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Recent Trends in Eradication of dyes from Wastewater Using activated carbon Anupama Sharma^{1*}, RC Chhipa¹, Mohd Ishaq¹

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Abstract

Using activated carbon (potato peel), this study examines the phenomena underlying the removal of reactive magenta and methyl red dye. Adsorption experiments were conducted in accordance with the bulk method. Investigating the adsorption behaviour in the study required the use of operating systems, which comprised the contact time required for stirring and the initial dye concentration. Experiments were conducted to evaluate the Freundlich isotherm and the Langmuir data. The findings of the research indicated that upon swaying for approximately forty minutes, equilibrium was achieved. Additionally, the sorption data revealed that saturation integration in the potato rind is mitigated when the initial CV concentration increase is greater than the percentage of reactive magenta and methyl red removal. Enhanced adsorption of pigments resulted from the initial enhancement in solution contact time. In accordance with the Freundlich and Langmuir frameworks, the isotherm adsorption data were deemed satisfactory. Furthermore, to illustrate the process of dye adsorption onto the potato rind, a model of pseudo-second-order kinetics was implemented. As a result of the research, it has been determined that potato peel can be utilized to effectively remove basic pigments from effluent.

INTRODUCTION

Environmental and biological hazards are significantly exacerbated by pollution on a global scale (Awadallah et al., 2016). A considerable influence of dyes is primarily observed in the environment's transformation as a result of their extensive use in the manufacture of numerous products, including food, cosmetics, textiles, leather, rubber, and papers (Akinola and Umar, 2015). About 7x metric tons of dye are produced each year by the textile sector (Carmen and Daniel, 2012). The extensive use and prevalence of these dyes contribute significantly to effluent pollution, which has adverse environmental consequences. Furthermore, the dyes' color effluents have an adverse effect on the ability of sunlight to penetrate, which is harmful to the aquatic environment. Research findings indicate that dyes possess intricate aromatic structures and synthetic origins, characteristics that enhance their resistance to light, heat, and oxidizing agents (Saini, 2018). The majority of studies corroborate that 2 to 20 percent of aqueous effluents are discharged into the environment during the withering process (Aneyo et al., 2016). The discharge of dye effluents into water results in detrimental consequences not only due to the color of the effluents but also because of the products they contain, which may include mutagenic, carcinogenic, or toxic substances that are harmful to other organisms (Crini and Lichtfouse, 2018). Inhalation or ingestion of the dye may result in irritation of the epidermis and toxicity (Kumar and Tamilarasan, 2013). These substances may include benzidine, naphthalene, and another aromatic element. The lack of sufficient treatment for their elimination is likely to have long-term consequences for the environment. As an illustration, the half-life of hydrolyzed Reactive Blue 19 is nearly 46 years at 25°C and a pH of 7. The utilization of water in various sectors including domestic, agricultural, and industrial gives rise to detrimental and undesired contaminants that have the potential to become noxious. Water resource protection requires active endeavors (Khalaf, 2016; Rathoure and Dhatwalia, 2016; Morin-Crini et al., 2017). A particular substance that finds extensive application in paper printing, textile dying, leather coloring (Jayganesh et al., 2017). Dye types are classified here according to the methods used to apply them. Dye types may be broadly classified as acid, basic, sulfur, vat, reactive, dispersion, and azo dyes (Kayode et al., 2015). Global water resource pollution is a matter of the utmost importance to academics, scientists, and government agencies. Numerous regions across the globe have contaminated surface and groundwater that is unfit for human consumption. The globe could experience severe freshwater scarcity by 2050 (Imran Ali et al., 2012; George et al., 2015), when the global population is projected to reach 9.3 billion (United Nations, 2011). To eliminate this issue or to discover a natural, practical pretreatment method for noxious dye

effluents (Robati et al., 2016) requires the researchers to devote considerable attention and effort.

A wide range of processes are employed to remediate wastewater, including but not limited to coagulation, reverse osmosis, flocculation, and biological methods. A number of these techniques have one or more deficiencies and are incapable of entirely eliminating the pigment from the water (Vijayakumar et al., 2012). On the contrary, the adsorption process exhibits several advantages over other methods for wastewater treatment, including its robustness in terms of design, cost, functionality, and resistance to the formation of hazardous sediment (Nageeb, 2013). In the current investigation, using inexpensive agricultural byproducts, diverse activated carbons were synthesized for the process of Adsorption of reactive magenta (RM) and methyl red (MR) dye substances.

MATERIAL AND METHODS

Activated carbon preparation: In order to eliminate dispersed impurities such as grit and soil, potato peels were collected from potatoes and subsequently rinsed with faucet water and double-distilled water before being desiccated in an air oven. Separately agitated at room temperature for twenty-four hours, 500 grams of carbon derived from potato rind is combined with 100 milliliters of concentrated sulfuric acid. It was then desiccated at 80 degrees Celsius in a hot air oven. To remove surplus acid, the desiccated substance was rinsed with distilled water (Heidarinejad et al, 2020). In an airtight container, charcoal was desiccated at 110 degrees Celsius for 12 hours to remove moisture content.

Chemical and Adsorbate preparation:

In the present study, the reactive magenta and methyl red dye was obtained from Loba Chemie, a chemical manufacturer. The efficacy of the activated carbons that were prepared was assessed by employing reactive magenta and methyl red dye as adsorbate. At 1418.94 g/mol, reactive magenta possesses a molecular weight. 530 nanometers is the maximal absorption wavelength of this dye.

Acid red 2 is the chemical symbol for methyl red dye. $C_{15}H_{15}N_3O_2$ is its molecular composition. 269.304 g/mol is the molecular weight. 410 nanometers precisely. Diazylbenzoic acid is designated by the IUPAC as (4-(Diethylamino) phenyl). Dark red crystalline powder, it is an Azo dye. Red at a pH below 4.4, yellow at a pH above 6.2, and orange at a pKa of 5.1, methyl red functions as a pH indicator. Histopathology distinguishes the presence of organisms with naturally occurring cell walls and acidic tissue by means of methyl red. The pigment (1gm) was dissolved in double-distilled water in 1000ml to create the stock solutions.

Adsorption experiments: Adsorption experiments were conducted in batch mode by combining 50 ml of a dye solution containing a specific concentration of adsorption with a contact time of 200 ppm. At predetermined intervals, the samples were extracted from the agitator, and the resulting solution was subsequently separated from the adsorbent. In order to ascertain the concentration of residual dye, the absorbance of the effluent solution was monitored using a double beam spectrophotometer both prior to and subsequent to treatment. To determine the impact of varying the initial dye concentrations in the test solution and the contact time on the adsorption kinetics, both parameters were altered.(Ruan,Zhang et al, 2022).

The calculation for determining the quantity adsorbed and the adsorption efficiency (percent removal) in a bulk experiment was as follows:

Adsorbed $(q) = (C_0 - C_e)/m - (1)$

(%) removal = $(C_0 - C_e)/C_0 \times 100$ ------ (2)

Where, C_o is the initial concentration (mg/L), C_e is the equilibrium concentration (mg/L), m is the mass of the adsorbent (g), q is the amount adsorbed (mg/g)

RESULTS AND DISCUSSION

Effect of concentration: As measured by the percentage of dye removal and the amount adsorbed (mg/g) using carbon PP (Table no: 1), the experimental outcomes of the influence of varying initial concentrations of RM and MR (26-40, 36-50, 52-66 ppm and 72-86, 58-72, 96-110 ppm, respectively) in addition to a constant dose and contact time were examined. A fixed dose of 1g/L and a constant contact time of 45 minutes were utilized in the bulk adsorption experiment. (26-40, 36-60, 52-66) for RM (potato peel) and (72-86, 58-71, 96-1110) for MR (potato peel) constitute the initial concentration (C_0) of the dye. A calibration curve can be utilized to determine the equilibrium concentration (C_0) of the dye by noting the absorbance and a known concentration of the dye devoid of carbon. A decline in the percentage of adsorption is increased since there are fewer active sites and the surface area of the carbon is less. The percentage of dye removal, however, is dependent on the initial concentration (Sivarajasekar et al., 2016) due to the reduced number of available adsorption sites at high concentrations. Dye molecules bind more strongly with the adsorbent surface when the initial concentration is higher, as shown in earlier research (Ai et al. 2011; Lee et al.

2019; Mondal and Kar 2018). These outcomes have also been documented in various scholarly works (Mondal and Kar 2018; Raval et al. 2016) and observed by other researchers.

Table : 1 Effect of initial concentration of Reactive Magenta(RM) and Methyl Red (MR) on PP

POTATO PEEL (PP)							
Reactive Magenta			Methyl Red				
Concentration	Adsorption Amoun		Concentration	Adsorption	Amount		
(ppm)	Efficiency	Adsorbed	(ppm)	Efficiency	Adsorbed		
	(%)			(%)			
26	98.10	128	72	96.24	3.45		
28	96.45	1.36	74	93.23	3.44		
30	95.12	1.41	76	92.78	3.50		
32	92.15	1.46	78	92.35	3.61		
34	89.10	1.52	80	91.21	3.66		
36	81.17	1.47	82	90.24	3.71		
38	80.20	1.53	84	89.64	3.75		
40	73.56	1.47	86	89.50	3.86		



(A)

(B)

Figure:1 Effect of initial concentration of Reactive Magenta (A) and Methyl Red dyes (B)

Analysis of contact time: The experimental findings pertaining to the kinetics and dynamics of dye adsorption onto carbon at a constant initial concentration (Table;2 and Fig:1). The particle size remains constant, while the pH of the solution remains constant. Both stopwatches were initiated concurrently with the commencement of the experiment. After 5 to 45 minutes, the flasks were removed from the agitator and the various ties were applied. The percentage of removal increases as the contact time increases, reaching its maximum at 45 minutes; thereafter, it reaches a state of stagnation. Adsorption efficiency diminishes with the passage of time as a result of desorption (George et al., 2016; Shengli et al., 2016; Elmoubarki et al., 2015).

 Table no : 2 Effect of contact time for Reactive Magenta(RM) and Methyl Red (MR)
 on PP (Potato peel)

POTATO PEEL (PP)							
Reactive Magenta			Methyl Red				
	Conc	Amount	Efficiency	Time	Conc.	Amount	Efficiency
Time	(ppm)	Adsorbed	(%)		(ppm)	Adsorbed	(%)
15	30	1.15	70.9	15	70	3.35	80.0
20	30	1.19	75.4	20	70	3.41	84.64
25	30	1.25	77.7	25	70	3.46	85.25
30	30	1.32	84.10	30	70	3.45	85.69
35	30	1.36	85.12	35	70	3.49	86.01
40	30	1.42	89.0	40	70	3.53	87.30
45	30	1.48	91.8	45	70	3.67	90.51



Figure: 2 Effect of contact time for Reactive Magenta and Methyl Red

ADSORPTION ISOTHERMS

It is via adsorption isotherms that the equilibrium interactions between adsorbent and adsorbate may be characterized. To suit the experimental data acquired in this investigation, two distinct adsorption isotherm models were utilized: the Freundlich (27) and Langmuir (26) isotherm equations. The sorption capacities of crystal violet were determined by comparing these two models with potato peel. The estimation of the most suitable model is conducted through the utilization of the correlation coefficient for regression (\mathbb{R}^2); an isotherm that produces an \mathbb{R}^2 value in closest proximity to unity is deemed to provide the most suitable fit (28).

Freundlich Adsorption Isotherm : The correlation coefficient R^2 for the RM and MR dyes is 0.986 and 0.957 respectively, on a log ce versus log qe plot, which features a straight line. The adsorption data were effectively fitted with Freundlich isotherm models based on the R^2 values. The information regarding the Freundlich adsorption isotherm is presented graphically in Figures 1 and is detailed in Table 3. The Freundlich constant KF and 1/n are determined, correspondingly, from the intercept and slope of the log ce versus log qe plot. Adsorption sites are distributed heterogeneously across the surface of the adsorbent when the heterogeneity factor 1/n approaches zero. In the Freundlich adsorption isotherm, all adsorbents exhibit experimental values of 'n' greater than 1. Therefore, chemical adsorption is the adsorption process. The affinity of the CR dye for both adsorbents is measured by the Freundlich constant KF (Table 3).

Table no : 3 Freundlich Adsorption Isotherm Parameter for Reactive Magenta and Methyl Red

Freundlich Isotherm constants	Activated	Activated carbon (PP)		
	Reactive Magenta	Methyl Red		
K _F (mg/g)	0.646	0.778		
1/n	0.279	0.139		
n	3.658	7.245		
\mathbf{R}^2	0.988	0.960		



Fig. 3 Freundlich Adsorption Isotherm plot of RM and MR DYES

Langmuir Adsorption Isotherm: The graphs in Figure 2 illustrate the Langmuir adsorption isotherm values pertaining to the adsorption of dye onto activated carbon, which are displayed in Table 4 The significance of the R^2 value approaching 1 suggests that the capacity of activated carbon to adsorb pigments has been confirmed through observation. From the intercept and slope of the linear plot between $1/q_e$ and $1/c_e$, the values of K_L and q_m were respectively calculated. As denoted by the separation factor RL, the fundamental trajectory of the Langmuir adsorption isotherm can be predicated. As shown in Table 4, the process was favorable based on the value of the dimensionless equilibrium parameters $R_L < 1$.

 Table no : 4 Langmuir Isotherm constants Parameter for Reactive Magenta and Methyl

 Red

Langmuir Isotherm constants	Activa	ated carbon (PP)
	Reactive	Methyl Red
	Magenta	
K _F (mg/g)	0.391	0.762
$q_m (mg/g)$	3.997	6.087
RL	0.181	0.099
\mathbb{R}^2	0.995	0.980



Fig. 4 Langmuir Isotherm plot of RM and MR DYES

Adsorption Kinetic. To determine the efficacy of the kinetic model's application procedure, the adsorption of reactive Magenta and methyl Red onto activated carbon (potato peel) was investigated. The kinetic model is implemented in order to facilitate the design and modeling of the adsorption system.

Utilizing pseudo-first-order and pseudo-second-order models, it was possible to ascertain which mechanism, such as mass transfer, chemical reaction, or diffusion, regulates the adsorption process. Lagergren provided the framework for the pseudo-first order kinetic. The following is its equation :

Log
$$(q_e - q_t) = \log q_e - k_1 x t$$

2.303

Where , q_e - The amount of dye adsorbed at equilibrium (mg/g) , q_t - The amount of dye adsorbed at any time t (mg/g) K₁ - First order rate constant (min-1)

Table 5 provides the kinetic adsorption correlation coefficient R^2 value of dyes reactive Magenta and methyl Red onto activated carbon for pseudo-first order kinetics. Figures 3 illustrate this value graphically. The rate constants K₁ and qe of the first order were calculated using the intercept and slope of the log (qe-qt) versus t graphs. The obtained correlation coefficient value R2 is relatively low, indicating that Lagergren's pseudo-first order kinetic model does not adequately describe the adsorption of dyes onto activated carbon.

Adsorption Kinetics	Parameters	reactive Magenta	methyl Red
Pseudo First	K ₁ (min-1)	0.051	0.05
Order Kinetics	q _e (mg g-1)	0.510	0.212
	R ²	0.874	0.976
Pseudo Second	h (g-1 mg-1 min-	4.150	1.034
Order Kinetics	1)		
	q _e (mg g-1)	11.12	5.775
	R ²	0.989	0.999

Table : 5 Adsorption	Kinetics Parameter	r for reactive Ma	agenta and r	methvl Red	dve
ruble i e mabor phon	i i i i i i i i i i i i i i i i i i i		agentia ana i	moung i neu	aje



Fig: 5. Pseudo First Order Kinetic plot of RM and MA dyes

The framework of pseudo-second-order kinetics is as follows:

$$t / qt = 1 / K^2 q_e^2 + t / q_e$$

In Figure 4, we can see the activated carbon kinetic plots of t/qt versus t, respectively. The coefficients 'h' and qe were calculated from the intercept and slope, respectively, as shown in the figures. Table 5 displays the kinetic data from the relevant plots for the adsorption of reactive Magenta and methyl Red dye onto PP. Compared to the faux first order rate equation, the pseudo second order rate equation has a greater correlation coefficient (\mathbb{R}^2). It seems that the pseudo second-order kinetic model is more suited to the rate of adsorption process, as shown by the larger determination of correlation coefficients \mathbb{R}^2 near to 1. Chemical reactions involving adsorbate and adsorbent seem to limit the total reactive Magenta and methyl Red dye adsorption rate.



Fig: 6. Pseudo Second Order Kinetic plot of RM and MA dyes

Conclusion

Using potato peel and operating under multivariate conditions, the present study examined the treatment of water for reactive Magenta and methyl red removal. In 45 minutes, equilibrium could be achieved with regard to the rate of magenta and methyl red sorption onto potato peel. Moreover, because of the saturation of active adsorbent sites, an increase in selected dye concentration during the initial phases decreases the removal percentage. The progressive percentage of selected dye removal facilitated by the potato peel was stimulated by the increased initial concentration of the solution. The obtained values of 3.997, 6.087 mg/g and 0.646, 0.778 mg/g for the maximal adsorption capacity of potato peel according to the Freundlich and Langmuir models, respectively, indicate that the data for the adsorption isotherm are sufficient. As demonstrated by the experiments, the adsorption kinetics indicate that pseudo-first and second order rate kinetics govern the adsorption of magenta and methyl

red dye onto potato peel. For the removal of fundamental dyes from water, the research establishes potato peel as a potentially effective adsorbent.

Consequently, in order to broaden the purview of research, the present study suggests that future investigations compare the capacity for regeneration (recycling) of comparable natural materials. Furthermore, this would aid in the assessment of the results' reproducibility.

Conflicts of Interest: The authors declare no conflict of interest.

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