbed versus different initial concentrations is plotted in fig.1. It was observed that the uptake capacity increased with initial concentration of the adsorbate. The different quantities adsorbed respectively are as follows (10.575, 56.59, 147.8, 285.18, and 409.78) mg/g for HCl treated husk. This could be attributed to the fact that initial dye concentration increased the driving force to overcome the mass transfer resistance of the dye ion between the aqueous and the solid phase, resulting to higher probability of collision between the dye ion and the sorbent molecules. (Chen. *et al.,* 2011). On the other hand, the rate of adsorption reduced between 20ppm and 25ppm, probably because the external surface was saturated, the dye molecules were adsorbed unto the porous structure (Safa and Bhatti, 2011) of the adsorbent. In comparison with, NH_4OH treated husk, the quantity adsorbed was very minimal, in addition it showed a descending trend. The quantities adsorbed respectively are as follows (3.01, 1.58, 1.14, 0.96, 0.35) mg/g.This could be due to the poor affinity of the sorbent for the fluid component which resulted from the poor Vander-waal forces and hydrophobic interaction that also existed between sorbent and the dye molecules.

Table 1a: showing effect of concentration of dye in Ppm and quantity adsorbed qe(mg/g) of HCl treated husk

Concentration (Ppm)	5	10	15	20	25
qe(mg/g)	10.575	56.59	147.8	285.18	409.78

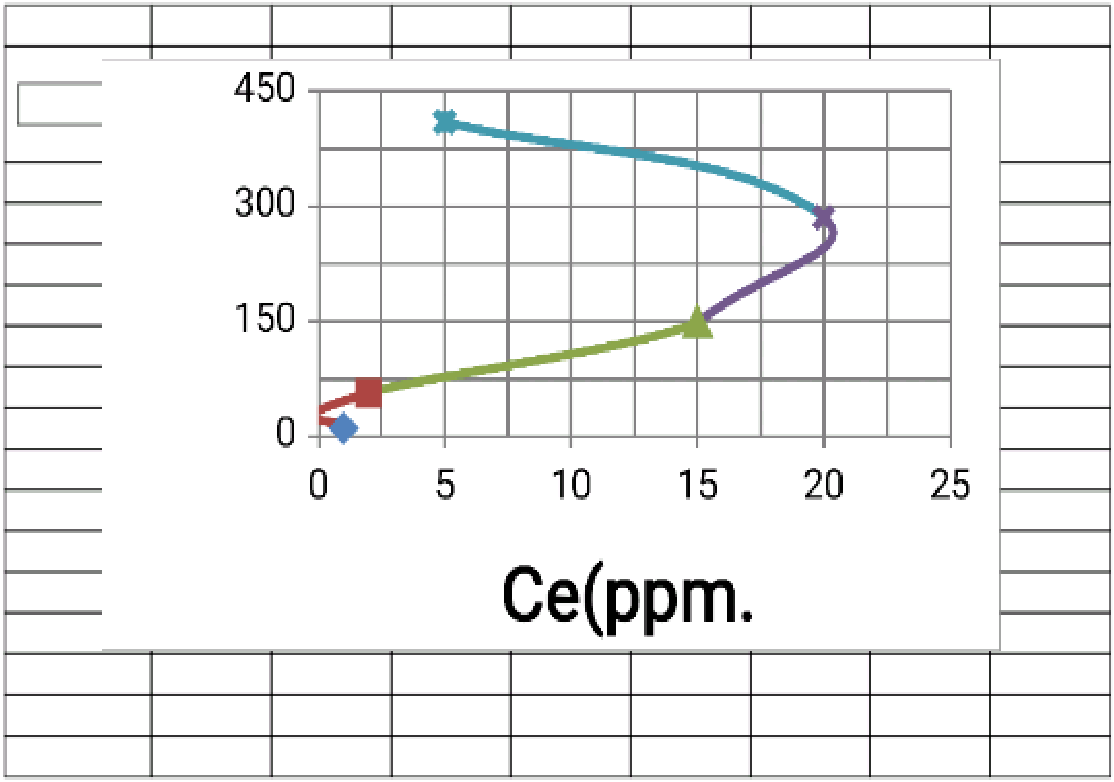

FIG 1a: A GRAPH SHOWING THE EFFECT OF INITIAL CONCENTRATION ON ADSORPTION CAPACITY OF HCl TREATED HUSK

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Table 1b: showing effect of concentration of dye in Ppm and quantity adsorbed qe(mg/g) of ammonium hydroxide treated husk

Concentration (Ppm)	5	10	15	20	25
qe(mg/g)	3.01	1.58	1.14	0.96	0.35

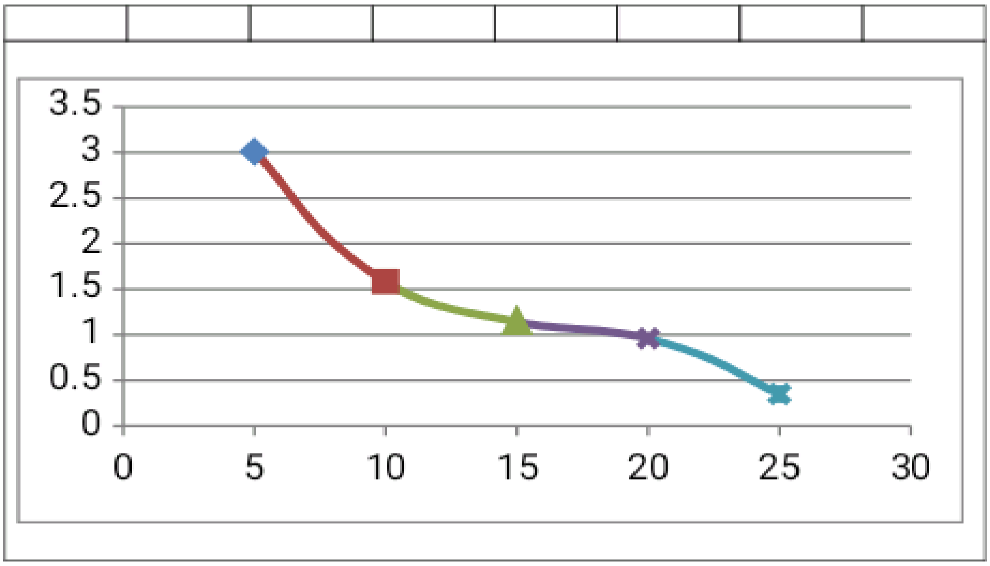

FIG 1b: A GRAPH SHOWING THE EFFECT OF INITIAL CONCENTRATION ON ADSORPTION CAPACITY OF NH_4OH TREATED HUSK

Effect of Contact Time

To investigate this effect on dye uptake varying time interval between 30mins - 150mins were employed, as shown in fig.2. The quantities adsorbed respectively were (50.080, 50.792, 52.000, 55.320, 56.590) mg/g for HCl treated husk. The highest rate was at 120mins, although adsorption capacity increased at 150mins. This showed that adsorption sites were exhausted due to repulsion forces between the solute molecules on the solid phase and bulk liquid phase. (Gulipalli, 2011)

NH_4OH treated husk only showed decreased adsorption capacity (4.520, 4.130, 2.860, 1.160, 0.110) mg/g. This can be attributed to decrease in electrostatic interaction which is a necessity for optimal adsorption.

Such interaction only exist between immobilized opposite charges such as occurs between SO_3^{2-}moeity of methyl orange and NH_4^+.

NH_4OH_{aq} (NH_{4aq}^+ + OH_{aq}^-[dissociation constant (K_1)= 1.8 $\times 10^{-5}$](Heys, 1975).

NH_{4aq}^{+}(NH_{3aq} + H_{aq}^{+}[dissociation constant (K_2)=5.6× 10^{-10}] (Bahl *et al*., 2007).

As illustrated above, K_1>K_2. Thus, the limited amount of NH_4^+ present gradually dissociates to liberate NH_3 a neutral molecule that cannot exhibit any electrostatic interaction with the SO_3^{2-} moiety, hence the decrease in adsorption with time.

Table 2a: showing time in minutes and quantity adsorped in mg/g of HCl treated husk

Time(mins)	30	60	90	120	150
qe(mg/g)	50.08	50.79	52.00	55.32	56.59

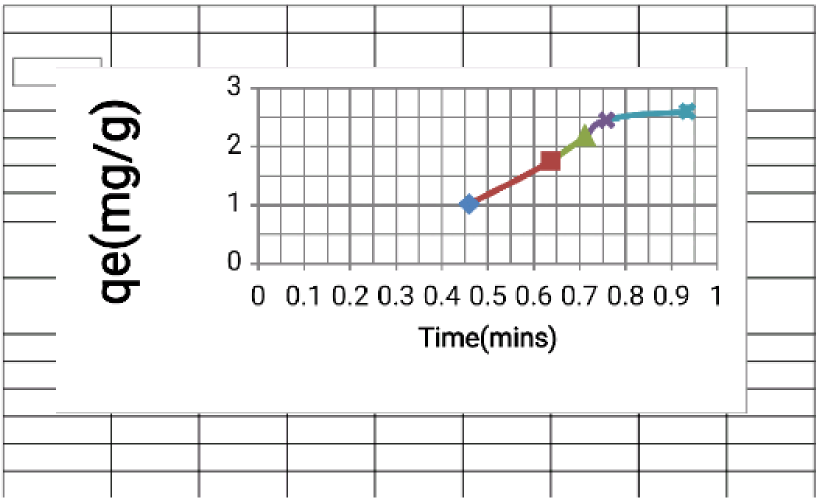

FIG 2a: A GRAPH SHOWING THE EFFECT OF TIME ON ADSORPTION CAPACITY OF HCl TREATED HUSK

Table 2b: showing time in minutes and quantity adsorped in mg/g of NH4OH treated husk

Time(mins)	30	60	90	120	150	
qe(mg/g)	4.52	4.13	2.86	1.16	0.11	

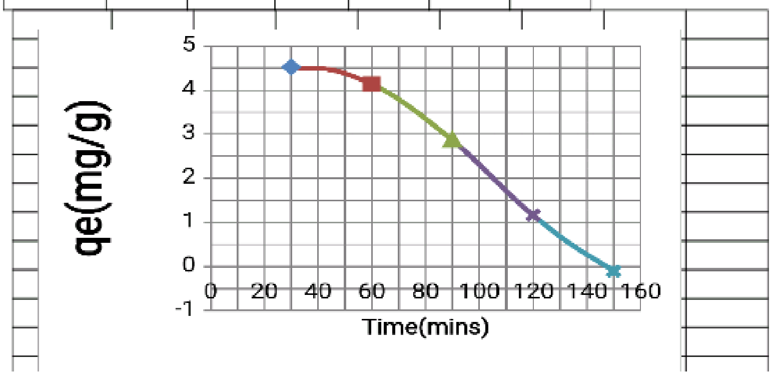

FIG 2b: A GRAPH SHOWING THE EFFECT OF TIME ON ADSORPTION CAPACITY OF NH4OH TREATED HUSK

Effect of P^H

To study the effect of p^H on the adsorption of methyl orange, p^H ranges between 3, 5, 7, 9, 11 were prepared. The P^H of the solutions was adjusted by adding 0.1M HCl and 0.02M NaOH as required.. Equal mass of adsorbent was added to the content in each flask. The highest adsorption was recorded at pH 3 for both HCl and NH_4OH treated husks. (74.96, 54.89, 8.65, 2.46, 0.170)mg/g.

In the case of NH_4OH treated husk adsorption capacities were (13.18, 8.8, 3.28, 0.51, 0.240)mg/g. Both showed decrease in adsorption capacity as pH values increased. This could be attributed to the protonation of the fibre at pH 3 in which the H^+provided a significant strong electrostatic interaction between fibre surface and dye molecules, leading to a maximum adsorption at pH 3.NH_4OH treated husk showed little adsorption capacity in comparison. This might be due to its poorly accessible pore volume (Saadi *et al.,* 2012).

Table 3a showing ph values and quantity adsorbed in qe(mg/g) of HCl treated husk

P^H	3	5	7	9	11
qe(mg/g)	74.96	54.89	8.65	2.46	0.17

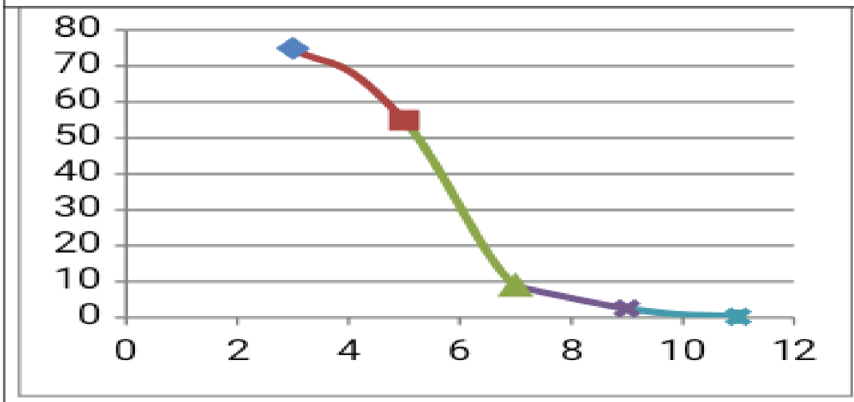

FIG 3a: A GRAPH SHOWING THE EFFECT OF P^H ON ADSSORPTION CAPACITY ON HCl TREATED HUSK

Table 3b showing pH values and quantity adsorbed in qe(mg/g) of NH_4OH treated husk

pH	3	5	7	9	11
qe(mg/g)	13.18	8.8	3.28	0.51	0.24

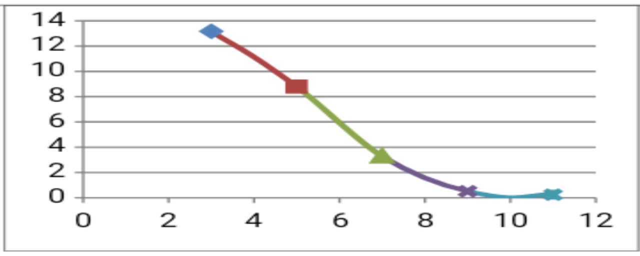

FIG 3b: A GRAPH SHOWING THE EFFECT OF P^H ON ADSSORPTION CAPACITY ON NH_4OH TREATED HUSK

Effect of Sorbent Dosage

The influence of sorbent dosage on adsorption of methyl orange was investigated using different sorbent doses of 1-5g. The quantities adsorbed were 58.7, 49.1, 49.56, 36.65, 10.997) mg/g respectively. For HCl treated husk the quantity adsorbed decreased with mass of the adsorbent as shown in fig. 4

Although increase in adsorbent dosage lead to increase in pore volume, this invariably might not lead to high adsorption capacity of the adsorbent due to the over loading and blocking of pore site for adsorption (Kanna,2002)

Ammonium hydroxide treated husk showed poor adsorption capacity but in the same trend. (3.99, 2.29, 1.28, 0.54, 0.7) mg/g

Table 4a showing mass of adsorbent in grams and quantity adsorbed qe(mg/g) of HCl treated husk

treated husk

mass(g)	1	2	3	4	5
qe(mg/g)	58.70	49.10	45.56	36.65	11.00

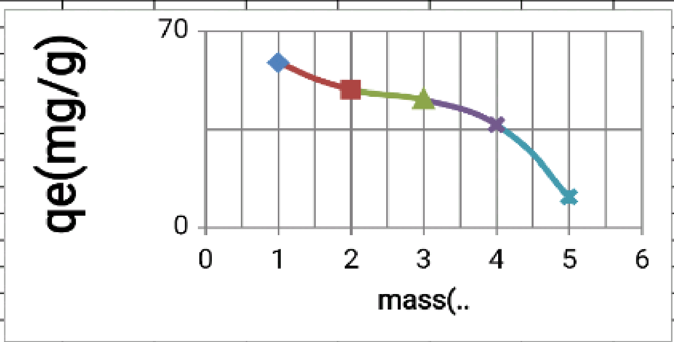

FIG 4a: A GRAPH SHOWING THE EFFECT OF DOSAGE ON ADSORPTION CAPACITY OF HCl TREATED HUSK

Table 4b quantity adsorbed qe(mg/g) of NH4OH treated showing mass of adsorbent in grams and husk.

mass(g)	1	2	3	4	5
qe(mg/g)	3.99	2.29	1.28	0.54	0.7

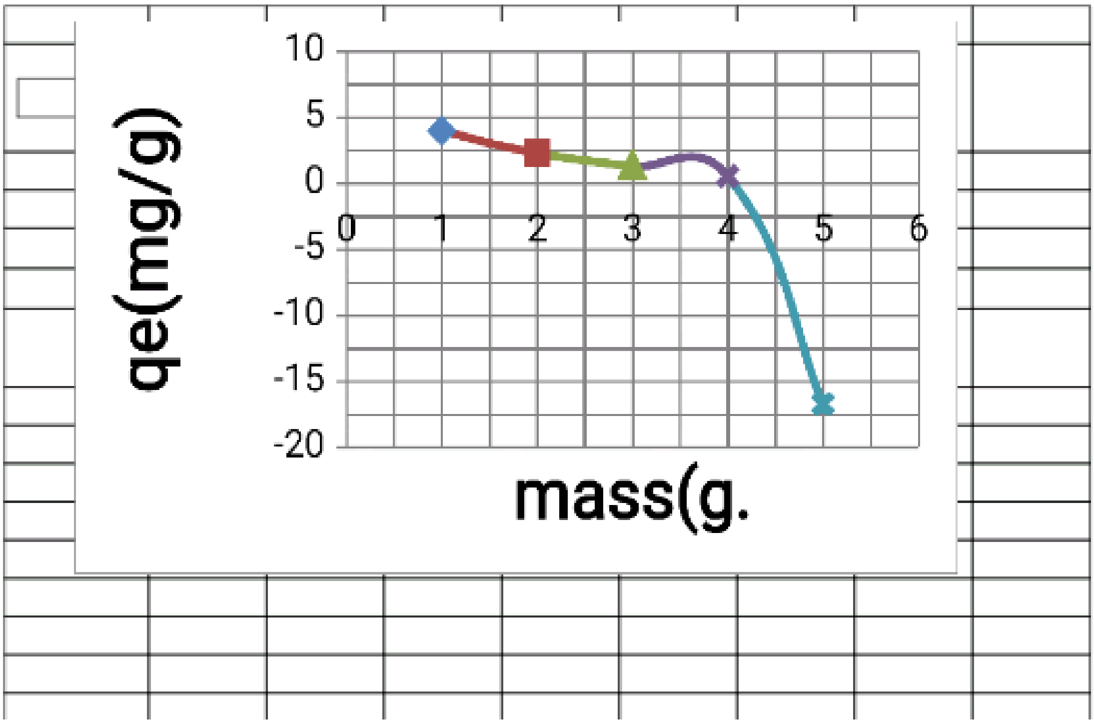

FIG 4b: A GRAPH SHOWING THE EFFECT OF DOSAGE ON ADSORPTION CAPACITY OF NH4OH TREATED HUSK

Freudlich Adsorption-Isotherm

The linear form of the Freundlich isotherm model is derived assuming a heterogeneous surface of adsorption capacity and adsorption intensity with a non-uniform distribution of heat adsorption. The Freundlich model can be given as

$qe=K_FC_e^{1/n}$

this equation can be linearized in logarithmic form of Freundlich isotherm model equation and is represented by In(Qe)=In(K_F)+ 1/nIn(C_e)where $K_F$and 1/n are Freundlich isotherm constant related to adsorption capacity. A plot of In(Qe) Vs In(C_e)yields a straight line with a slope of 1/n and intercept of $K_{f..}$

The magnitude of exponent 1/n gave an indication of the favourability of adsorption capacity of the rice husk adsorbent of methyl orange adsorbate values n>1 represented favourable adsorption conditions (McKay *et al.*, 1980, Ozer and Pirincci 2006).

Table 5: freudlich adsorption values for HCl treated husk.

InCe(mg/L)	1.059	1.469	1.638	1.747	2.153
InQe(mg/g)	2.734	4.025	4.990	5.653	6.016

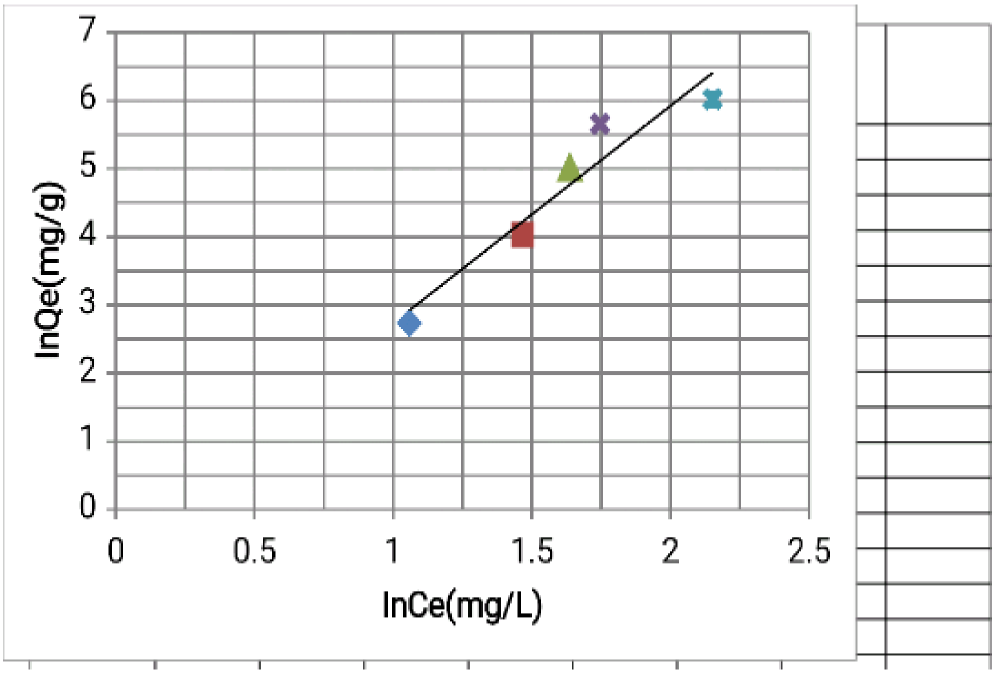

Fig 5: THE FREUNDLICH ADSORPTION ISOTHERM FOR METHYL ORANGE USING HCl TREATED HUSK

Conclusion

To find the most appropriate model for methyl orange dye adsorption, data were fitted into Langmuir and Freudlich isotherms and the results were consistent with only the latter. Langmuir adsorption model deviates significantly probably because it fails to account for the surface roughness of the adsorbent- a major consideration when working with small molecules as typified in our study. Furthermore, the inconsistency with Langmuir's model may also be due to the energetic heterogeneity of adsorption sites.

On the basis of the linear form of Freudlich equation, if n=1, then the adsorption is linear. If n<1, then the adsorption is a chemical process and if n>1 then adsorption is a physical process (Diesta, 2013). In our current study, n=1.52. A clear indication of good adsorption which is a physical process that portends environmental friendliness.

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