Removal of Malachite Green and Crystal Violet Dyes from Aqueous Solution with Bio-Materials: A Review

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Abstract- Malachite Green and Crystal violet are among millions of dyes which are being used in every aspect of day to day life of a human being. Approximately 12% of synthetic dyes are lost during manufacturing and processing operations and 20% of the resultant color enters the environment through effluents from industrial wastewater. They are toxic and having extremely harmful consequences; hence many governmental and environmental agencies have put in place very strict regulation and restriction on discharge of industrial waste water/effluent containing dyes into the natural water bodies. There are various technique available for removal of dyes from waste water but adsorption is the process of choice. Activated carbon is the best known adsorbent. But its use in treating the industrial waste water especially in developing countries is restricted due to very high cost. This high cost of activated carbon has forced the researchers to find out low cost and effective adsorbent which may be used as an efficient alternative of activated carbon. In this paper an attempt has been made to compile the work of various researchers on removal of crystal violet and malachite green dyes from aqueous solution by using biomaterials and agricultural waste during the last five years.

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Binod Kumar [α] & Upendra Kumar [σ]

Abstract- Malachite Green and Crystal violet are among millions of dyes which are being used in every aspect of day to day life of a human being. Approximately 12% of synthetic dyes are lost during manufacturing and processing operations and 20% of the resultant color enters the environment through effluents from industrial wastewater. They are toxic and having extremely harmful consequences; hence many governmental and environmental agencies have put in place very strict regulation and restriction on discharge of industrial waste water/effluent containing dyes into the natural water bodies. There are various technique available for removal of dyes from waste water but adsorption is the process of choice. Activated carbon is the best known adsorbent. But its use in treating the industrial waste water especially in developing countries is restricted due to very high cost. This high cost of activated carbon has forced the researchers to find out low cost and effective adsorbent which may be used as an efficient alternative of activated carbon. In this paper an attempt has been made to compile the work of various researchers on removal of crystal violet and malachite green dyes from aqueous solution by using biomaterials and agricultural waste during the last five years.

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I. Introduction

Dyes in different form are being used in every aspect of day to day life of a human being. At present there are more than 1,00,000 Commercial dyes with rough estimates of production range between 7×10^5 tons to 1×10^6 tons per year[1] Among them Crystal Violet and malachite green are one of the widely used synthetic and cationic dyes. The molecular formula of crystal violet and malachite green are $C_{25}N_3H_{30}Cl$ and $C_{23}N_2H_{25}Cl$, the molecular mass are 407.979 g mol^{-1} and 364.91 g mol^{-1} and melting point are 205 °C and159 °C respectively. Both the dyes are soluble in Water and Alcohol. They are Stable, Incompatible with strong oxidizing agents, strong acids, Light-sensitive and Combustible [2]. Color Index Number (CI) of crystal violet and malachite green are 42555 and 42000 respectively. When crystal violet is dissolved in water the dye has a blue-violet colour with an absorbance maximum at 590 nm. Similarly when malachite green is dissolved in water the dye has a green colour with an absorbance maximum at 617 nm. Both the dyes are extensively used as a dye in paper and pulp industries, leather industries, and textile industries. They are also widely used for various medicinal purposes like as a biological stain for microscopic analysis of cell biology and tissue samples. Approximately 12% of synthetic dyes are lost during manufacturing and processing operations and 20% of the resultant color enters the environment through effluents from industrial wastewater [3].The presence of very small amounts of dyes in water (less than 1 ppm for some dyes) is highly visible and undesirable on aesthetic ground. [4]. It also interferes with transmission of light and upset the biological metabolism process which causes the destruction of aquatic communities present in Eco-system. Further, dye has the tendency to sequester metal and may cause micro toxicity to fish and other organism. Due to these harmful consequences many countries have put in place very stringent regulation. Due to enforcement of very stringent regulation by the various environmental and governmental agencies upon the industries ,the interest of researcher have moved towards to find the cost effective methods for removal of dyes from aqueous solution. The waste water containing dye(s) is difficult to treat since the dyes are very complex organic molecule, resistance to aerobic digestion and are stable to light, heat and oxidizing agents. [5]. during the past three decades, several physical, chemical and biological decolourization processes have been reported. They are Coagulation, Flocculation, Biodegradation, Adsorption on activated carbons, Membrane separations, Ion-exchange, Oxidation, Advanced oxidation process, Biomass, Selective biosorbents. However, these methods have several disadvantages that include incomplete dyes removal, high reagent and energy requirements and generation of toxic sludge or other waste products that requires proper disposal and further treatment. These methods are very costly, making them uneconomical and unviable. Amongst the numerous techniques of dye removal, adsorption is the procedure of choice and gives the best results. [6] Commercially Activated carbon adsorption has been cited as one of

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the best dyes control technology by the US Environmental protection Agency [7]. The very high capacity of Commercially Activated carbon for removal of dye through adsorption is mainly due to their structural characteristics and their porous texture which gives them a large surface area, and their chemical nature which can be easily modified by chemical treatment in order to increase their properties. However, activated carbon presents several disadvantages. It is quite expensive, the higher the quality, the greater the cost, non-selective and ineffective against disperse and vat dyes. The regeneration of saturated carbon is also expensive, not straightforward, and results in loss of the adsorbent [8]. Due to the problems mentioned above, research interest into the production of alternative sorbents to replace the costly activated carbon has intensified in recent years. Attention has focused on various natural solid supports, which are able to remove pollutants from contaminated water at low cost. Cost is actually an important parameter for comparing the adsorbent materials. According to Bailey et al. (1999) [10] a sorbent can be considered low-cost if it requires little processing cost, is abundant in nature or is a by-product or waste material from another industry. Recently attention has been diverted towards the biomaterials which are byproducts or the wastes from large scale industrial operations and agricultural waste materials. The major advantages of biosorption over conventional treatment methods are: low cost, high efficiency, minimization of chemical or biological sludge, requirement of additional nutrient, and regeneration of biosorbents, and possibility of dyes recovery. Presently, agricultural waste materials have been proposed as economic and eco-friendly adsorbents. Agricultural materials are particularly those containing cellulose which shows a high potential in dye biosorption capacity. The adsorption process of dyes presently in aqueous solution by low-cost adsorbents from plant wastes can be carried with or without chemical modifications. Generally, chemically modified plant wastes are exhibiting the higher adsorption capacities than unmodified forms. More recently, the great efforts have been directed to develop a new adsorbent and improving the existing adsorbents to have an alternative to activated carbon.

In this paper an attempt has been made to compile the work of various researchers on removal of crystal violet and malachite green dyes from aqueous solution by using biomaterials and agricultural waste during the last five years.

II.   Literature Review

On scanning the available literature on the subject matter it has been observed that researchers have investigated the effectiveness of biomaterials and agricultural wastes in removal of crystal violet and malachite green dyes from aqueous solution by adsorption in batch mode isotherm experiment. They have examined the effect of rotational speed of the shaker, pH value of the solution, contact time, initial concentration of dyes in the solution, dose of adsorbent, temperature of solution on the adsorption of dyes by biosorbents. Adsorption isotherm modeling, rate kinetic modeling, intra- particle diffusion analysis, thermodynamic analysis have been done by them on the experimentally observed data. Wang et al (2008) investigated the removal of malachite green from aqueous solution using agricultural by–products (wheat bran and rice bran). It was found that adsorption increases with increase in solution pH and attained equilibrium at 90 min. The equilibrium data of malachite green fitted better to Freundlich model. The kinetic data fitted better to pseudo-second order equation. While the external diffusion was the rate controlling step of the initial fast adsorption ($<$ 15minutes) and in the next stage the intraparticle diffusion dominated the mass transfer. The thermodynamic analysis revealed that the adsorption of MG onto wheat bran and rice bran is spontaneous and favorable process [11]. Baseri et al (2012) investigated the adsorption of basic dyes (malachite green, crystal violet and rhodamine B) from synthetic textile effluent by activated carbon prepared from *Thevetia peruviana.* It was found that the amount of dye adsorbed increased with increasing initial dye concentration. The process was endothermic in nature. Kinetic studies showed that the adsorption of these dyes followed pseudo-second order model with multi-step intra particle diffusion model. The data obtained from adsorption isotherms are well fitted with Langmuir model, the negative ΔG^O value obtained suggested the process was spontaneous in nature [12].

Prasad et al (2012) studied the adsorption of cationic dyes (crystal violet and rhodamine B) from aqueous solution onto Acacia nilotica leaves as an eco-friendly adsorbent. The result showed that the optimum pH was 6 and the equilibrium time was 120 minutes. The removal efficiency increased with increase in agitation time and initial dye concentration. The equilibrium data were best described by Langmuir isotherm model with maximum monolayer capacity of 33 and 37 mgg-1 for crystal violet and rhodamine B respectively. The adsorption kinetics can be successfully fitted to pseudo–second order kinetic model. The result of the intraparticle diffusion model suggested that intraparticle diffusion might not be the only rate controlling step. Desorption study revealed that the recovery of the dye from adsorption was possible [13]. Tahir et al. [2009] investigated the removal of malachite green by using household used black tea as an adsorbent. The adsorbent was used in raw form and impregnated form. The equilibrium time of adsorption came out to be 10 minutes. Also, the data showed that there was decrease in the amount of the dyes

adsorption with increase in temperature. The thermodynamic parameter showed that the process was exothermic and spontaneous. Furthermore, the result showed that the raw form of the adsorbent showed better adsorption capacity compared to its impregnated form [14]. Kumar et al. (2005) investigated the adsorption of malachite green onto Pithophora sp., fresh water algae. The algae were used raw and some were thermally activated at 300°C for 50 minutes. The equilibrium data was very well represented by Redlich-Peterson isotherm. It was found that the thermally activated adsorbent possess a higher sorption capacity of 117.647mg/g than the raw one with 64.4mg/g. The kinetic data followed the pseudo-second order model closely and the negative value of Gibb's free energy change ($\Delta G\circ$) indicated that the sorption process was spontaneous [15]. Remenarova et al. [2009] studied the sorption of Malachite Green from aqueous solutions by moss Rhytidiadelphus squarrosus. The results showed that the equilibrium was reached within 1-2 hours. The equilibrium data best fitted the Freundlich isotherm model [16]. Uma et al.(2013) used Sawdust a timber waste as a bio-sorbent for the removal of a cationic dye, malachite green from aqueous solutions. Point zero charge (pHzpc) of raw sawdust was calculated by titrimetric method and that was 7.37. FTIR was performed to determine various functional groups attached to the adsorbent surface. The experimental results indicate that 5g/L g of sawdust was able to remove 93% of dye from an initial concentration of 20 mg/ L. Equilibrium was achieved in 100 min and the maximum adsorption of malachite green occurred in the higher (alkaline) pH range. The data was better fitted in Freundlich isotherm model. It was observed that dye removal decrease with increasing concentrations of dye solution. The maximum adsorption capacity of adsorbent was found to be 13.87 mg$g-1$ at 298 K. The dye adsorption followed the pseudo second- order kinetics. Removal process was endothermic in nature [17]. Jiao Li et al. (2013) investigated the removal of malachite green (MG) from aqueous solution using modified peanut shell (MPS). The SEM and FTIR showed that some components of raw peanut shell (RPS) had been removed during the chemical modification, and many cavities of various dimensions were clearly evident on the surface of MPS. Adsorption experiments showed that MG adsorption uptake was increased with an increase in initial concentration, contact time, solution temperature, and adsorbent dosage. Furthermore, neutral pH was optimum for the removal of MG. The adsorption of MG onto MPS agreed well with the nonlinear Langmuir and Sips isotherm models. The monolayer capacity (Q_{max}) was 32.73 or 35.85mg/g as calculated from Langmuir or Sips isotherm models, respectively. The adsorption kinetic studies showed that the adsorption process followed the pseudo-second-order kinetic model with a multi-step

diffusion process [18]. Chen Z et al. (2014) used the Pleurotus ostreatus (a macro-fungus) as a new biosorbents to study the biosorption of hazardous malachite green (MG) from aqueous solutions. The equilibrium data best fitted with Freundlich isotherm model. The biosorption process followed the pseudo-second-order kinetic model. The Fourier transform infrared spectroscopy (FTIR) showed the presence of the functional groups such as, carboxyl, hydroxyl, amino and phosphonate groups on the biosorbents surface which could be the potential adsorption sites for MG biosorption [19].

Ashish S. Sartape et al. (2013) investigated successfully Wood apple shell (WAS) alternative adsorbent for the removal of hazardous dye malachite green. The removal of MG dye was found to be 98.87% with initial concentration 100 mg/L at pH 7–9 in 3.30 h by shaking at 150 rpm at 299 ± 2 K. The shifting of peaks in FTIR spectrum confirmed the MG dye adsorption onto WAS. The SEM study also made support to it by observing difference in surface morphology of adsorbent before and after adsorption of MG. The adsorption equilibrium data showed good fit to the Langmuir isotherm model as compared to the Freundlich isotherm model. The adsorption capacity for WAS was increased from 12.35 to 80.645 mg/g as the MG concentration in the test solution was increased from 100 to 700 mg/L. The adsorption kinetics followed pseudo first-order kinetic equation for sorption of MG onto WAS. Thermodynamic study demonstrates the spontaneous and endothermic nature of biosorption process due to negative values of free energy change $\Delta G\circ$ and positive value of enthalpy change $\Delta H\circ$, respectively. [20]

Mi-Hwa Baek et al. (2010) studied the degreased coffee beans as an adsorbent for removal of MG from aqueous solutions. The adsorption was highly dependent on initial dye concentration, temperature and pH. MG adsorption onto DCB reached almost equilibrium in about 4 h MG removal by RCB reached equilibrium in about 8h. The optimal pH was 10–12. The result of the present investigations showed that degreased coffee beans (DCB) have higher adsorption efficiency than raw coffee beans. The adsorbed amount of MG increased as initial MG concentration increase. The kinetic data best fitted the pseudo second-order kinetic model though the correlations coefficients from the pseudo first-order kinetic were as well relatively high for the range of concentrations studied. On the basis of Correlation coefficients ([R2]) values it is revealed that the sorption of MG onto DCB followed both Freundlich and Langmuir models. Freundlich parameter, n value at equilibrium was 0.51, indicating a chemosorption adsorption of MG onto DCB. The maximum adsorption (monolayer) capacity of DCB for MG is 55.3 mg/gm at temp 2^{50}C. Thermodynamic studies showed that the adsorption processes were spontaneous and

endothermic since ΔG◦ value was negative and ΔH◦ value was positive. In this study, activation energy (Ea) = 78.5 kJ/mol for the adsorption of MG onto DCB, indicating the process as chemiosorption. [21]. Y.C. Sharma et al. (2009) investigated the activated carbon developed from rice husk for the removal of malachite green from aqueous solutions. Percentage removal of MG by RHAC increased with decrease in the initial concentration of dye. Time of equilibrium was found to be 40 min. The process of removal follows pseudo first order kinetics. Equilibrium studies were performed and the data fitted well in Langmuir and Freundlich adsorption isotherm equations. The n value was found greater than one (>1) at different temperature, indicating high intensity of adsorption of malachite green onto rice husk activated carbon. The maximum adsorption (monolayer) capacity of rice husk activated carbon for MG is 63.85 mg/gm at temp 30°C. [22]

M. A. Ackacha et al. (2012) studied a new agriculture waste (Tamarix aphylla leaves) treated with sulfuric acid, sodium hydroxide and acetone as adsorbent for the removal of malachite green from aqueous solution in batch kinetic experiment. Tamarix aphylla leaves were first treated with sulphuric acid (0.225N H_2SO_4) then with sodium hydroxide (0.225N NaoH) and finally with acetone. t The optimal pH was found in the range of 5 to 9. The adsorption process reached the equilibrium after 90 and 105 minute at initial concentration of malachite green solution 4.9 and 7 mg/l, respectively. The process of removal follows pseudo second order kinetics. Equilibrium data fitted well in Langmuir isotherm model. The maximum adsorption capacity (monolayer coverage) was 303.03 (mg/g) at temperature 30°C. The intra particle studies suggested the intra particle diffusion as rate controlling process. The negative values of $ΔG^0$ and $ΔH^0$ obtained from thermo dynamical analysis of the experimental data indicated the spontaneous and exothermic nature of the adsorption. [23] T. Santhi et al. (2009) studied a sample of raw (PR-Raw) and activated carbon (PR-Carbon) from prawn waste as an adsorbent for removal of malachite green (MG)) from aqueous solution at 28°C. It was found that the amount of MG adsorbed increased as the sorbent particle size decreased. The percentage of adsorption increased as the adsorbent concentration increased. The value of initial pH 7 for PR-Carbon and pH 8 for PR-Raw, were found optimal for removal of MG effectively. When the dye concentration was increased the percentage of dye adsorbed decreases. The equilibrium adsorption capacity of MG onto the PR-Carbon is significantly larger than those onto the PR-Raw. From the values of R^2 it was concluded that the equilibrium data best fitted the Freundlich isotherm model. The biosorption processes followed the Pseudo –first order rate kinetics. Intra particle diffusion modeling indicating that Surface adsorption and intra particle diffusion were likely to take place simultaneously. [24]. Le Phan Linh et al.(2012) studied the removal of malachite green from aqueous solutions by adsorption onto rubber wood *(Hevea Brasiliensis)* sawdust in batch kinetic experiment. The equilibrium study showed that adsorption process of malachite green reached equilibrium after 2.5 hours and optimal pH was 5. As the temperature increases the adsorption amount increased. Equilibrium data fitted well in Langmuir isotherm model (R^2=0.9902) in compare to Freundlich isotherm model (R^2=0.7776). The maximum adsorption capacity (Q_0) (monolayer coverage) was found 27.4 (mg/g) at temperature 40°C. [25] Shabudeen P.S. syed (2011) studied Kapok hull activated carbon (KHAC) as an adsorbent for removal of malachite green from aqueous solution. Here they used sulfuric acid (1:1) to activate the adsorbent. The adsorption was found independent of pH of the medium. It was also observed that the adsorption increased as temperature increases from 300 to 318K and further the increase in temperature did not have any influence upon adsorption. It was found that the data fitted well in Langmuir adsorption isotherm model as well as Freundlich adsorption isotherm model. Further, it was revealed that R_L values lay between 0 and 1 and the value of Freundlich parameter n lay between 2 to 10 at various temperature and particle sizes showing the adsorption of MG onto KHAC was fovourable. Adsorption followed the pseudo first order rate equation and the intra particle diffusion model indicated that more than one mode of sorption mechanism was in operation. From the thermo dynamic analysis of the experimental data the value of ΔG° , ΔH° and ΔS° were found which come out to be negative, positive and positive indicating the process as spontaneous, endothermic and there was a decrease in randomness at the surface of adsorbent after adsorption. It was observed that the ΔH° and ΔS° values increased with decrease of particle size. The positive and increased ΔS° values for smaller particle size indicated that the KHAC showed greater affinity towards the dye. It was observed that, the value of energy of activation for malachite green by KHAC was in between 5 to 20 kJ/mol confirms the activated adsorption.

Response surface method using Box- Behnken design of experiments was adopted and gives a mathematical model for the adsorption of dye stuff. The results obtained by adapting Box-Behnken model in the study of absorption of MG dyes on KHAC proves, absorption of dye depends only upon the particle size of absorbent and it was not influenced by pH or temperature. The experimental values and the predicted values of Box-Behnken design model were in close agreement with quadratic regression >98%. [26]. Jagdish Singh et al. (2013) studied the removal of malachite green from aqueous solutions by adsorption onto agricultural waste rice straw in batch kinetic

experiment. The optimal pH of the solution was found to be 8 and the equilibrium time was about 15 min. The removal of MG was found increases as the initial concentration of the MG increases. The adsorption of MG increased with increase in temperature. The adsorption was found to follow the Pseudo –first order rate kinetics. The equilibrium data best fitted the Freundlich isotherm model. The Freundlich parameters n and K_F were obtained as 9.3, 10.3, 11.3 and 87, 90 and 92 mg/gm respectively at different temperature 25,30 and 35^{0}C.   The values of ΔG^0, ΔH^0 and ΔS^0 obtained from thermo dynamical analysis of the experimental data were found negative, positive and positive respectively. [27]

S. Sivamani et al. (2009) investigated the removal of malachite green from its aqueous solution by Pithophora sp., fresh water algae by means of a batch system. The optimum pH was found to be 5 and equilibrium time as 10 min and the maximum dye removal rate was found to be 94.35%. It may be that the zero point charge for the prepared adsorbent could be found at a pH of 5. [28]. Anna Jasińska et al.(2013) studied the waste of rapeseed press cake (WRPC), obtained after the preparation of microbial culture medium, in a batch system as an adsorbent of malachite green (MG). The highest sorption of MG was observed after 180min in solution containing 50mg/L of MG and 2.5mg/L of WRPC at pH 6.5. The equilibrium data best fitted with the Langmuir isotherm model. MG sorption followed the pseudo-second-order rate kinetics. MG desorption efficiency (94.5%) from WRPC with the use of 0.1M NaoH solution was determined. [29]. Chowdhury .S et al. (2013) investigated thermo chemically modified Wheat bran with citric acid as a potential adsorbent for removal of Malachite Green (MG) from aqueous solutions in batch experiment. It was found that operational parameters, such as solution pH, adsorbent dose, initial adsorbate concentration as well as temperature, greatly influenced the adsorption efficiency of the adsorbent. The Langmuir isotherm model showed excellent fit to the adsorption data of MG. The sorption processes followed the pseudo-second-order rate kinetics. Thermodynamic study showed spontaneous and exothermic nature of the sorption processes [30]. Jia Tan et al (2012) used Waste newspaper fiber (WNF), separated and deinked it(denoted by DWNF) for use as an absorbent for removal of Malachite Green (MG) from aqueous solutions in batch kinetic experiment. The equilibrium study showed that adsorption process of malachite green reaches equilibrium after one hour but 88% of removal took place within 10min. the optimal pH of the solution was found to be 7. Equilibrium data was found fitted well in Langmuir adsorption isotherm model. The maximum adsorption capacity (Q_0) (monolayer coverage) was found 85.25 (mg/g) at temperature 40^{0}C. Sorption kinetic analysis revealed that adsorption of MG

onto DWNF followed the pseudo second order rate model. From thermodynamic analysis they obtained value of ΔG° Gibbs free energy, ΔH° change in enthalpy, and ΔS° change in entropy were found negative, negative and positive respectively. [31]. Shanthi et al.(2012) studied adsorption of methylene blue and malachite green dyes from aqueous solution of their binary mixture on Commerical Activated Carbon (CAC), and Tamarind Kernel Powder (TKP), a biological waste material under different experimental conditions (Initial concentration, dose by varying of adsorbent, initial pH and contact time. Experimental values indicate that the rate of removal of dye decreases with the increase in the initial concentration of dye and vice versa .The amount of dye adsorbed increased exponently with the increase in the dose of adsorbent. The effect of initial pH of dye solution was studied at different pH value (Range of pH: MG & MB = 3 – 6.8 for CAC, MG & MB = 3 – 6.8 for TKP).The adsorption of these dyes on CAC & TKP in found to be highly pH dependent. The percentage removal of binary mixture of dyes (MG and MB) at 60 min. of contact time, is 97.51 for MG and 94.86 for MG by CAC, and 96.25 for MG and 93.45 for MB by TKP respectively, This reveals that the optimum contact time is 60 min for MG & MB for both the adsorbents (CAC and TKP). Sorption kinetic analysis revealed that adsorption of MG & MB binary mixture onto CAC and TKP followed the pseudo first order rate kinetic expression. The rate constant value is higher in TKP than in CAC. This shows that rate of adsorption is higher in TKP. This gives support for the efficiency of TKP. Adsorption data obeyed both Freundlich and Langmuir adsorption isotherms. Intra particle diffusion plots for the removal of dyes from their binary mixture by adsorption revealed the intraparticle diffusion was found to be rate determining step. [32]. K. RajasekharJia (2014)) used corn cob as an absorbent for removal of Malachite Green (MG) from aqueous solutions in batch kinetic experiment. The contact time needed for dye solution to reach equilibrium was found 100min. The result shows that there was no significant change in the present removal of dye over the entire pH range. The study reveals that percentage of adsorption increases with increasing the adsorbent dosage. IT was foumd that as the initial concentration of dyes increased the removal of % of dyes decreased. [33]

Sharma et al. (2013) studied the adsorption potential of agricultural waste material sugarcane baggase to remove malachite green dye from aqueous solution. The adsorbent was characterized by BET surface area measurement and FTIR analysis. It was observed that more than 95% removal efficiency was obtained within 120 min at adsorbent dose of 1 g/L for initial dye concentration of 50 mg/L. It was observed that with increase in temperature, adsorption capacity decreases indicating the adsorption is exothermic in nature. The high values of R^2 ($\sim$ 1) and good agreement

between two q_e Values indicate that the adsorption system followed pseudo-second-order kinetic model and hence the process is chemisorptions controlled. From thermodynamic analysis the value of ΔG°, ΔH°, ΔS° were found which came out to be negative, negative, negative respectively at every temperature under study. Adsorption mechanisms were investigated with intra-particle diffusion model, Furusawa and Smith model and Boyd's model which shows that both film diffusion and intra particle diffusion were simultaneously occurring during the adsorption. Langmuir isotherm model was fitted the best for the adsorption system with an adsorption capacity of 190 mg/g of adsorbent. [34]. Makeswari et al. (2013) studied and analysed the Competitive adsorption of malachite green (MG) in single and binary system on microwave activated epicarp of Ricinus communis (MRC) and microwave assisted zinc chloride activated epicarp of Ricinus communis (ZRC). It had indicated that ZnCl2 was a suitable activating agent for the preparation of activated carbon from epicarp of Ricinus communis by microwave radiation. SEM micrographs showed that the external surface of the chemically activated car-bon was full of cavities compared with untreated Ricinus communis. The activated carbon prepared could effectively used as adsorbent for the removal of basic dye from aqueous solutions. 5 was the optimum pH value observed for the adsorption of MG onto MRC and ZRC. It was observed that the percentage of adsorption increases with increase in adsorbent dose from 0.2 g to 1 g in MG with the concentration of dye solution of 100 mg/L. It was seen that the percentage removal decreased with the increase in initial concentration. Adsorption Isotherm Studies for adsorption of MG onto MRC (S), MRC (B), ZRC (S), ZRC (B) revealed that the obtained data was best fitted in Langmuir isotherm model compare to Freundlich isotherm model, Dubinin-Radushkevich model, Temkin model. The maximum adsorption capacity (monolayer coverage) for adsorption of MG onto MRC (S), MRC (B), ZRC (S), ZRC (B) were found 12.6500, 11.7647, 24.3900 and 20.4081 mg/gm respectively. The higher R^2 values confirm that the sorption process of dyes onto MRC and ZRC follow a pseudo-second-order kinetic model. From Intra Particle Diffusion Model it was observed that the plot between q_e Vs $t^{1/2}$ did not pass through the origin for both the single and binary system which indicated that surface adsorption and intra-particle diffusion were concurrently operating during the MRC and ZRC interactions. MG adsorption rate onto MRC and ZRC was greater in single system (S) than in binary system (B) due to the competitive adsorption of dye onto the active site of the activated carbon. Among MRC and ZRC, ZRC shows most adsorption ability than MRC in single and binary system. [35]

Rajeshkannan et al. (2010) studied the Hydrilla verticillata, a cheap and widely available biomass as a potential adsorbent to remove malachite green from the aqueous solutions. The effects of operating parameters such as temperature, adsorbent dosage, contact time, adsorbent size, and agitation speed on the sorption of Malachite green were analyzed using response surface methodology (RSM). The proposed quadratic model for central composite design (CCD) fitted very well to the experimental data that it could be used to navigate the design space according to ANOVA results. The optimum sorption conditions were determined as temperature - 43.5°C, adsorbent dosage - 0.26g, contact time - 200min, adsorbent size - 0.205mm (65mesh), and agitation speed - 230rpm . Freundlich isotherm fits the data better with R^2 0.991 than Langmuir isotherm with R^2 0.963. Freundlich parameters are K_f - 3.17, n- 1.299. The maximum adsorption capacity was obtained from Langmuir isotherm (91.97 mg/g) at a solution pH ~8.0. From the kinetic and equilibrium studies it was found that pseudo second order kinetics and Freundlich isotherm fits the data well respectively. Intra particle diffusion models analysis revealed that both the external diffusion as well as intra particle diffusion contributes to the actual sorption process. [36]. Subbareddy Y et.al.(2012) investigated the potential use of a low-cost Fuller's Earth (FE) for removal of Malachite Green oxalate (MG) dye from an aqueous solution. The experimental equilibrium data were found best fitted with the Langmuir model. The maximum adsorption capacity of FE was found to be 1.96 x10-4mol/g for MG at room temperature. The energy of adsorption was 25.828 kJ/mol indicating chemisorptions. Adsorption data of MG onto FE was fitted well by the pseudo second order model. From thermodynamic analysis ΔG° and ΔH^0 were found negative and positive respectively suggesting the process of removal of MG by FE is a spontaneous and endothermic nature. [37]. Madrakian .T et al. (2012) investigated the removal of crystal violet, CV, onto the Magnetite nanoparticles loaded tea waste (MNLTW) obtained from treatment of tea waste as naturally occurring waste by FeCl3_6H2O, FeCl2_4H2O and NH_3 solution. It was observed that the dye became adsorbed after 35 min and under the optimized conditions, up to 98% of dyes can be removed from the solution onto the MNLTW surface and the optimal pH was found 10. The equilibrium data of adsorption of CV onto MNLTW best fitted with Langmuir model with R_L lying between 0 to 1($0 < RL < 1$). Maximum adsorption capacities at 25°C for removal of CV were found to be 129.87 mg/g. It was observed that that adsorption data followed the pseudo second-order kinetic model. [38]. Karla Aparecida Guimarães Gusmãoa et al. (2012) have investigated the adsorption of crystal violet onto the Succinylated sugarcane bagasse (SCB 2) prepared from sugarcane bagasse, an important agricultural waste, after only one chemical modification under several operating conditions. Equilibrium adsorption times was found to be 20 hours for CV and optimum pH for removal of CV

was found to be equal to 8.0. The experimental data fitted very well to the Langmuir model. Maximum adsorption capacities for removal of CV were found to be 1273.2 mg/g. The adsorption process was well described by pseudo-second-order model; however the intraparticle diffusion model yielded three linear regions suggesting multiple sorption rates. [39]

Prasad and Santhi (2012) studied the adsorption of cationic dyes (crystal violet and rhodamine B) from aqueous solution onto *Acacia nilotica* leaves as an eco-friendly adsorbent. The equilibrium adsorption was practically achieved in 120 minutes. The highest removal of dyes was obtained at pH 6. The removal efficiency increased with increase in agitation time and initial dye concentration. The equilibrium data were best described by Langmuir isotherm model with maximum monolayer capacity of 33 and 37 mg g-1 for crystal violet and rhodamine B respectively. The adsorption kinetics can be successfully fitted to pseudo–second order kinetic model. The result of the intraparticle diffusion model suggested that intraparticle diffusion might not be the only rate controlling step. Desorption study revealed that the recovery of the dye from adsorption was possible. [40]. M. M. El. Jamal .et al. (2011) investigated the adsorption of crystal violet onto the Chaetophora Elegans Alga under several operating conditions. Equilibrium adsorption times was found to be 20 minutes for CV and optimum pH for removal of CV was found to be greater than 8.0. The experimental data fitted very well to the combined Langmuir-Freundlich model. Maximum adsorption capacities for removal of CV were found to be 158.7 mg/g at temperature 25^0C. The adsorption process was well described by pseudo-second-order model; besides the thermodynamic analysis revealed that the present adsorption process is endothermic and spontaneous as ΔH^0 and ΔG° were found positive and negative respectively. [41]

Satish Patil et al. (2011) have investigated the naturally available materials viz. the Mangrove plant (Sonneratia Apetala) leaf powder (MPLP), Mangrove plant (Sonneratia Apetala) fruit powder (MPFP), Mango (Mangifera Indica) leaf powder (MLP), Tamarind (Tamarindus indica) fruit shell powder (TFSP), Teak tree (Tectona Grandis) bark powder (TTBP), Almond tree (Terminialia cattapa) bark powder (ATBP) as an adsorbent for removal of crystal violet from aqueous solution. The monolayer (maximum) adsorption capacities (Q_0) of MPLP, MPFP, MLP, TFSP, TTBP, ATBP were found to be 200, 250, 200, 142.857, 200, 166.667 mg/g respectably. The pseudo second order model best fits the kinetics of adsorption. Intra particle diffusion plot showed boundary layer effect and larger intercepts indicates greater contribution of surface sorption in rate determining step. Adsorption was found to increase on increasing pH, increasing temperature and decreasing particle size. ΔG, ΔH and ΔS values showed favorable, spontaneous, endothermic physical

adsorption with increased disorder and randomness at the solid solution interface of CV with biosorbents. Adsorption capacities of different adsorbents towards CV were found to be of the order of MPLP > MPFP > TTBP > MLP > ATBP > TFSP. [42]. Nagda, G. K et al (2008), Studied Raw tendu waste (TLR), sulfuric acid carbonized tendu waste (TLR-CM) and tendu waste treated with dilute sulfuric acid (TLR-2N) as sorbent for uptake of crystal violet from aqueous solutions. The experimental result showed that it followed the pseudo-second-order kinetics and followed the Langmuir adsorption isotherm. The maximum adsorption capacities for crystal violet for TLR-2N, TLR and TLR-CM are 67.57, 42.92 and 22.47 mg/g respectively. Interestingly, milder acid treatment of the tendu waste enhanced biosorption, whereas drastic acid carbonization of tendu waste resulted in reduced adsorption of dye. [43]

Verma and Mishra (2010) used rice husk carbon to adsorb dyes (crystal violet, direct orange and magenta). It was found that the optimum time was 45 minutes and there was decrease in adsorption capacity in the low pH region. Also, the removal of dyes increased with increase in temperature and there was increase in removal of dyes with increasing adsorbent dose. The removal percentage decreased with increase in initial concentration of dyes. [44]. Bharathi K. S. et al.(2012) used Citrullus lanatus (Watermelon) rind, an agricultural solid waste as a bio-sorbent for the removal of crystal violet from aqueous solutions. The maximum amount of CV adsorbed corresponding to the equilibrium time of 180 min was found to be 87% for a dose of 1.0 gm/lit of the adsorbent. The optimal pH value for the sorption of CV was found to be in the range of 8.0-12.0. The extent of adsorption of CV was found to increase with increase in temperature in the range of 30-500C, indicating the process to be endothermic in nature. The experimental equilibrium data best fitted to the Freundlich isotherm model. The adsorption capacity was found to be 4.82 mg/g at 30°C. The kinetics of adsorption was found to follow pseudo-second-order kinetic model. From thermodynamic analysis the value of ΔG^0, ΔH^0 and ΔS^0 were found negative, positive and positive respectively. [45]. Sagnik Chakraborty et al. (2011) studied, equilibrium, kinetics and thermodynamics of Crystal Violet (CV) adsorption onto NaoH modified rice husk (NMRH). The adsorption was favored at higher pHs and lower temperatures. Adsorption data were well described by the Freundlich model, although they could be modeled by the Langmuir model as well. The adsorption process followed the pseudo-second order kinetic model. It was found that intraparticle diffusion was not the sole rate controlling step. The activation energy (Ea) of the system was calculated as 50.51 kJ mol−1. Thermodynamic parameters suggest that the adsorption is a typical chemical process, spontaneous, and

exothermic in nature. (Sagnik Chakraborty, Shamik Chowdhury, Papita Das Saha, Adsorption of Crystal Violet from aqueous solution onto NaoH-modified rice husk, Carbohydrate Polymers 86 (2011) 1533– 1541).

Rice husk carbon was used to adsorb dyes (crystal violet, direct orange and magenta) by Verma and Mishra [2010]. It was found that the equilibrium time was 45 minutes and there was decrease in adsorption capacity in the low pH region. Also, the removal of dyes increased with increase in temperature and there was increase in removal of dyes with increasing adsorbent dose. The removal percentage decreased with increase in initial concentration of dyes. [46]

III. Further Scope of Study

From the above review it can be observed that a number of biomaterials have been tested as an adsorbent for the removal of CV and MG in batch mode experiment. These studies will be proved useful only when suitable technology is being evolved for their actual use in removal of these dyes from industrial effluents containing CV and MG. Though lots of works have been done to find out the effectiveness of biomaterials in removal of CV and MG by means of adsorption but very little work has been done to understand the actual mechanism of adsorption of these dyes onto the various biomaterials. This is one of the areas where researchers have to put their attention. There is the need to develop mathematical model to predict the effect of various parameters like the rotational speed, pH value of solution, initial concentration of dye, dose of adsorbent, temperature. Response surface methodology (RSM) is an attempt in this direction but still much more is required to evolve mathematical models which fully explain the various factors. During the last five years a number of biomaterials/agricultural waste have been tested as an adsorbent for the removal of the crystal violet and malachite green dye from its aqueous solution by researchers. These biosorbents shows excellent adsorption capacity for the CV and MG dyes and can be used as an alternative of activated carbon.

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