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Adsorption of Recalcitrant Malachite Green Dye from Aqueous Solution Using Cabbage Waste powder

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Abstract. Malachite green (MG) dye is a toxic cationic, azo soluble organic dye blamed for grievous health complications and aquatic pollution. The present study assesses the potential of cabbage waste powder (CWP) in the adsorptive removal of malachite green dye from aqueous solution. Batch experiments were designed to evaluate the impact of dye concentration, temperature. pH, adsorbent dose, particle size and contact time in dye removal. Adsorption equilibrium was realized within 80 minutes with adsorption efficiency of 92.5% at pH 8. The percentage dye removal improved with rise in time of contact, adsorbent dose and surface area to volume ratio but declined with rise in temperature. FTIR analysis established numerous functional groups of lignocellulosic compounds on adsorbent, which greatly influenced dye removal. The sorption kinetics obeyed pseudo-second order kinetic model while the equilibrium data followed Freundlich isotherm model. These results prove that the cabbage waste powder is indeed a worthwhile, overabundant and environmentally safe biosorbent for adsorptive removal of organic dyes from textile wastewaters.

Keywords: Malachite green dye, Isotherm, Kinetics, Adsorption. Cabbage Waste powder

INTRODUCTION

Rapid industrialization has led to immeasurable utilization of dyes and other colorants in manufacturing industries like textile, food, tanneries, paper, rubber, print and cosmetic for colouring products [1]. Apart from using dyes, these industries also consume a lot of water resulting in discharge of large volumes of dye-contaminated wastewater into aquatic environments. Approximately 7.5 x 10^5 tonnes of wastewaters containing dyes are generated yearly with textile industry alone discharging over $1.5x10^5M^3$ of coloured waste annually [2]. The dye containing effluents once discharged into natural waters interfere with water clarity, sunlight transmission, photosynthesis and the aesthetic nature of the waters. Dyes have also been found to be carcinogenic, mutagenic and unsafe [3]. Therefore, there is a need to look for an efficient treatment and disposal methods to reduce water pollution.

Malachite oxalate green dye ([4-[[4-(dimethylamino)phenyl]-phenylmethylidene]cyclohexa-2,5-dien-1-ylidene]-dimethylazanium;2-hydroxy-2-oxoacetate;oxalic acid) (Fig.1) is a triarylmethane dark green cationic, azo, water soluble dye (MW 929.58) that has been found to be mutagenic, carcinogenic and toxic but is still widely used as an antimicrobial in aquaculture, histology, antifungal drug and in textile industries [4]. The dye can get into the body through many avenues such as skin, eyes, consumption of treated fish or by inhalation especially for works in dying industry. The dye can cause severe eye irritation, damage of vital body organs such as kidney and liver [5].

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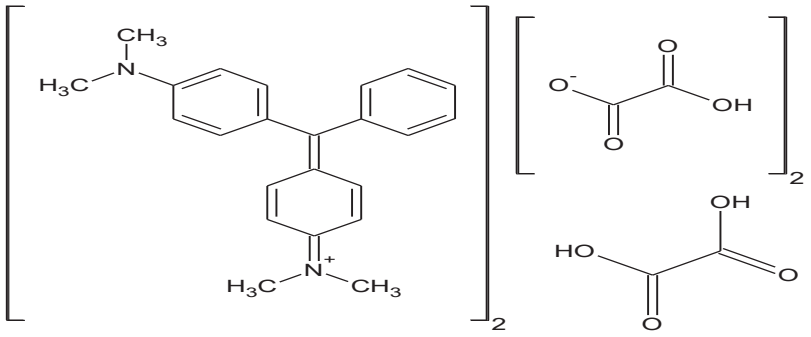

FIGURE 1. Structure of Malachite Green Oxalate (MG) dye.

Several technologies such as biological treatment, coagulation, membrane separation, reverse osmosis and chemical oxidation among others have been used to treat wastewaters [6]. However, the above methods suffer various limitations such as high cost, sensitivity to sludge, are very slow and none is effective in entirely removing colour from wastewaters [7]. Adsorption has gained prominence over the above methods because it is cheap, biomaterials are easily available and there is possibility of recycling the adsobent and dye. Adsorption has the potential to remove other contaminates such as toxic metals, and pesticides hence comprehensive applicability in controlling water pollution. Activated carbon is regularly exploited as an effective adsorbent but its outrageous cost makes it economically nonviable. This has provoked researchers to search for a substitute affordable adsorbents like; rice husk [8], carbon nanotubes [9], *Eichhornia crassipes* [10], penicilium [11], spirogyra [12], fish waste [13], hematite [14], *rhizophora mucronata* stem-barks [15] and macadamia seed husks [16]

The cost and adsorption capacity of adsorbents is mainly responsible for efficiency of the adsorption process. Agro-wastes have shown great potential in dyes uptake from wastewaters due to their plentiful, affordability and effectiveness. Cabbage is a common vegetable that proliferate on fertile fine drained loam-sandy soil within a pH ranging from of 6.4 to 7.0. High demand for vegetables has considerably contributed to the increasing attractiveness of this crop and consumption mainly in city towns [17]. Cabbage is known as a source of vitamin C and many other health benefits such as prevention of cancer, anti-inflammatory agent, improves vision, skin care and regulates blood pressure and body detoxifier among others [18]. Cabbage waste being an agricultural by-product can also be employed in useful processes like dye removal. Increasing demand for cabbage has led to disposal menace of the waste in urban areas. Currently, methods such as burning, landfilling have been employed to get rid of the waste but has ended up causing more pollution to the environment. The dumping space have not only diminished but have become sources of pathogens which cause diseases and comes along with bad odour [19]. Establishing an alternative technology of adding value to the abundant cabbage waste by utilizing in solving environmental problems would be a welcomed move toward environmental conservation. In this study, batch experiments was accomplished to determine the efficiency of CWP in sorption of MG dye. The study explores the practicability of recycling cabbage waste, which is an environmental menace into inexpensive biomaterials for biosorption of organic dyes from contaminated industrial wastewater

MATERIALS AND METHODS

Materials

Core cabbage stalks wastes was sourced from Kericho town dumping site. They were rigorously washed and sun dried for two weeks to remove moisture and prevent decay. Dried samples were crushed using a ball mill machine (Lasany-20160301201Y) into a powder. The ground particles were again soaked in clean water for 18 hrs after which, they were washed and rinsed thoroughly using distilled to remove soluble compounds. The cabbage wastes powder was dried in the sun, sieved in different particle sizes and kept in airtight containers ready for sorption experiments. Malachite green (MG) dye of analytical purity was purchased from Sigma-Aldrich, Nairobi-Kenya and used without extra purification.

Batch Experiments

Batch experiments were contacted to establish impact of time of contact, concentration, temperature, dose and pH on dye removal. 50 ml of MG dye solution was put in 100 ml conical flask with a weighed load of

adsorbent. The flasks were placed on a mechanical shaker at 140 rpm. During the adsorption process, a dye concentration in the solutions was examined at intervals of 10 minutes. An aliquot was withdrawn from the flask and concentration assessed using UV-visible spectrophotometer (HALO RB-10) at λ_{max}618 nm. The complete set of experiments was done at altered dose, pH, contact time, dye concentration, size of particle and temperatures. All the experiments were performed in triplicates and mean value divulged. The quantity of dye removed (Q_e) was computed by equation;

$$Q_e = V\frac{(C_o - C_e)}{M} \qquad (1)$$

Where C_o and C_e are initial and equilibrium malachite green dye concentrations (moles per litre), V is the volume of dye solution (L) and M is the mass of cabbage waste powder used (g). Percentage dye removed was determined using equation:

$$\%\ \text{dye removal} = \frac{(C_o - C_e)}{C_o} \times 100 \qquad (2)$$

Kinetics studies were examined using 50ml of MG dye in 100 ml flask at optimum pH. Accurately weighed CWP were mixed with dye solution in the flasks for adsorption studies and the amount of dye adsorbed determined. This procedure was repeated till the attainment of equilibrium.

RESULTS AND DISCUSSION

Effect of Contact Time and Initial MG Concentration

The duration of interaction is an essential factor in an industrial set up because it control the time required to clean wastewater and the cost effectiveness of the process [20]. Effect of contact time and concentration on uptake of MG onto CWP was determined at 25˚C and result presented in Fig.2. MG dye removal was fast in the first 20 minutes then progressively slowed down as time elapsed until attainment of equilibrium. The quick dye removal at the begging of experiment can credited to the existence of bare active sites for adsorption that slowly reduced with time. Once most of the active sites had been occupied, additional adsorption was hindered owing to the repulsive forces between MG molecules on CWP surface and solution phase which further slowed dye removal. The time taken to reach equilibrium strongly depended on dye concentration solution. As the dye concentration upsurge from 1.288 to 11.77 mgl^{-1}, the time required to achieve equilibrium improved from 10 to 50 minutes. The deviation in time of contact was due to the boundary layer that dye molecules are to overpower so as to move from the bulk solution phase to the CWP surface. Consequently, the quantity of dye removed rose from 0.124 to 1.082 mgg^{-1} when dye concentration increased from 1.288 to 11.77 mgl^{-1}. This findings can attributed to rise in concentration slope that is the driving force to conquer all mass transfer resistances betwixt the dye solution and CWP phase [21].

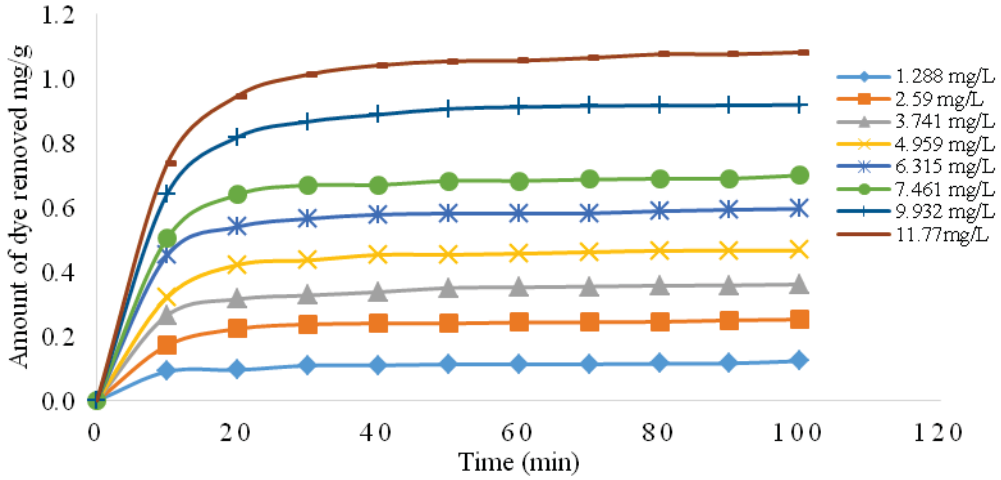

FIGURE 2. Effect of contact time and concentration on removal of MG dye at equilibrium. Conditions: (size of particle: 300 - 600µm, at 25 ˚C).

In order to verify that adsorption MG occurred, image of CWP before and after MG dye removal were taken as shown in Fig 3. It is evident from the image that the grey white CWP particles assumed the dark green colour of the MG dye after adsorption proving that physical adsorption occurred.

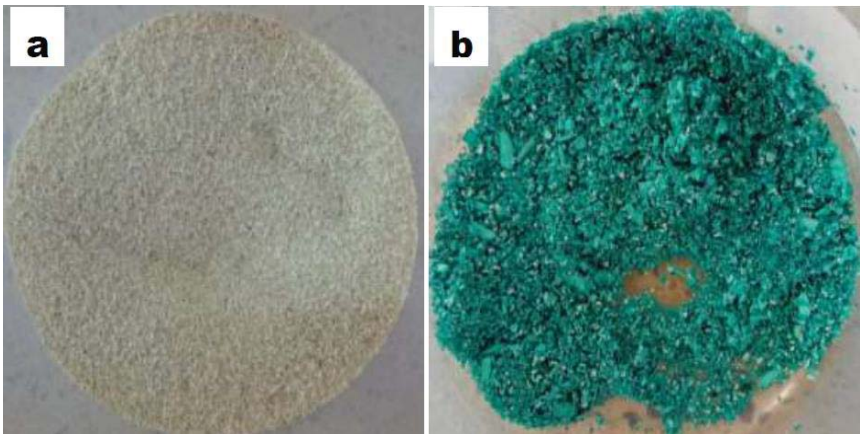

FIGURE 3. CWP Image before and after adsorption of MG dye

Effect of CWP Dose

The results for effect of CWP dose on sorption of MG dye are shown in Fig. 4. The percent sorption increased from 80 % to 95.1 % as CWP quantity rose from 0.1 to 1.5 g. This was due to more adsorption sites provided by extra dose of the CWP. Beyond 1.0 g of CWP the percentage removal remained constant because the adsorption sites on CWP surface were more than molecules of MG dye present in solution. A similar observation has been reported in adsorption of MG dye by pulverized teak leaf litter [22].

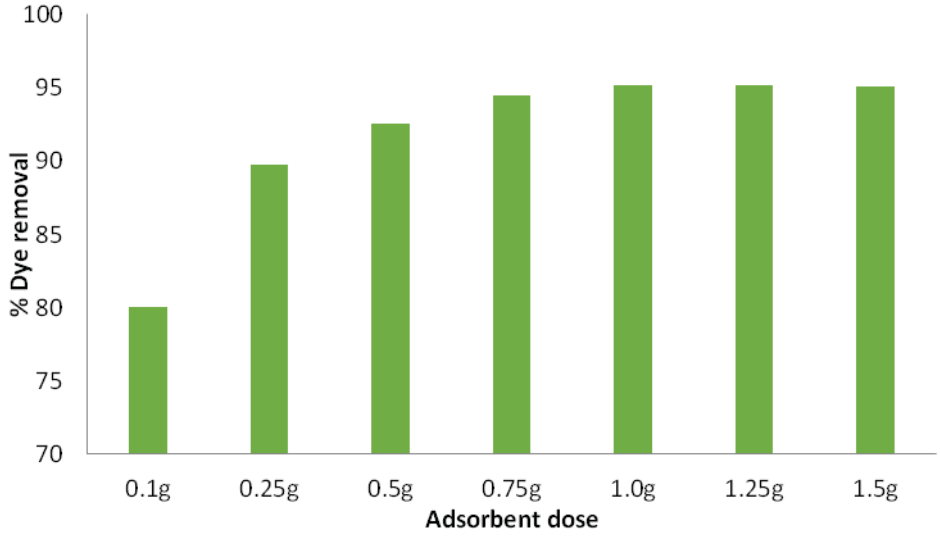

FIGURE 4. Influence of adsorbent dose on MG dye sorption. Conditions: (MG 11.77 mg/l, CWP: 0.5g, size of particles: 300 - 600µm, at 25 ˚C).

Effect of pH

pH is a principal aspect that controls sorption progression since it dictate charge on sorbent surface and determines the magnitude of dye ionization [23]. Influence of pH on biosorption of MG dye was established and outcomes displayed in Fig. 5. Dye removal rose as the pH increased up to pH 4, then slowed down slightly before gradual rise with optimum adsorption of 92.2% at pH 8. This is due to increased electrostatic force of attraction between positively charged sorbent surface and negatively charged dye molecules. The reduced MG dye sorption from pH 4 to 6 could be due to competitiveness for adsorption sites by hydroxyl ions and the dye molecules.

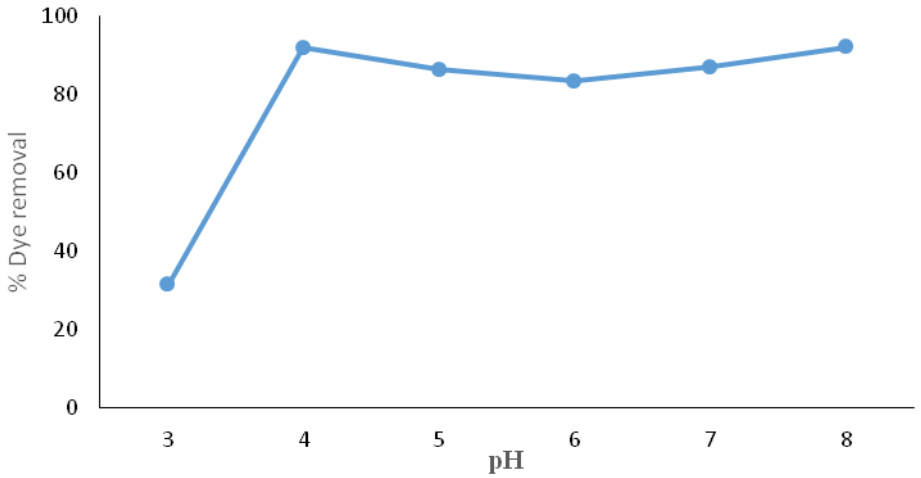

FIGURE 5. Influence of pH on % removal of MG dye. Conditions: (MG dye: 11.77 mg/l, cabbage waste powder: 0.5 g, particle size: 300-600 µm, at 25 ^{0}C)

Effect of Particle Size

Size of particles play a key function in sorption since it determines free surface area accessible on the adsorbent for attachment dye molecules [24]. Particle size influence on biosorption of MG dye was evaluated and results showed in Fig. 6. The rate of dye removal declined as size of particle surged. This observation could be accredited to presence of hefty surface area to volume ratio available on small sized particles as compared to large particles which have a small surface area for attachment of MG dye molecules [25]. These results are in line with related study previously reported where MG dye removal declined with rise in size of particles [26].

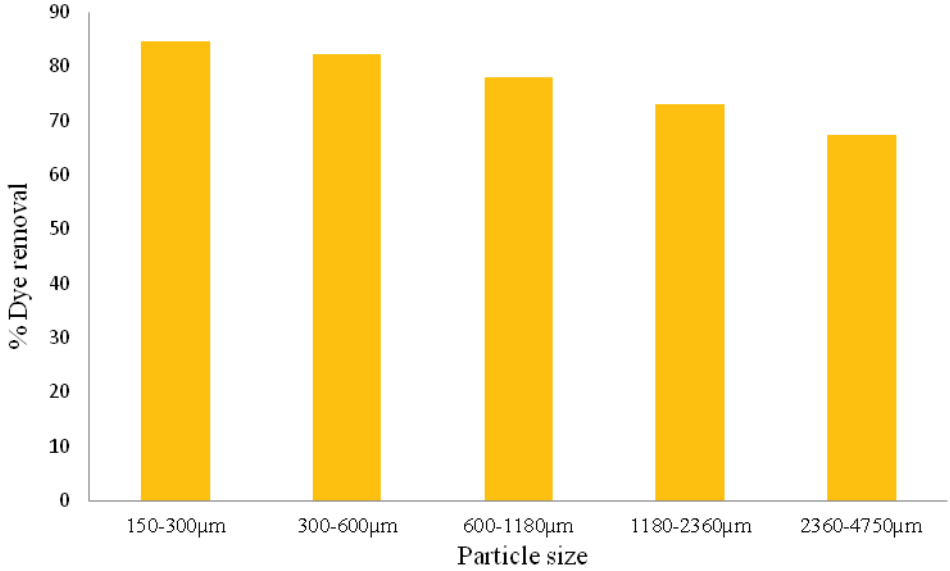

FIGURE 6. Influence of particle size on sorption of MG dye. Conditions: (MG dye11.77 mg/l, cabbage waste particles 0.5g, at 25˚C).

Effect of Temperature

Temperature performs an essential function in dye uptake as it impacts diffusion rate and dye solubility in the aqueous solution [27]. The impact of temperature on sorption of MG was researched and the findings exposed in Fig.7. The rate of MG dye removal improved from 88.4 to 92.8% with rise in temperature from 25 to 35˚C. This could be accredited to the rise in kinetic energy of MG dye molecules. Above 35˚C percent dye removal declined with rise in temperature. This is because physical adsorption process involves weak van der Waals forces of

attraction and hydrogen bonding which are destroyed by high temperatures thus diminishing dye removal at higher temperature [28]. Similar findings have been obtained in biosorption of MG by rice husks [29] and sorption of CV dye by coffee husks [28] .

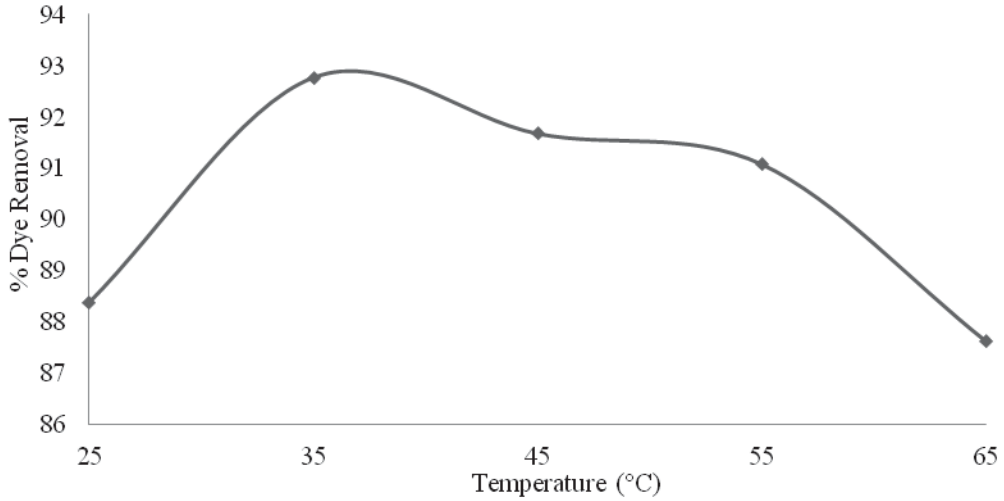

FIGURE 7. Effect of temperature on % MG dye removal. Condition: (MG dye: 11.77 mg/l, cabbage waste particles: 0. 5g, Particle size: 300 - 600 µm).

Adsorbent Characterization

FTIR is an important spectrometric technique used in qualitatively determining the characteristic functional groups on the adsobent that control binding of the dye [30]. Fig.8. displays FTIR spectra of CWP before and after interaction with MG dye. A wide band at 3298 cm^{-1} is assigned to O-H stretch which designates existence of O-H groups on CWP surface majorly of which are observed in cellulose and phenolic compounds of lignin [31]. A shift was detected in the bands after adsorption of MG dye as; 3876.92 to 3861.49 cm^{-1} which represents the O-H stretch, 3799.77 to 3714.90 cm^{-1} for monomeric alcohols, phenols and amine stretches. A shift from 2897.08 to 2927.94 is ascribed to C-H stretch and flexion of alkyl groups (methyl group) and 1029.99 to 1026.31 cm^{-1} is allotted C-O stretch present in cellulose which appears as wide intense bands. The band at 1689 cm^{-1} can be assigned to stretching of C=O group of conjugated and non-conjugated aromatic rings in carboxylic acids, ketones and aldehydes [32]. Existence of methyl and aromatic groups favours aquaphobic interactivity with MG dye. Similar findings have been reported where lignocellulosic compounds greatly influenced biosorption of MG and MB dyes onto degreased coffee beans [33].

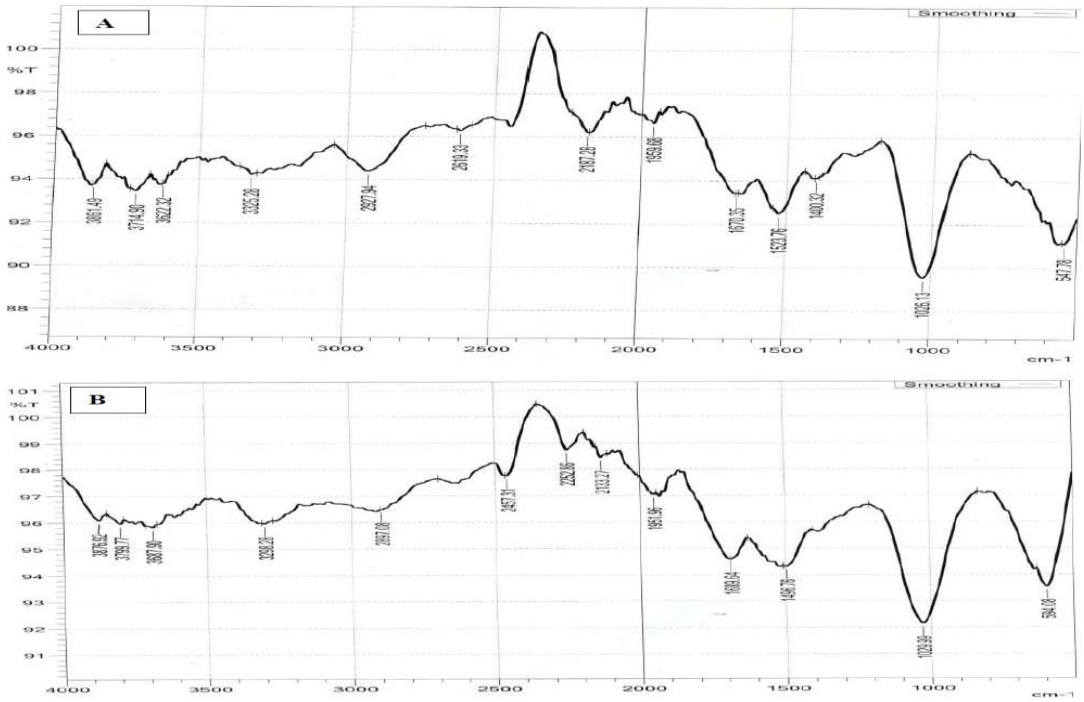

FIGURE 8. FTIR analysis for unreacted (A) and reacted (B) cabbage waste particles with MG dye

Adsorption Isotherms

Dye molecules don't bind to different adsorbents in a similar way. Isotherm plots conveys the spreading of dye molecules between the two phases with respect to time [34]. Langmuir and Freundlich adsorption isotherms were employed to determine the practicality of adsorption as a technique in sorption of MG dye from aqueous environment using cabbage waste powder. The Langmuir isotherm is based on the notion of a single layer adsorption onto a surface with fixed value of indistinguishable site [35]. The linearized form of the Langmuir isotherm [36] is shown by equation 3.

$$\frac{1}{q_e} = \frac{1}{Q_m} + \left(\frac{1}{Q_m b}\right)\frac{1}{C_e} \quad (3)$$

Where q_e is the sorption density mgg^{-1} of MG dye at equilibrium, C_e is the equilibrium concentration of MG dye, Q_m is the monolayer adsorption capacity mgg^{-1} and b is the Langmuir constant (c/mg) related to force energy adsorption. Q_m and b are calculated from the intercepts ($1/Q_m$) and slopes ($1/bQ_m$) of the linear plots $1/q_e$ vs $1/C_e$. Further analysis of the Langmuir equation was also made on the basis of a separation factor, R_L shown by equation 4.

$$R_L = \frac{1}{1+b(C_0)} \quad (4)$$

The values of R_L shows that the isotherms are either favorable ($0<R_L<1$), linear ($R_L=1$), unfavorable ($R_L>1$) and irreversible ($R_L = 0$). The plots for $1/q_e$ vs $1/C_e$ for adsorption of MG dye on cabbage waste powder are shown in Fig. 9 . Freundlich assumes that the adsorption is multilayer and takes place on heterogeneous surfaces [37]. The linear form of the Freundlich isotherm [38] is shown by equation 5.

$$\ln q_e = InK_f + \left(\frac{1}{n}\right) InC_e \quad (5)$$

Where K_f and n are Freundlich constant associated to adsorption capacity and adsorption intensity of adsorbent. Values of K_f and n can be calculated from the intercepts (Ink_f) and slopes (1/n) of the graph ln q_e vs InC_e. 1/n shows how favorable the adsorption process is and values of n>1 indicates favorable adsorption conditions. The plots of Inq_e verses lnC_e for the adsorption of MG dye on cabbage waste powder is displayed in Fig.10.

The isotherm constants and the correlation coefficient values for the two isotherm models are presented in Table 1. Basing on the correlation coefficient value (R^2) the Freundlich isotherm fitted well to the experimental data as compared to Langmuir isotherm with R^2 value of 0.9393. This also indicates that the surface of the cabbage waste powder was heterogeneous responsible for a multilayer adsorption due to presence of heterogeneous adsorption sites. In terms of the separation factor (R_L), its value in this study was 0.0418 which indicates favorable adsorption process.

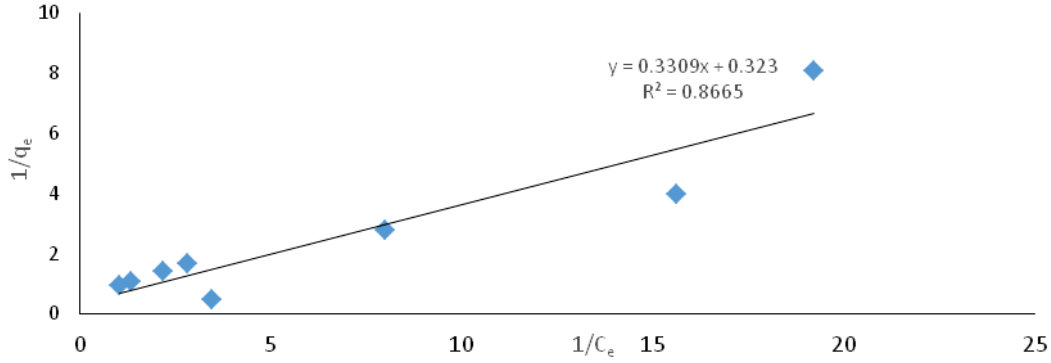

FIGURE 9. Langmuir adsorption isotherm for MG on CWP

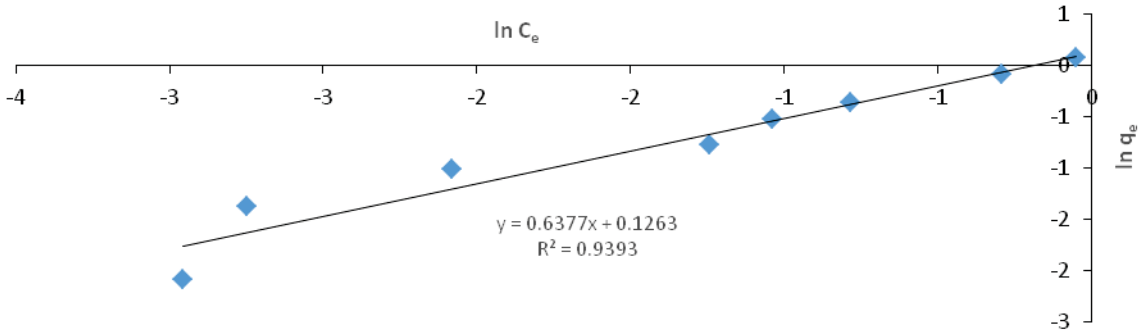

FIGURE 10. Freundlich adsorption isotherm MG dye on CWP

TABLE 1. Langmuir and Freundlich isotherm constants for adsorption of MG dye CWP.

Langmuir adsorption isotherm				**Freundlich adsorption isotherm**		
Q_m	b	R^2	R_L	K_F	n	R^2
1.551	1.948	0.8665	0.0418	1.108	1.568	0.9393

Kinetics of Dye Adsorption

The kinetics of adsorption is a significant characteristic to describe the efficacy of adsorption. The kinetics of the adsorption were investigated to establish how quick the process was and whether it was controlled by chemical or physical adsorption [8]. Pseudo-first and pseudo-second order kinetic models were used to study adsorption of MG dyes on cabbage waste powder. Pseudo-first order model is expressed by equation 6

$$\ln(q_e - q_t) = lnq_e - K_1 t \qquad (6)$$

Where, q_e and q_t are amounts of dye adsorbed at equilibrium at time t (mg/g) respectively, k_1 (min^{-1}) is rate constant adsorption. The plots of $\ln(q_e-q_t)$ vs t had lower coefficient correlation values (R^2) as shown in table 2 and the q_e values differed widely with the experimental values. The pseudo-first order model was therefore not appropriate for relating the kinetics for adsorption of MG on CWP. The experimental data was also subjected to pseudo-second order model shown by equation 7.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (7)$$

Where k_2 is the rate constant of adsorption (g/mg min), q_e and q_t are amounts of MGadsorbed at equilibrium at time t(mg/g) respectively. The values of k_2 and q_e were calculated from the intercepts ($1/k_2q_e$) and slopes ($1/q_e$) of the plots t/q_e vs t. Fig. 11 shows the plots of pseudo-second order kinetics for sorption of MG dye onto cabbage waste powder at various concentrations. The values of the rate constant (k_2), equilibrium adsorption capacity (q_e) and their respective correlation coefficients were determined and presented in Table 2. The correlation coefficients for all the studied concentrations were high (r^2>0.99) while the theoretical $q_{e.cal}$ values were close to the experimental $q_{e.exp}$ values. This shows that sorption of MG dye onto cabbage waste powder follows the pseudo-second order kinetic model. This further suggests that the rate limiting factor is chemisorption which embroils sharing and exchange of electrons through valence forces between the adsorbent and the dye molecules [37]. It was also noted that the rate constant k_2 decreases with rise in concentration. Comparable findings have been registered on kinetic study of walnut shell [39], activated macadamia nut shell [20] and rice husk for malachite green dye.

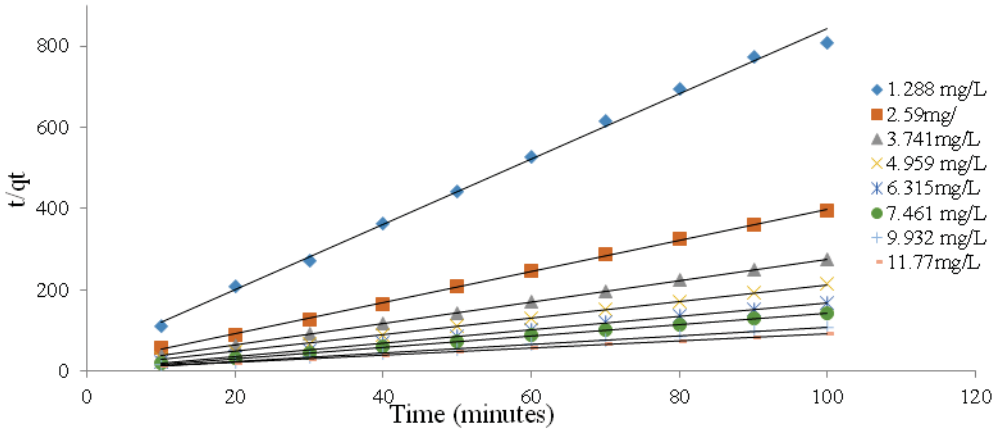

FIGURE 11. Pseudo-second order model plots for sorption of MG dye on CWP

TABLE 2. pseudo second order model parameters for adsorption of MG on CWP

C_o (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)	k_2(min-1)	R^2
1.288	0.124	0.050	-0.0252	0.7729	0.122	2.365	0.9960
2.590	0.253	0.102	-0.0403	0.8535	0.256	1.468	0.9986
3.741	0.362	0.178	-0.0488	0.9541	0.369	0.979	0.9989
4.959	0.467	0.288	-0.0651	0.9839	0.478	0.857	0.9989
6.315	0.596	0.222	-0.0473	0.8841	0.604	0.829	0.9994
7.461	0.700	0.228	-0.0410	0.9250	0.708	0.704	0.9992
9.932	0.919	0.545	-0.0712	0.9838	0.942	0.450	0.9989
11.77	1.082	0.538	-0.0537	0.946	1.108	0.334	0.9988

CONCLUSION

Adsorption experiments were performed to ascertain the efficacy of cabbage waste powder in adsorption of MG dye. The result clearly illustrates that CWP is an efficient adsorbent for removal of MG dye by over 93 %. The sorption of MG on cabbage was influenced by biosorbent dose, contact time, pH and particle size. The percentage MG dye uptake improved with rise in dosage, time of contact and diminished with increase in particle size and temperature. The quantity of dye removed in mg/g increased with increase in initial dye concentration. The results showed that Freundlich isotherm best fit on experimental data displaying high correlation coefficient (R^2 = 0.9393) that implyed multi-layer sorption process. The values of R_L and n values indicated that the adsorption process was favorable. The sorption kinetics showed that the sorption of MG onto cabbage waste powder followed the pseudo-second order model with high correlation coefficients (R^2 = 0.99) for all the concentrations studied. It can therefore be fulfilled that cabbage waste powder may be employed as an alternate cheap adsorbent for removing organic dyes such as MG from wastewater due to its high surface area, abundance and low cost.

Acknowledgement

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