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Research Article

AN ADSORPTIVE STUDY ON REMOVAL OF MALACHITE GREEN (MG) FROM AQUEOUS SOLUTION USING AN ECO- FRIENDLY BIOADSORBENT ACTIVATED *PONGAMMIA PINNATA* POD POWDER (AP4)

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ABSTRACT

The present investigation has been aimed to develop a cheap adsorption method for the removal of contaminants from wastewater using an eco-friendly bioadsorbent. Activated *Pongammia pinnata* pod powder (AP4) was used as an adsorbent which is extracted from ground shells of *Pongammia pinnata* pods (karanj tree). Systematic batch adsorption studies of Malachite Green (MG) on activated *Pongammia pinnata* pod powder (AP4) were carried using different parameters such as effect of initial adsorbate concentration, dose of adsorbent (AP4), pH, contact time and temperature. The adsorptive behaviour of MG onto AP4 was studied using Langmuir adsorption isotherm model. Thermodynamic analysis was also done to find out the nature of adsorption procedure. The estimated value of Gibb's free energy $\Delta G°$ (-11.22×10^3) reveals spontaneous nature of the process which involves pseudo first order kinetics controlled by particle diffusion process and the positive value entropy ($\Delta S°$) shows the randomness of the adsorption process.

Keywords: Adsorption, Malachite Green (MG), Activated pongammia pinnata pod powder (AP4), Isotherms, Equilibrium Study.

1. INTRODUCTION

The introduction of waste products into the environment has become a universal problem in recent time. Wastewater is a liquid waste which is discharged by different sources like commercial properties, industries, domestic residences, agriculture areas etc. [1]. On the basis of these origins, wastewater can be classed as commercial waste, sanitary waste, agricultural waste, industrial waste or surface runoff. The sources of industrial wastewater includes pharmaceutical industries, food industries, cement industries, pulp paper industries, textile industries, rubber industries, leather industries, organic compost, cosmetics industries, plastic industries and other industries [2, 3]. From the above mentioned sources of wastes, textile industrial waste, waste generated by use of a large variety of chemical and dyes wastes have resulted in a public health threat. Now a day's different types of dyes are being used in industries to color the products such as textiles, rubber, paper, plastics, cosmetics, etc. [4]. These industries released the remaining dye waste in water stream which is aesthetically detrimental and can produce serious environmental impacts.

Numbers of studies have been done to measure the harmful impacts of these types of materials on the ecosystem and it was found that they can cause several troubles in water bodies in many ways:

- Dyes can produce acute or chronic effects on the organisms which depend on the dye concentration and exposure time.
- Dyes have an affinity to sequester metal ions which can produce micro toxicity to fish and other aquatic organisms.
- Dyes have naturally extremely visible characteristics therefore their minor release of effluent may cause unusual coloration of surface waters.
- When dyes enter in wastewater, they can consume dissolved oxygen from the stream and can do some chemical and biological changes also in water bodies and consequently it can destroy the aquatic life.
- The dyes have ability to absorb and reflect the sunlight entering the water so it affects the growth of bacteria and prohibit their biological activity.
- Every dye has different and complex molecular structures therefore it is difficult to treat these types

of waste with simple municipal waste treatment operations and it required a innovative technique.

Due to these reasons, it is necessary to develop a technique which can treat these types of contaminants from waste water. A number of techniques have been discovered for this reason such as coagulation and flocculation, reverse oxidation [5], osmosis [6], biological treatment [7], photocatalysis [8] and adsorption [9]. Among these techniques, Adsorption is most promising method, which has wide applications in wastewater treatment. Adsorption is a mass transfer process which involves the accumulation of substances at the interface of two phases, such as, liquid-liquid, gas-liquid, gas-solid, or liquid-solid interface. Adsorption is economically cost effective, sludge free and simple method which is efficiently capable to treat the dyes in more concentrated form [10, 11]. Therefore it has superiority over other removal techniques. Our Co-workers have also been contributed in this field [12]. A number of studies have been done on adsorptive and photocatalytic removal of organic and inorganic contaminants from waste water [13, 14]. One of author of this research work has also done study on the adsorptive [15, 16] and photocatalytic [17-19] removal of pharmaceuticals from waste water. The present study is also a contribution in the field of adsorptive removal of dyes from water bodies. An environmental friendly bioadsorbent has been developed from *Pongammia pinnata* seed shell and the removal efficiency of the developed adsorbent was studied over the adsorbate Malachite Green (MG). A batch adsorption kinetic study has been done over the different concentration range of adsorbate and adsorbent to evaluate the effect of various parameters such as dye concentration, adsorbent dosages, contact time, pH of the medium to present adsorption dynamics. After that Adsorption isotherm models has also been evaluated to find the adsorptive behaviour and removal efficiency of the adsorbent. Thermodynamic studies have also been investigated to find out the free energy of adsorption ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) by assessing the experimental data.

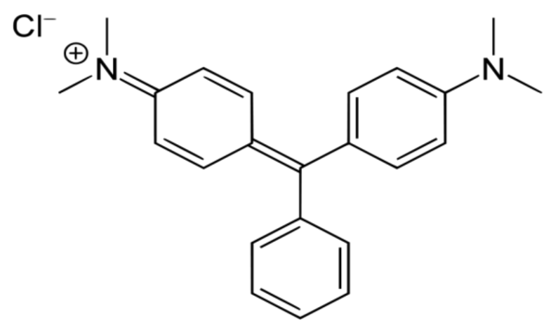
2. EXPERIMENTAL

2.1. Development of Eco-friendly Biosorbent

In the present investigation, the adsorbent was prepared by the seed shells of *Pongammia pinnata* (Karanj). For this purpose, the *Pongammia pinnata* pods were collected from Madhav Institute of Technology and Science (MITS), Gwalior, India. The pod's shells were compacted in fine particles and sieved to a particular mesh size. It was then soaked in hydrogen peroxide (30%) at 60°C for 24 h for the oxidization of the adhering organic impurities. After that it was washed with doubly distilled water and kept in an oven at 150°C for heating. Now it was sodden overnight in the solution of $NaHCO_3$ (1%) to take away any acid. Thus developed material was again washed with distilled water and again dried in oven at 150°C. Finally, developed adsorbent material was stored in separate air tight container.

2.2. Adsorbate

All the chemicals used in this study were of analytical grade and double distilled water was used throughout the experiment. Malachite Green (MG) (Scheme 1) (Table 1) was obtained from E. Merck, India and was used without further purification. A stock solution of MG (1mg/mL) was prepared by dissolving 500 mg of MG dye in 500 mL of double distilled water. After that working solutions of required concentrations were prepared by suitable dilution of the earlier prepared stock solution in double distilled water.



Scheme 1: Structure of Malachite Green

Table 1: Main properties of the Malachite Green

Property	Malachite Green
Molecular formula	$C_{23}H_{25}ClN_2$ (chloride)
Molecular weight	364.911 g/mol
Solubility	Water & Alcohol
Water Solubility	0.00138 mg/mL
Melting Point	158-160°C
Appearance	Green color powder
Density	1 g/mL
λ_{max}	617 nm

2.3. Instrumentation

A digital pH meter (DB 1011 India) fitted with glass electrode was used to measure the pH of the solutions. Adsorption measurement has been done on a spectrophotometer (Systonic model S-922 over the wavelength range of 340 to 960 nm) with a 1.0 cm light path quartz cells at λ max 617 nm. A Sartorius CP224S analytical balance (Gottingen, Germany) and ultra sonic cleaner (Frontline FS 4, Mumbai, India) were used during the study.

2.4. Adsorption studies

A batch method permits convenient evaluation of parameters that influence the adsorption process. Batch adsorption kinetic studies were performed at 30, 40 and 50°C temperatures. In this method, a fixed amount of the adsorbent (10 mg) was added to 30 mL of MG solution of varying concentrations from 1×10^{-5} to 8×10^{-5} M. The solutions were stirred continuously at constant temperatures. After a definite time (determined initially) the samples were withdrawn and the solution was separated using Whatmann filter paper (No. 42) and absorbance was determined spectrophotometrically at λmax 617nm.

Afterwards when equilibrium was achieved, the adsorption capacity q_e (mg g^{-1}) of the adsorbent at any time was calculated using the following mass balance relationship equation:

$$q_e=(C_o-C_e)\times(V/W) \qquad (1)$$

Where, C_o and C_e (both in mg L^{-1}) are the MG initial concentration and concentration of MG at any time respectively. V is the Volume of Adsorbate (MG) and W is the weight of adsorbent.

2.5. Quality assurance/quality control

Accuracy and precision are also necessary in an experiment, therefore, all the experiments were performed thrice to establish the accuracy, reliability, and reproducibility of the data. All the glasswares which were used in this study were soaked in 5% HNO_3 solution for a period of 3 days then doubly rinsed with distilled water and oven dried before use.

3. RESULTS AND DISCUSSIONS

3.1. Characterization of Bioadsorbent

3.1.1. Surface morphology and characteristics

Scanning electronic microscopy (SEM) study is one the most popular, primary, and widely used characterization technique used for the study of surface properties and morphology of biosorbent material. SEM study tells about porosity and texture of biosorbent material. The morphological structure of biosorbent activated *Pongammia pinnata* pod powder (AP4) was observed under SEM (Zeiss EVO 50 instrument) and the micrograph is shown in fig. 1 which indicates it has small cavities on the surface or quite rough surface and there are asymmetrical shaped pores present. It has a porous texture that may provide bulky surface for the adsorption of the dye molecules.

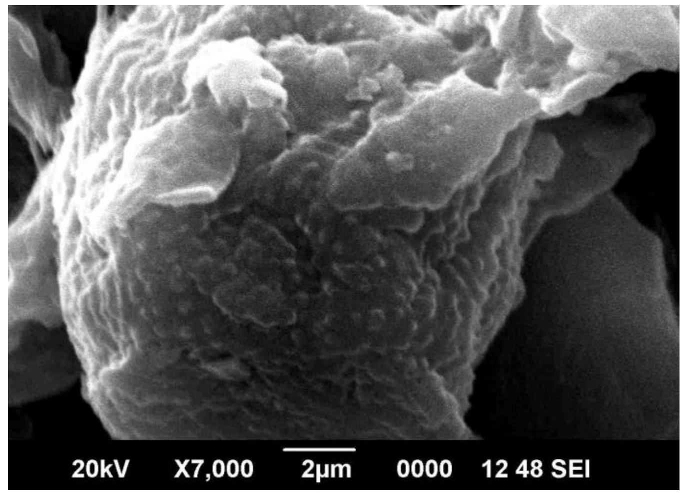


Fig. 1: Scanning electron microscope image of Bioadsorbent

3.2. Effect of bioadsorbent dose on adsorption of MG

Effect of adsorbent dosage is as an important parameter to study the adsorptive behaviour of any adsorbent. In the present study, this factor was studied by varying the amount of bioadsorbent from 0.066 to 0.53 g L^{-1} on keeping other parameters (pH, initial concentration, and contact time) constant. When we increase the adsorbent dose, the rate of adsorption is increased to 0.33 g L^{-1} and on further increase in adsorbent doses, a sudden decreased in adsorption rate of MG occurred. Hence 0.33 g L^{-1} was taken as optimum amount of adsorbent dose for evaluation of other parameters. The results are shown in fig. 2 which concludes that on increasing the adsorbent dosage uptake capacity decreases.

3.3. Effect of temperature

The effect of temperature is also an important parameter because it changes the equilibrium capacity of the adsorbent for the adsorbate. In this study, it was found that removal efficiency of MG was directly proportional to temperature hence when the temperature was increased from 30°C to 50°C, the maximum efficiency was found at 50°C which indicate the endothermic nature of the reaction.

3.4. Effect of pH

The charges present on dye molecules and the surface of the adsorbent interact with each other and reaction occurred [20]. Some parameters such as surface charges, adsorption capacity and active sites which are present on adsorbent might be attributed to the adsorption behaviour of the adsorbent at different pHs. Therefore the experiments were carried out at pH range from 2.48 to 12.3 and it was found that the percent removal of MG was different at every pH range. When the pH range was increased from acidic medium to basic medium, it was found that percent removal also increased from 42% to 90% till pH 9.2 and on further increasing it almost get constant, therefore, 9.2 was taken as optimum pH value for further study.

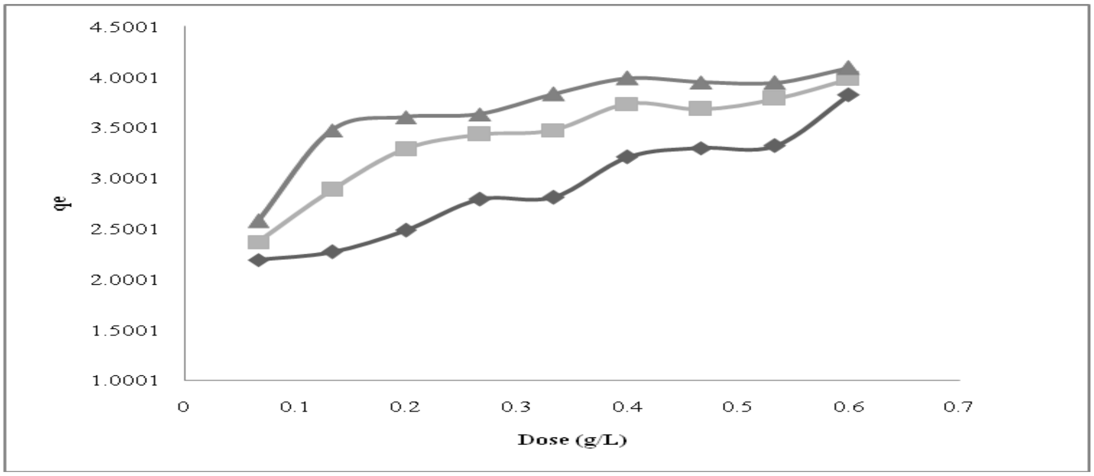


Fig. 2: Effect of amount of adsorbent for the removal of Malachite Green at 4×10^{-5} M at pH 9.2 and different temperatures

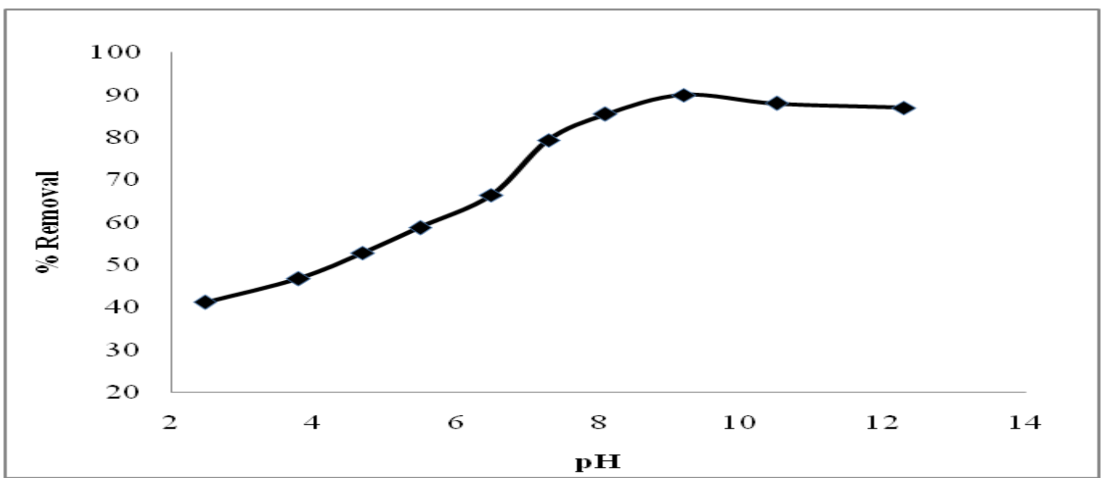


Fig. 3: Effect of pH on the removal of Malachite Green at 4×10^{-5} M and 0.33g/L dose of adsorbent.

3.5. Adsorption isotherm studies

The adsorption isotherms define the distribution of adsorption molecules between the liquid phase and the solid phase at equilibrium [21]. Adsorption isotherms also play an important role to study the adsorptive behavior for solid-liquid adsorption systems. In the present investigation Langmuir isotherm model has been studied.

3.5.1. Langmuir adsorption isotherm

Langmuir adsorption isotherm model was given by Irving Langmuir in 1916 [22]. This model refers to adsorption of a homogeneous monolayer to a surface containing a limited number of adsorption sites having identical qualities with no transmigration of adsorbate in the plane of the surface. The mathematical expression of Langmuir model is as following [23]:

$1 / q_e = 1/Q° + 1bQ°C_e$ (2)

Where C_e is the equilibrium concentration of the adsorbate (mol L^{-1}) and qe is the amount of adsorbent adsorbed (mol g^{-1}). b and Q° are the Langmuir constants related to energy adsorption and maximum adsorption capacity, respectively. When 1/qe is plotted against $1/C_e$, a straight line with slope 1/bQ° is obtained, which shows that the adsorption of MG follows the Langmuir isotherm (Fig. 4). Langmuir constants were calculated at 30, 40, and 50°C and reported in table 1.

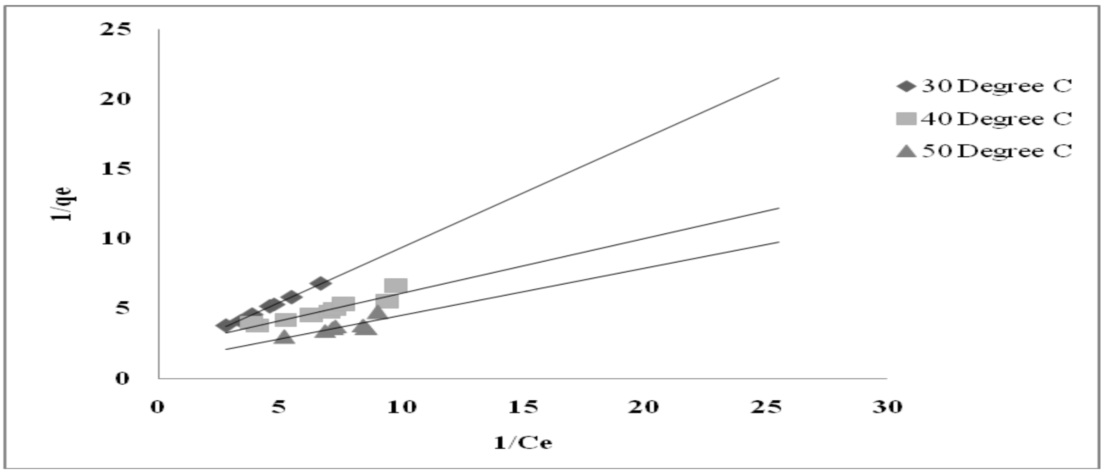


Fig. 4: Langmuir adsorption isotherms for adsorption of Malachite Green at pH 9.2 and different temperatures

Table 2: Langmuir constants for MG over bioadsorbent at different temperatures

Temp.(°C)	b(molg^1)	Q°(Lmol^1)	bQ°	R^2	%RSD$^\#$
30	1.628	118.12	2.016	0.998	0.983
40	1.416	84.32	3.621	0.932	0.901
50	1.388	69.30	3.434	0.915	0.898

3.6. Adsorption kinetics studies

The kinetic study in adsorptive procedure is important factor to understand the adsorption dynamics in terms of order of the rate constant and it provides useful information regarding the efficiency of the adsorption of solid/liquid systems. It can be determined by many mathematical calculations but Lagergren's rate equation plays major role in it. Lagergren and Svenska [24] suggested the kinetic model to study the efficiency of adsorption of any system. In the present investigation the kinetics study of the MG adsorption was analyzed using the following first-order rate equation [25].

$\text{Log} (q_e-q_t) = \log q_e-k_{ad} \times t/2.303$ (3)

Where q_e and q_t are the amount adsorbed at equilibrium and at any time t, respectively.

Lagergren plot was found by plotting graph between log (qe-qt) versus time which exhibit straight line at different temperatures and constant pH 9.2 and that confirms the first order kinetics of the adsorption process.

3.7. Thermodynamics studies

Thermodynamic parameters [26] are the key features of any adsorption procedure. These are studied to find out the feasibility and nature of the process. Different types of thermodynamic parameters such as change in enthalpy (ΔH°), entropy (ΔS°) and gibb's free energy (G°) were calculated in the present investigation using the following thermodynamic relations [27].

$\Delta G° = -RT \ln b$ (4)

$\Delta H° = -R (T_{2*}T_1)/T_2-T_1)\ln(b_2/b_1)$ (5)

$\Delta S° = (\Delta H° - \Delta G°)/ T$ (6)

Here b, b_1 and b_2 are the equilibrium constants calculated from the slopes of straight lines which was obtained in case of Langmuir adsorption isotherms and given in table 3. The negative values of ΔG° confirm the spontaneous nature of the adsorption process. The positive value of ΔH° shows that the reaction is endothermic in nature while the positive value of ΔS° suggests increasing randomness at the solid/solution interface during the adsorption process.

Table 3: Thermodynamic parameters of MG over bioadsorbent

$\Delta G°$(kJ mol^{-1})			$\Delta H°$(kJ mol^{-1})	$\Delta S°$(JK^{-1} mol^{-1})
30°C	40°C	50°C	30°C	30°C
-11.22×10^3	-14.19×10^3	-15.09×10^3	3.153×10^3	29.478

4. CONCLUSION

Adsorption of Malachite Green onto developed bioadsorbent was studied experimentally in a batch adsorber. The investigation reveals that activated *Pongammia pinnata* pod powder (AP4) can be an excellent, inexpensive and environment friendly biosorbent for the removal of dye contaminants from aqueous solutions. The parameters such as pH of solution, dose of AP4 and temperature determined in the present study, were effective in determining the efficiency of MG onto the AP4. Langmuir isotherm model agreed very well with the equilibrium isotherms. It was also found that the reaction followed the pseudo first-order kinetic model with the dynamical behavior for the adsorption of MG onto AP4 at different temperatures. The value of thermodynamic parameter $\Delta G°$ (Gibbs free energy) was negative which confirm that the nature of the adsorption process was spontaneous while the positive value of $\Delta H°$ states the endothermic nature of the adsorption process. Hence it can be concluded that developed activated *Pongammia pinnata* pod powder (AP4) can be used as a cost effective, highly efficient and eco-friendly bioadsorbent for the removal of Malachite Green.

Conflict of interest

None declared

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