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Synthesis and Charecterisation of Nanocrystallite Embedded Activated Carbon from *Eichornia Crassipes* and its use in the Removal of Malachite Green

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Abstract : Activated carbon was prepared from *Eichornia crassipes* by pyrolysis at 250°C. The plant biomass was impregnated with transition metal salt solution prior to pyrolysis. The activated carbon was charecterised by XRD, SEM and EDAX. The activated carbon was found to contain nanocrystallites embedded in it. Batch experiments were carried out for the adsorption of malachite green onto the prepared carbon. Equilibrium data for the adsorption process was fitted to two parameter and three parameter isotherm models, including Langmuir, Freundlich, Temkin and Dubinin-Radushkevich, Redlich-Peterson, Toth, and Koble-Corrigan. Linear and Non-linear regression methods were used to determine the best fit model to the equilibrium data. The data obtained was fitted to different kinetic models namely, pseudo first order, pseudo second order, intraparticle diffusion and Elovich model. Nanocrystallite embedded activated carbon was found to have superior adsorption capacity for malachite green, through physisorption, and can be used to treat waste water containing dyes. The kinetics follows pseudo second order mechanism under favourable adsorption conditions.

Keywords: activated carbon, nanocrystallites, linear regression, non-linear regression, adsorption, malachite green.

Introduction

Industrial effluents are a major cause of environmental pollution. The use of a large number of dyes in textile industry is mandatory. In most cases the textile industry discharges untreated effluents into receiving water bodies causing damage to aquatic organisms, plant and animal life and also human beings. Wastewater containing dyes is difficult to treat because dyes are organic molecules, resistant to aerobic digestion, stable to light, heat and oxidizing agents due to their structure and molecular size.

Conventional wastewater treatment methods for removing dyes include physical, chemical and biological methods. Adsorption has gained favour in recent years for its efficiency in removing pollutants from effluent water. Activated carbon as an adsorbent for dyes has been widely investigated. The use of biomass as a source of activated carbon is also being investigated in recent years.

Malachite green (MG) is classified as a basic dye and is used mainly as a pigment in several industries.

It is used as a dye for materials such as silk, leather and paper [1]. Malachite green is an organic compound that is extensively used in aquaculture. It is an active agent against infections in fish eggs in commercial aquaculture. Malachite green is toxic, carcinogenic and known to cause reproductive problems.

Many physical and chemical treatment methods including adsorption, coagulation, precipitation filtration, electrodialysis, membrane separation and oxidation have been used for the treatment of dye-containing effluents [2] [3] [4]. Adsorption process is one of the most effective and economically feasible methods for the removal of dyes from aqueous solutions.

Activated carbon is widely used in removal dyes from textile effluent due to its relatively high sorption capacity for a wide variety of dyes. The selection of precursors for producing activated carbon determines the adsorptive, physical and chemical properties that can be attained in the carbon. Carbon used for adsorption can be designed depending on the structure of the adsorbate by selecting an appropriate precursor and optimising the carbonising and activation process conditions.

Eichornia crassipes is a plant that is found in water bodies like lakes and rivers in profusion. It is considered a weed and its potential for preparing activated carbon has been investigated earlier. The use of *Eichornia crassipes* to prepare activated carbon embedded with nanocrystallites and its potential for the removal of MG is being investigated in this paper.

Materials and Methods

Adsorbent and Adsorbate

10 g of the dried and powdered biomass was soaked in 0.1 M solution of cobalt nitrate in w:v ratio of 1:15 for 24 hours. The mass was then filtered and washed with distilled water and dried in air for 24 hours and in an air oven at 100ºC till completely dry. The dried biomass was then transferred to a stainless steel container and heated at 250ºC for 20 minutes, quenched with 200 ml of distilled water and dried in air for 24 hours and further in an air oven at 100ºC till completely dry. The activated carbon thus obtained, AC-Co, was stored in an air tight container.

Preparation of Synthetic Solution

A stock solution of 1000 mg L^{-1} was prepared in distilled water by dissolving appropriate amount of MG. Synthetic dye solutions of different concentrations, 60, 80, 100 and 120 mgL^{-1}, were prepared by diluting appropriate amount of stock solution. All the adsorption experiments were carried out at room temperature (30 ± 2 ºC).

Charecterisation of the Adsorbent

Crystalline structure, surface morphology and elemental constituents were obtained by XRD, SEM and EDAX analysis respectively. X-ray diffraction (XRD) measurements were performed using a powder X-ray diffractometer, PANanalytical X'Pert powder XRD system with Cu K radiation (wavelength = 1.5405Å) at 45 kV and 30mA. Electron Micrographs for SEM were recorded using scanning electron microscope (JSM-6330TF) operated at 10 kV. The scanning electron microscope image is used in conjunction with energy-dispersive X-ray microanalysis to determine the elements present in the sample.

Batch Adsorption Experiments

Batch mode experiments were carried out using the prepared activated carbon as adsorbent as described in [5].

Contact Time and Initial Dye Concentration Studies

Studies were carried out by shaking the adsorbent with 25 ml of synthetic dye solutions of different concentrations at pH 7 at room temperature (30 ± 2 ºC) in 250 ml iodine flask.

Adsorption Dynamics

The rate at which the basic dyes are adsorbed on the prepared carbon is significant. This determines the suitability of this process for treatment of waste water containing dyes.

Isotherm Modelling

The relationship between the amount of dye adsorbed at constant temperature and its concentration in the solution at equilibrium is called the adsorption isotherm. Equilibrium isotherm equations are used to describe the experimental sorption data. To optimize the design of an adsorption system to remove the dye, it is important to establish the correlations of the equilibrium data of each system. The parameters obtained from the different models provide important information on the sorption mechanisms and the surface properties and affinities of the adsorbent to the dye molecule.

In this study, equilibrium data were fitted into two-parameter isotherms namely Langmuir, Freundlich, Temkin and Dubinin-Radushkevich. Three parameter isotherm models including Redlich-Peterson, Toth and Koble-Corrigan models were also employed for fitting the equilibrium data. The equations for each isotherm and their linear expressions are as given in [5].

Linear regression and non-linear regression is used to determine the best-fitting isotherm. The applicability of isotherm equations was judged by comparing the correlation coefficients, the coefficient of determination, MPSD and HYBRID error functions. When the value of r^2 and R^2 lie closer to 1, the experimental data is said to fit with the data calculated by the isotherm models. The smaller values of MPSD and HYBRID indicate a better fit between experimental data and the equilibrium capacity obtained by calculation from the isotherm models. MPSD and HYBRID functions were chosen as the number of parameters in the isotherm are also accounted for in calculating error.

Adsorption Kinetics

The study of kinetics is important in waste water treatment because it describes rate of uptake of MG. The equations used to calculate the parameters for the various kinetic models have been given in [5].

Results and Discussions

Charecterisation of t he Adsorbent

X-Ray Diffraction

X-ray diffraction is a powerful technique to analyse the crystalline and amorphous nature of the prepared carbons. In crystalline materials [6] well defined peaks are observed whereas in amorphous materials the peaks are broad and not sharply defined. Fig 1 shows the powder XRD of AC-Co. The peaks observed at values of 2θ corresponding to 19°, 30°, 37°, 43°, 59° and 65° correspond to peaks observed [7] [8] [9] in Co_3O_4 as they match with the standard spectrum JCPDS No – 073-1701. The nanocrystallites are present between the graphitic layers of the carbon char from the bioprecursor. The minor shift and broadening of diffraction peaks may be attributed strain. There are no peaks corresponding to CoO and Co [10] and their formation during pyrolysis is ruled out.
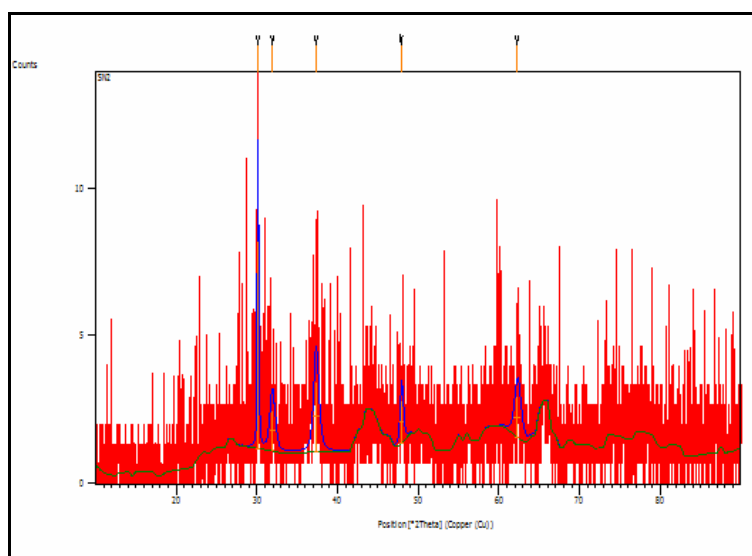

Fig 1 - Powder XRD of AC-Co

The XRD pattern of AC-Co has broad peaks at 2θ value [11] of 26° and 44° which correspond to peak of graphite [12] . There is noise in the powder XRD signals, revealing a predominantly amorphous structure [13] of carbon. The diffused peaks appearing at low 2θ values between 13° to 24° are indicative of the amorphous nature of the material [14] having some degree of crystallinity in the molecular chains.

XRD crystallite size is calculated using Debeye Scherrer formula [15]

$$D = \frac{K\lambda}{\beta Cos\theta}$$

where K is the shape factor, λ is the wavelength of the x-ray used, β is the line broadening at half maximum intensity (FWHM) in radians and θ is the Bragg's angle. The dimentionless shape factor K has a typical value of 0.9, but varies with the actual shape of the crystallite. A variety of factors can contribute to the width of a diffraction peak besides instrumental effects and crystallite size; the most important of these are usually inhomogeneous strain and crystal lattice imperfections. The size of the nanocrystallite particle calculated using Debeye Scherrer formula is given in Table 1.

Table 1 - XRD results estimate the average particle size in AC-Co.

Name of the Carbon	2θ of the intense peak (deg)	FWHM of the intense peak	Size of the particle (nm)
AC-Co	30.0934	0.1968	7.2957

Scanning Electron Microscopy

SEM image of the activated carbon was recorded and is given in Figure 2. The SEM image of AC-Co shows that the particles have a fluffy morphology. The activated carbon has extremely heterogeneous surfaces with large number of voids, cracks and enlarged pores. This is due to the escape of easily volatile substances from the raw biomass [16] and the decomposition of $Co(NO_3)_2$ during carbonisation. The SEM images of the activated carbon shows the formation of macro and meso pores, favouring their use in the study of adsorption of MG.
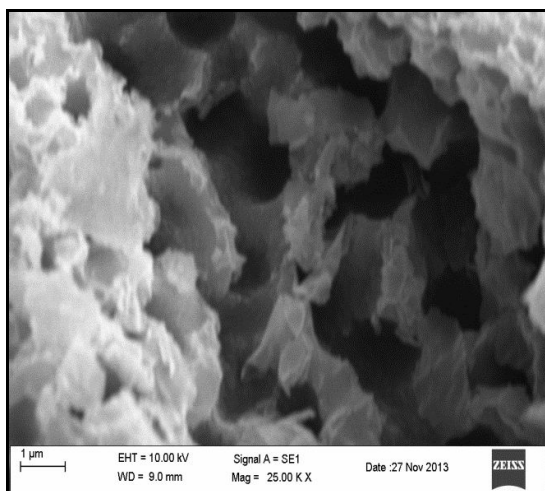

Fig 2 - SEM of AC-Co

X-Ray Microanalysis Edx

The results of EDX analysis of the activated carbon show that these materials primarily consist of carbon and oxygen. There is a significant amount of Co as expected, from the salt used for activation. It may be inferred that AC-Co consists of irregularly arranged graphite sheets which acts as the macroscopic material. The nanocrystallite Co_3O_4 are present embedded between the graphite layers. The nano size transition metal oxide formed, as ascertained in XRD analysis may affect the process of dye adsorption.
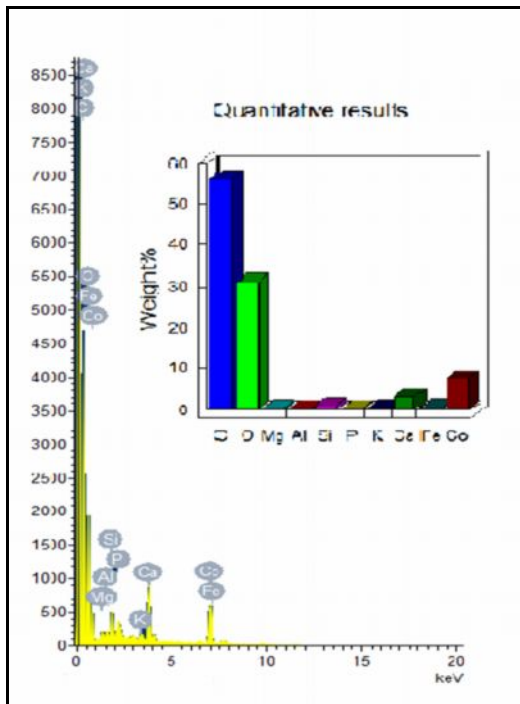
Fig 3 - EDX of AC-Co

Effect of Contact Time and Initial Dye Concentration

The data for the uptake of MG onto AC-Co is shown as a function of contact time for different initial dye concentration and presented in Figure 4. It can be seen that the amount of MG adsorbed per unit mass of adsorbent increased with the increase in initial concentration and attained saturation after equilibrium time, although percentage removal decreased with the increase in initial concentration. The result clearly indicates that the amount of dye adsorbed increases with increase in time till equilibrium is reached, for all concentrations investigated.
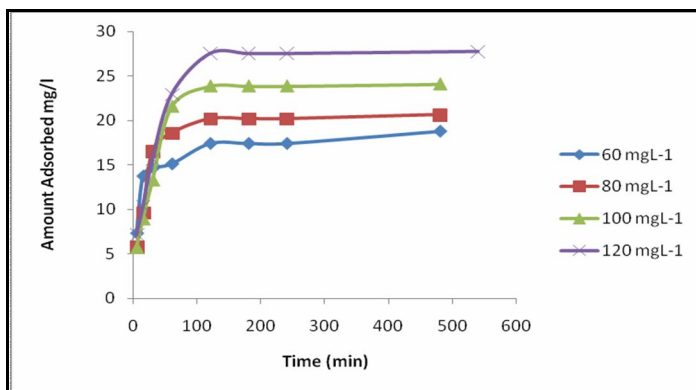

Figure 4 – Effect of contact time and concentration of the adsorbate on the adsorption of MG on AC-Co (0.05g of AC-Co dose/25ml of adsorbate solution, temperature 30°C, pH 7)

From figure 4, it has been found that the amount of dye removed at equilibrium increases with increase in dye concentration of MG. This is so because the initial dye concentration provides the driving force to overcome the resistance to mass transfer of the dye molecule between the aqueous and solid phase.

The data also reveals that as the contact time increases, rate of adsorption first increases and then becomes almost constant. This is due to the aggregation of dye molecules with the increase in contact time, which makes it almost impossible to diffuse deeper into the adsorbent structure and occupy sites having higher energy. This aggregation nullifies the influence of increase in contact time. The pores get filled up and start offering resistance to diffusion of aggregated dye molecules in the adsorbents [17]. The adsorption percentage also decreases with increase in concentration of the adsorbate MG. A maximum of 92.9% of MG was removed at adsorbate dose of 100 mg L^{-1} by AC-Co.

Isotherm Modelling

The fitness of the equilibrium data obtained for the adsorption of MG onto AC-Co was analyzed using various models viz., two-parameter isotherms namely Langmuir, Freundlich, Temkin and Dubinin-Radushkevich and three parameter isotherm models including Redlich-Peterson, Toth and Koble-Corrigan isotherm models.

In the present study, the experimental data for the adsorption of MG onto AC-Co was found to fit the Freundlich isotherm model among the two parameter models and Toth isotherm [18] among the three parameter models.

It can be seen from Table 2 that Freundlich isotherm fits the data better than Langmuir isotherm. This is also confirmed by the higher value of R^2 in case of Freundlich compared to Langmuir. The Langmuir maximum adsorption capacity is higher for AC-Co is 121.1 mg g^{-1}. This indicates a high degree of affinity of AC-Co towards MG.

Table 2 – Isotherm parameters calculated by linear regression (LR) and non linear regression (NLR) for the sorption of MG by AC-Co.

Isotherm		Parameters	LR	NLR
Langmuir	r^2		0.7777	-
	R^2		0.4944	0.8881
	MPSD		746	43.43
	HYBRID		5564	18.87
	Parameters	q_m (mg g^{-1})	65.44	121.1
		K_L (L mg^{-1})	0.0814	0.03513
Freundlich	r^2		0.9336	-
	R^2		0.8699	0.9344
	MPSD		209	180
	HYBRID		437	325
	Parameters	K_F (mg g^{-1})(L mg^{-1})	6.941	24.79
		N	1.587	17.5
Temkin	r^2		0.9166	-
	R^2		0.4930	0.8622
	MPSD		656	46.58
	HYBRID		4305	21.7
	Parameters	q_m (J mol^{-1})	0.7635	16.95
		K_T (L g^{-1})	14.25	0.5911
Dubinin-Radushkevich	r^2		0.8779	-
	R^2		0.7356	0.6572
	MPSD		204	259.6
	HYBRID		417	671
	Parameters	q_m (mg g^{-1})	30.20	99.09
		β (mol^2 KJ^{-2})	2.1x10^{-6}	1.26x10^{-5}
		E (J mol^{-1})	-492.9	-198.9
Redlich-Peterson	r^2		0.8371	-
	R^2		0.9275	0.8714
	MPSD		304	80.75
	HYBRID		462	32.6
	Parameters	G	0.02515	0

		A_{RP} (mg g^{-1})(L mg^{-1})	0.658	1.702
		B_{RP} (L mg^{-1})^g	0.9243	0.5002
Toth	r^2		0.9336	-
	R^2		0.8889	0.888
	MPSD		300	62.1
	HYBRID		449	19.28
	Parameters	K_T (mg g^{-1})(L mg^{-1})	30.11	125
		a_T (L mg^{-1})^d	7.01	30.55
		D	1.46	1.008
Koble-Corrigan	r^2		0.9481	-
	R^2		0.9276	0.9278
	MPSD		305	45.97
	HYBRID		454	10.57
	Parameters	A_{KC} (mg g^{-1})(L mg^{-1})^P	0.4104	0.5399
		B_{KC} (L mg^{-1})^P	0.9531	0.9388
		P	0.01534	0.02

The value of n is greater than 10 indicating a high degree of heterogeneity of the adsorbent surface. The value of K_F, the adsorption or distribution coefficient, representing the quantity of dye adsorbed onto adsorbent for unit equilibrium concentration is related to bonding energy. The K_F values indicate that the adsorption of MG onto the prepared carbons is favourable.

Temkin isotherm [19] model considered that the effect of adsorbate interactions on adsorption isotherms. The heat of adsorption of all the molecules in the layer is assumed to decrease linearly with coverage. The heat of adsorption values indicate that adsorption occurs through physisorption.

The theoretical saturation capacity q_m estimated from the Dubinin Radushevich is 99.09 mg g-1 corroborates the values of Langmuir maximum monolayer adsorption capacity. The calculated apparent energy of adsorption value is -198.9 J mol^{-1} indicating physisorption.

The Redlich–Peterson isotherm is an empirical three parameter isotherm equation combines elements from both the Langmuir and Freundlich equations. The proposed mechanism of adsorption is a hybrid of Langmuir and Freundlich models and does not follow ideal monolayer adsorption. The values of G is 0 implying multilayer adsorption of MG on the surface of AC-Co. From the R^2, MPSD and HYBRID values, it is clear that this isotherm does not explain the adsorption process completely.

The Toth isotherm model [19] gave the best fit for the adsorption of MG. It is often useful for describing heterogeneous systems. The Toth isotherm model approaches the Henry region at infinite dilution. The application of Toth isotherm equation is best suited to multilayer adsorption, which is a special type of Langmuir isotherm and has very restrictive validity. These facts clearly indicate the existence of a great degree of heterogeneity in the surface of AC-Co.

The R^2, MPSD and HYBRID values for Koble Corrigan model indicate a good fit to the experimental data. But the values of the Koble Corrigan exponent P are less than 1. Therefore, we cannot apply this model to explain the adsorption process.

The difference between the values calculated by linear and non linear regression is due to the inherent bias resulting from linearization. It may be concluded that the adsorption of MG is governed by the formation of monolayer. The adsorption of MG involves adsorption sites of different energies on the heterogeneous surface of the prepared carbon. The adsorption energy as calculated by Dubinin Radushevich isotherm is -198.9 Jmol^{-1} indicating stronger bond formations between MG and the prepared carbon.

Langmuir constants for the adsorption MG by a number of adsorbents are presented in Table 3. These include the published values as well as the Langmuir constants obtained in the present study.

Table 3 - Comparison of adsorption capacity of various adsorbents for adsorption of MG by linear regression (LR) and non-linear regression (NLR)

Source of Carbon	Dye	Chemical used for activation	Temperature of carbonisation	Langmuir Adsorption Capacity mg g-1	References
Prawn waste	MG	H_2SO_4	Room temperature	9.2	[25]
Borassus bark	MG	-	600°C	20.7	[26]
Jack fruit peel	MG	H_2SO_4	160°C	166.4	[27]
Degreased coffee beans	MG	-	Room temperature	55.3	[28]
Thevetia peruviana	MG	H_3PO_4	800°C	133.1	[22]
Eichornia crassipes	MG	$Co(NO_3)_2$ AC-Co	250°C	65.44 (LR) 121.1(NLR)	Present study

Adsorption Kinetics

     Study of adsorption kinetics provides important information on sorption rate and the factors affecting the sorption rate, which is extremely important in designing batch sorption systems. Equilibrium data of malachite green adsorption onto AC-Co obtained from batch adsorption experiments were analysed.

     In the present study, pseudo-first order and pseudo-second order, Elovich and Intraparticle diffusion models were employed to analyse the kinetics of malachite green adsorption onto the adsorbent. The linear equations of the various kinetic models studied as given in [5]. The linear regression correlation coefficient values were used to determine the goodness of fit to the different kinetic models.

Pseudo-first-order equation

     The data obtained were analyzed with the Lagergren pseudo-first order kinetic model equation are given is Table 3. The pseudo first order Langergren equation predicts that the variation in rate should be proportional to the first power of concentration. However, this is not found to be true. The correlation coefficient r^2 varies between 0.8763 and 0.923 for the adsorption of MG onto AC-Co.

     The values of qe obtained theoretically from this equation do not agree with those obtained experimentally. Thus the rate of removal of MG from solution by AC-Co does not follow the pseudo-first-order equation. Indeed this is the general trend in most adsorption studies reported in literature [20].

Pseudo-second-order equation.

     The pseudo second order rate equation [21] was used to calculate the value of K_2, the second order rate constant of adsorption. The values obtained are given in Table 3. The value of r^2 is between 0.9988 and 0.9997 for the adsorption of MG. The results show that the values of qe calculated using pseudo second order rate equation and qe determined experimentally are almost equal. The correlation coefficients r^2 are closer to unity, which confirm that adsorption of MG onto AC-Co follows pseudo-second order kinetic mechanism. The applicability of pseudo second order kinetic model to adsorption process has been reported in previous studies using low cost adsorbents [22].

Intraparticle diffusion model.

     The kinetics was further analysed by intraparticle diffusion model using Weber – Morris equation [23]. The intra particle diffusion is a very important technique that could be used for confirming the mechanism of the adsorption process. The value of K_{id} is evaluated from the slope of the linear plot of q_t versus $t^{1/2}$ (Figure 5).
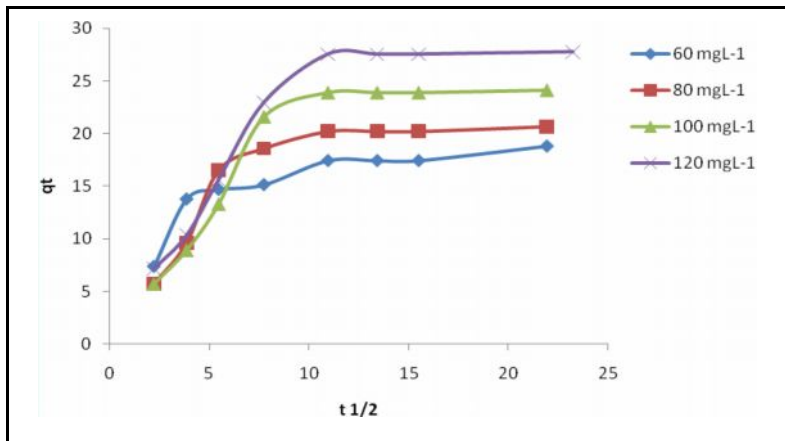
Figure 5 – Plot of intraparticle diffusion model for adsorption kinetics of MG on AC-Co at different initial concentrations.

If the plot of q_t versus $t^{1/2}$ is linear and passes through the origin, then intraparticle diffusion is the sole rate limiting step. It is clear from figure 5 that the lines do not pass through the origin. Larger the value of the intercept, greater is the contribution of the surface sorption in the rate limiting step. Hence, the presence of both surface adsorption and intraparticle diffusion is confirmed.

The initial curved portion is probably due to the boundary layer effect and the second linear portion represents the intra particle diffusion. The intercepts reflect the boundary layer effect. The two phases of the intra particle diffusion in the plot suggest that the mechanism of adsorption process was by adsorption and intra particle diffusion. . This model gives correlation coefficient values between 0.7848 and 0.8317, which are lower than the pseudo second order kinetics, but is also an indicator that several processes may be involved in the uptake of MG by AC-Co. Also the uptake depends on the concentration of the dye available which changes with time.

Elovich model.

In the Elovich equation [24], B_E is the initial adsorption rate and A_E is the adsorption constant related to extent of surface coverage and activation energy. A comparison of the values of A_E and B_E for MG shows that their values are higher at lower concentrations (Table 4). Diffusion of MG inside the pores may be the limiting step for the adsorption at higher concentrations of MG.

Table 4 - Kinetic parameters calculated for the various models for the prepared activated carbon AC-Co.

Adsorbent	Conc mgL^{-1}	qe (exp) mg.g^{-1}	Pseudo First Order Kinetic Model			Pseudo Second Order Kinetic Model			
			q_e (cal) mg.g^{-1}	K_1 min^{-1}	r^2	q_e (cal) mg.g^{-1}	K_2 g.mg^{-1}. min^{-1}	r^2	h mg g^{-1}.min^{-1}
AC-Co	60	18.81	6.326	0.00797	0.8763	18.98	0.004674	0.9993	1.684
	80	20.64	8.253	0.01519	0.8972	21.19	0.004279	0.9997	1.922
	100	24.08	13.58	0.02115	0.9171	25.26	0.002312	0.9988	1.475
	120	27.75	17.3	0.02218	0.923	28.94	0.002054	0.9991	1.719

Adsorbent	Conc mgL^{-1}	Intraparticle Diffusion Model		Elovich Model		
		K_{id} mg g^{-1} min$^{-1/2}$	r^2	A_E g.mg^{-1}	B_E mg.g^{-1}. min^{-1}	r^2
AC-Co	60	0.4459	0.8154	0.4314	33.09	0.9365
	80	0.6714	0.7848	0.2906	6.276	0.9301
	100	0.9551	0.8307	0.2124	3.399	0.9466
	120	1.021	0.8317	0.1907	4.156	0.9531

Elovich equation does not help in providing any mechanism for the adsorption process, we may conclude that the surface of the adsorbents are heterogeneous. This model gives correlation coefficient values between 0.9301 and 0.9531. These values are lower when compared to pseudo second order kinetic model. This shows that Elovich model cannot describe this adsorption system entirely.

Proposed Adsorption Mechanism

The main factors that influence the adsorption behaviour are structure of dye and adsorbent surface properties. MG is a cationic dye having two amine groups in its structure and one nitrogen atom carrying a positive charge, in an aqueous solution.

The adsorption of MG on AC-Co occurs through physical adsorption (Dubinin Raduschvich model) as concluded from adsorption studies. It occurs through the formation of a monolayer (Langmuir model) followed by multilayer adsorption of MG (Toth model). The surface of AC-Co is heterogeneous (Freundlich and Toth model) providing a large surface area dominated by the formation of macro and mesopores as seen in the SEM image of the adsorbent. Adsorption of MG is a favourable process (Freundlich model) occurring on adsorption sites having different energies (Toth model).

Kinetic studies show that the data of adsorption kinetics fitted well to the pseudo-second order linear model for different MG concentration for AC-Co. The biosorption process was a multi-steps process which included a fast step and a slow step as concluded by intraparticle diffusion model. In the first step, the adsorption active sites on external surface were enough for a fast biosorption. After the first step, the biosorption would get to a steady phase which the intraparticle diffusion was diffusion-controlled. The intraparticle diffusion plots do not pass through the origin, thus, it demonstrated that intraparticle diffusion was not the only rate control step.

Adsorption of MG proceeds by film diffusion followed by pore diffusion. Physisorption occurs at the macro and meso pores seen on SEM image of the adsorbent. The presence of nanocrystallites in the activated carbon may have a catalytic effect.

Conclusion

The present study shows that nanocrystallite embedded activated carbon derived from *Eichornia crassipes* can be used as a low cost adsorbent for the removal of MG from waste water. The adsorbent, AC-Co used in this work had a relatively large adsorption capacity compared to some other adsorbents reported in the literature (Table 3) indicating its effectiveness for the removal of MG from aqueous solutions.

Adsorption equilibrium correlated reasonably well by Freundlich and Toth isotherm models. The adsorption of malachite green onto AC-Co is spontaneous, exothermic and physical in nature. The pseudo second order kinetic model agrees very well with the dynamic behaviour for the adsorption of MG. Non-linear regression method is a better way to obtain the isotherm parameters.

The adsorption of MG by the nanocrystallite embeddded carbon is governed by the formation of monolayer and involves adsorption sites of different energies on the heterogeneous surface followed by diffusion of MG into the mesopores.

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