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KINETIC STUDY OF ADSORPTION OF METHYL RED DYE ON PERICARP CHARCOAL OF ADANSONIA DIGITATA(BAOBAB)

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ABSTRACT

Activated charcoal prepared from Adansonia Digitata(baobab) pericarp has been used for the removal of methyl red dye from simulated aqueous solutions employing adsorption method. The effect of adsorption was studied by using different parameters such as pH(2-4), contact time(50-200min), initial dye concentration(50-200mg/L) and adsorbent dosage(1-4g). The extent of adsorption was determined by employing uv-vis spectrometer. The experimental data was verified by Freundlich model and found to be satisfactory. Under the experimental conditions the parameters at the maximum adsorption ability have been determined for the dye and reported.

Keywords: Biosorption, methyl red dye, baobab pericarp charcoal

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1. INTRODUCTION

Dyes are synthetic aromatic compounds that are stable and difficult to be degraded (yenikaya, et al., 2010). Most of the dyes are complex organic molecules. According to the chemical structure, dyes can be divided into Azo dyes, Aryl dyes, Acridine dyes etc. Azo dyes are the mostly used in industrial activities. Dyes are used in production of the essential consumer products of modern life such as textile, leather, cosmetic, foods and beverages, papers and pulp which cause the environmental pollution problems and threat to the ecological balance (Ulas, et al., 2017).

Synthetic dyes are extensively used for coloring and printing in variety of industry (mohanraj, 2009). The dye based effluent is a considerable source of non-aesthetic pollution since the presence of small amount of dye (below 1 ppm) is clearly visible. Many researchers found that colorant may cause problems in aquatic ecosystem in several ways (yenikaya, et al., 2010). Worldwide, infectious diseases such as water-borne diseases are the number one killer of children under five years old and more people die from unsafe water annually than from all forms of violence, including war (Edogbanya, et al., 2013a). The problem of water pollution has become an issue drawing global attention. Every day, two million tons of sewage, industrial and agricultural waste are discharged into the world's waste water bodies (WWAD, 2006). There are several ways for removal of dyes; adsorption has been considered for the removal of textile dyes effluents due to its low cost, easy availability, simplicity of design, high efficiency, ease of operations and ability to treat wide variety of dyes (Ramalkashmi, et al., 2012). Activated carbon is a carbonaceous adsorbent with a highly crystalline form and internal pore structure (Kavitha 2019). A wide variety of activated carbon products are available depending upon a starting raw material and activation techniques (Gupta, 2003). It is used to recover organic solvent, purify carbon dioxide from fermentation process, purification of drinking water, amine, and glycol treating, decolorizing of water and various other chemical and petrochemical process (Sircar, et al., 1996). The mount of dyes absorbed per unit mass of absorption increase with increase with concentration (Omprakash, et al., 2019). At lower pH of solution, the percentage of dye removal decreases for cationic dye adsorption while for anionic dyes the percentage of dye removal increases and vice versa (singh, 2019).

The Baobab tree mostly found in the equatorial area such as Gabon, Democratic Congo Zaire and the area with marked dry season (Gebauer, et al., 2002) such as Dodoma region in Tanzania. It is a tree of multiple uses and it is said that all parts of the tree are useful. Generally baobab fruits and seed oil are used for human consumption and the rest of the tree parts are used as traditional medicine (simon, 2015). The baobab tree is known to human beings for 200 years. Baobab trees are grown in thirty two African countries, they live for up to 5000 years and reach upto 30 meters high (Anna, et al., 2019). Baobab belongs to genus:Adansonia and Species- Adansonia digitata. In the present study, methyl red is used as a simulated adsorbate and baobab fruit pericarp charcoal as adsorbent.

2. MATERIALS AND METHODS

2.1 Preparation of dye solution

Stock solution of dye concentration 1000 mg/L was prepared by dissolving 1g of 100% pure methyl red in 1000mL of distilled water by using standard flasks. Solutions of different concentrations were prepared by dilution method between 20 and 200 mg/L using the stock solution of the dye. All chemicals of 99.9% purity have been used in the present study.

2.2. Preparation of Pericarp biosorbent

Fruits of adansonia digitata were collected from a single tree in Dodoma region at Kongwa district. The dried fruits were broken and the seeds were removed. The pericarp pieces were properly washed with distilled water, dried under the sun, pulverized into powder using grinding machine, sieved through a pore size of about 1mm. The dried pericarp sample was treated with sulfuric acid with constant stirring. Then the sample was kept in hot air oven at 200±50k temperature for twelve hours. The sample was washed with distilled water and soaked in sodium bicarbonate solution and then allowed to stand overnight to remove the residual acid from the pores of carbon. The sample was washed again with distilled water, until the pH of the adsorbent becomes neutral (7±0.2). Then the sample was dried in a hot air over at 100±5℃ for twelve hours. The dried sample was ground to get a powder of particle size about 125-250µm range and stored in an airtight container for further experiments.

2.3 Batch mode biosorption studies

A standard calibration plot between the adsorbate concentration and absorbance was drawn. Batch biosorption equilibrium experiments were conducted in 250 mL conical flasks at a constant agitation speed (180 rpm). All the experiments were carried out at room temperature (30^0C). The concentrations of the dyes both before and after adsorption were determined using Agilent 60 carry UV- Vis spectrophotometer, USA through monitoring the absorbance for the dye used. Initial concentration of the dye, adsorbent dosage, pH of solution, temperature and contact time between adsorbent and adsorbate are the most important factors that affect adsorption process. The effect of initial dye concentration was studied in the concentration range 50-200 mg/L at optimized conditions. The pH was studied in the intervals of 2, 4, 6 and 8. The effect of mass of adsorbent was studied in the range 1gram to 4gram at constant dye concentration 200mg/L and optimized conditions. The effect of contact time was studied in the constant dye concentration of 200 mg/L and time range from 50 minutes to 200 minutes

3. RESULTS AND DISCUSSION

3.1 Effect of initial concentration of dye

The effect of initial dye concentration was studied in the concentration range 50-200 mg/L at optimized conditions. The extent of adsorption of dye per gram of activated

carbon was calculated and reported in Table No:1. A plot is drawn between adsorbate concentration and adsorption ability and shown in Fig.1.
x/w = extent of adsorption (mg/g), V = Volume of dye solution (L), Ci = initial concentrations (mg/L), Cf = final concentrations of dye (mg/L) , w = dry weight of the activated carbon (g)

Table 1: Data showing initial concentration of dye solution and adsorption ability

S/N	Ci (ppm)	w (g)	Absorbance	Cf (ppm)	Ci-Cf (ppm)	x(mg)	x/w (mg/g)
1	50	1.02	0.1077	23	27	0.317	0.311
2	100	1.05	0.1139	33	67	0.766	0.729
3	150	1.00	0.1215	46	104	1.25	1.25
4	200	1.14	0.1305	61	139	1.46	1.281

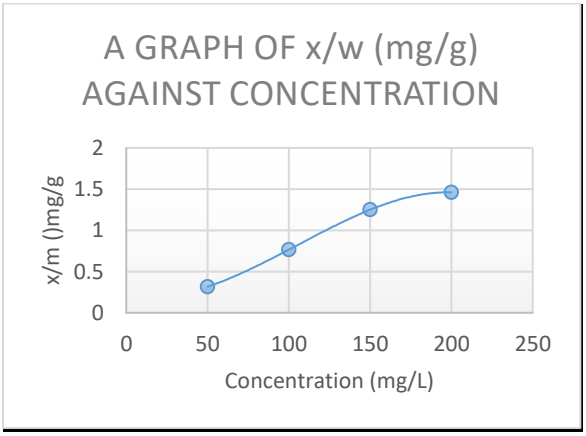


Fig:1 Adsorbate concentration vs. Adsorption ability

It is observed from the graph that as the initial concentration of adsorbate increases, adsorption ability increase to a certain extent and thereby remains constant. This may be due to the saturation of the active sites due to adsorption on the surface of adsorbent.

3.2 Adsorption isotherm

Adsorption isotherm has been studied on the extent of adsorption of adsorbate on the adsorbent by using Freundlich adsorption model. According to the Freundlich isotherm model, the amount of adsorption at low concentration varies linearly, at moderate concentration become dependent on the Freundlich constant and at higher concentration becomes independent of the adsorbate concentration. From the Fig:1 above, it shows that the experiment obeys the Freundlich model satisfactorily. Further

it is verified by plotting a logarithmic graph (Fig:2) and found to be a straight line which is expected of the above results.
x/w – extent of adsorption, C – equilibrium concentration of solute in aqueous medium K and n are Freundlich constants which depend upon the nature of adsorbent and adsorbate.

Table 2: Effect of concentration of adsorbate on adsorption

S/N	x/w (mg/g)	Ci (mg/L)	Log x/m	Log Ci
1	0.311	50	-0.51	1.7
2	0.729	100	-0.14	2
3	1.25	150	0.0969	2.17
4	1.281	200	0.11	2.3

From the Freundlich adsorption isotherm, the value of n and K are found to be 1 and $4.445x10^{-3}$ mg/L respectively.

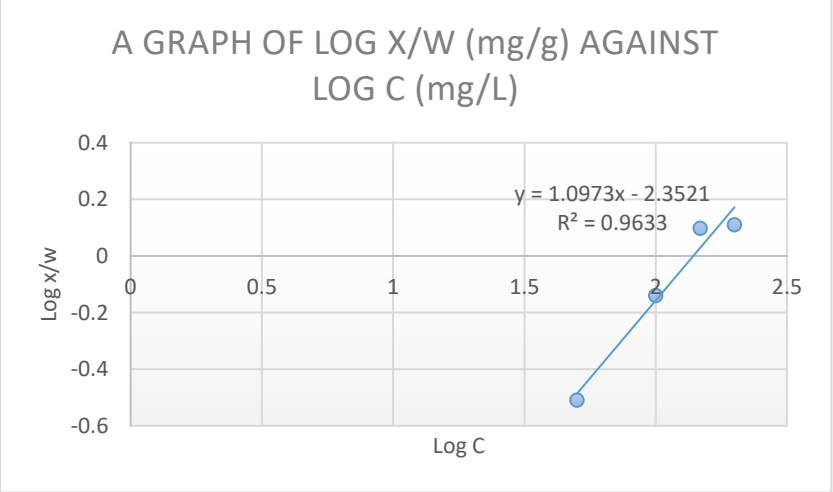


Fig 2: Freundlich adsorption isotherm

3.3 Effect of adsorbent dosage

The effect of mass of absorbent was studied in the range of 1gram to 4gram at constant adsorbate concentration of 200mg/L and optimized conditions. The extent of

adsorption of dye per gram of activated carbon was calculated and reported in Table No: 3. A plot is drawn between adsorbent dosage and adsorption percentage is shown in the Fig.3.

Table 3: Adsorbent dosage vs. absorbance data

S/N	Ci (ppm)	W (g)	Absorbance	Cf (ppm)	Ci-Cf (ppm)	X (mg)	x/w (mg/g)	q %
1	200	1.10	0.1220	46.83	153.17	3.68	3.35	76.6
2	200	2.01	0.1177	38.67	161.33	3.87	1.93	80.66
3	200	3.03	0.1101	27	173	4.15	1.37	86.5
4	200	4.14	0.1091	25.3	174.7	4.19	1.01	87.3

It was observed that the extent of adsorption increases with an increase in the mass of adsorbent (activated carbon) from 1-4 gram which may be due to the availability of unsaturated surface area (active sites).

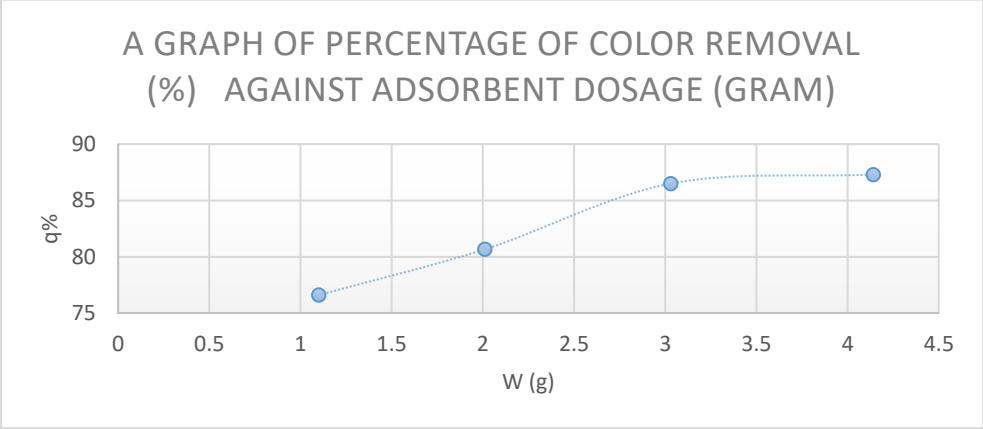


Fig 3: Graph between adsorbent dosage and adsorption percentage

3.4 Effect of pH

The effect of pH was studied at a constant concentration of 200 mg/L of adsorbent and pH range 2-8. The extent of adsorption of dye per gram of activated carbon was calculated and reported in table No.4
x/w = extent of adsorption (mg/g)
V = Volume of dye solution (L), Ci = initial concentrations (mg/L), Cf = final concentrations of dye (mg/L) , W = dry weight of the activated carbon (g)

The percentage of adsorption of the dye was calculated as, $q\% = \frac{(Ci-Cf)}{Ci}$.

Table 4: Data showing the variation of absorbance with change in pH at a constant mass of adsorbent

S/N	W (g)	pH	Absorbance	Cf (ppm)	Ci-Cf (ppm)	X (mg)	x/w (mg/g)	q%
1	4.12	2.46	0.0952	2.16	197.84	4.75	1.15	98.9
2	4.25	4.37	0.0969	5.00	195	4.68	1.10	97.5
3	4.16	6.57	0.0982	7.17	192.83	4.63	1.11	96.4
4	4.03	8.42	0.1000	10.2	189.80	4.55	1.13	94.8

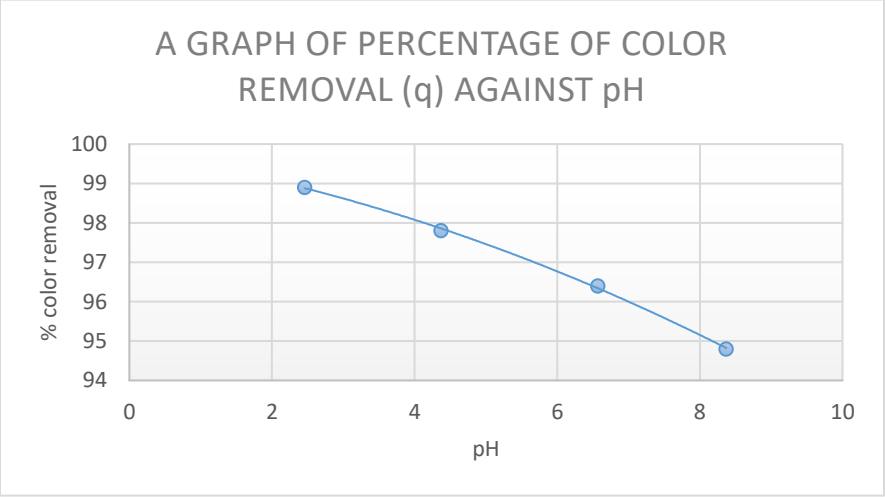


Fig 4: Effect of pH on the adsorbate concentration

The adsorbate shows a maximum adsorption at pH 2.46 with maximum percentage of adsorption of 98.9%, because it works efficiently on the acidic medium than in a basic medium. Methyl red is an anionic azo dye, hence at lower pH it shows higher adsorption due to the positively charged surface of the adsorbent.

3.5 Effect of contact time

The effect of contact time was studied at a constant concentration of 200 mg/L and time range from 50 minutes to 200 minutes. The extent of adsorption of dye per gram of activated carbon was calculated and reported in Table no:5 below.

The percentage of color removal in the dye solution after adsorption was calculated as $q\% = \frac{(Ci-Cf)}{Ci}$.

Table 5: Data showing the effect of contact time on adsorption ability

S/N	W (g)	Contact time (minute)	Absorbance	Cf (ppm)	Ci-Cf (ppm)	X (mg)	x/m (mg/g)	q%
1	4.09	50	0.1216	46.17	153.83	3.69	0,90	76.92
2	4.11	100	0.1207	34.7	155.3	3.73	0.91	77.65
3	4.02	150	0.1101	17	173	4.15	1.03	86.5
4	4.18	200	0.0960	3.5	196.5	4.72	1.13	98.25

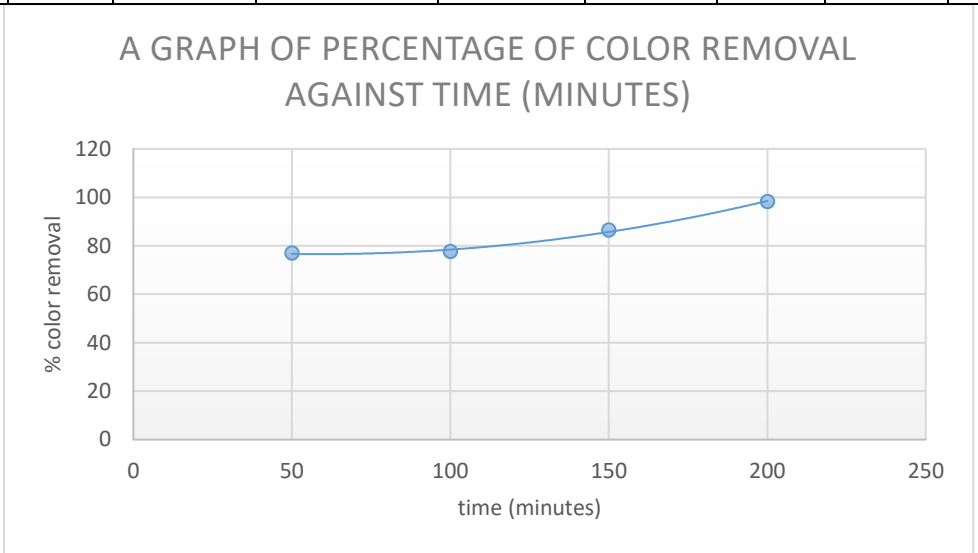


Fig 5: Effect of contact time on the adsorption ability

The removal of methyl red by activated carbon as a function of time was observed. Initially, the adsorption of dye is measurable during the time interval of 50 to 150 min and later, the adsorption process becomes less significant and remains nearly constant. The adsorption efficiency was found to be 98.25%.

4. CONCLUSION

The data obtained from the adsorption studies showed that a contact time of 200 min was sufficient for the maximum removal of methyl red dye from aqueous solution using baobab pericarp charcoal. The experimental data of biosorption of the dye on the baobab charcoal biosorbent fits well with the Freundlich adsorption model. This indicates that the biosorption of the dye on the baobab charcoal is favourable. The

maximum removal efficiency was predicted to be 98.25% at a temperature of 303K, solution pH of 2.45, and initial dye concentration of 200 mg/L and biosorbent dosage of 4.0g. Further investigation of the adsorption characteristics like surface area of the adsorbent and adsorption thickness are suggested to understand the adsorption mechanism.

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