

REMOVAL OF ACID GREEN 25 DYE BY USING ACTIVATED CARBON PREPARED FROM *Passiflora Foetida*[PAC-MnO₂-NC] NANOCOMPOSITE IN BATCH ADSORPTION-KINETIC STUDY

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SUMMARY

The elimination of tint from wastewater contains dye requires a successful technique to treat the sewage. Due to its simplicity adsorption is most popular for the removal of dyes. This paper reveals that the deletion of Acid Green-25 (AG-25) containing wastewater was performed through group adsorption in which Nano Composite was used as an adsorbent. The elimination of Acid Green-25 (AG-25) by adsorption on Activated carbon-MnO₂-Nanocomposite, under an optimized environment, has been considered. Kinetics and a Thermodynamic parameter, for example, ΔH° , ΔS° and ΔG° were also designed. The study has found that for removing the Acid Green-25 (AG-25) starting its aqueous solution the Nanocomposite adsorbent plays an effective role.

Keywords: Acid Green 25, PAC-MnO₂-NC, Kinetics.

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INTRODUCTION

In numerous industries, such as leather, plastics, cosmetics, foods, printing and textiles the dyes are used widely as coloring agents. Owing to their struggle to deprive them, they are found near wastewater at a significant amount. A major quantity of devastating water is generated having chlorine, COD concentration, sulfides, a highly fluctuating pH, salts, a large number of suspended solids, heavy metals and temperature¹. Many of the organic dyes are dangerous and may distress the food chain and even aquatic life. Discharge of these dyes in a watercourse is aesthetically undesirable². The release of tint in the surroundings is disturbing for both esthetical and toxicological reasons as dyes delay light diffusion, spoil the value of the getting stream and are poisonous to foodstuff organisms³. The rapid development of the textile industry in developing countries has triggered an increase in pollution of the aquatic environment⁴. Numerous techniques have been investigated for the exclusion of dyes from wastewaters. At present, the principal methods of treatment involve physical and/or chemical, biological processes such as chemical oxidation, microbial degradation and adsorption knowledge with activated carbon geared up from a variety of agricultural wastes⁵.

In a challenge to answer dye contamination tribulations, methods like biological treatments, photodegradation, reverse osmosis, coagulation, chemical oxidation, membrane separation and adsorption have been used; the adsorption procedure is single of the most successful method for the exclusion of dyes from wastewater⁶. Adsorption on activated carbon is one of the mainly useful processes but the elevated rate of such adsorbent has aggravated a lot of researchers to investigate for substitute low cost adsorbents⁷. As a result activated carbon, as an adsorbent, has been broadly applied to eliminate pollutants from aqueous solution⁸.

These adsorbents were ready from natural resources such as leaf and seed like neem leaf powder⁹, Guava leaf powder¹⁰, Typha Angustata L¹¹, plant roots, cotton fibre¹², wheat and rice¹³, Jambonut¹⁴, Borassusflabellifer L¹⁵ and Passiflora Foetida¹⁶etc, worn for amputation of dye removal studies. Therefore, adsorption is suggested as a feasible way for Acid dye removal.

In current days, nanotechnology has been measured as a talented knowledge to care for water. In at hand effort of adsorption capacity of the passiflorafoetida plant material [PAC-MnO₂-NC] be considered in favor of the removal of Acid Green-25 at temperature, P^H and particle size, dissimilar dye concentration, contact time, and adsorbent dosage,. The kinetic group adsorption study was agreed away to realize the adsorption process. The adsorption dynamics and thermodynamic parameter ΔH° , ΔS° , and ΔG° for such systems have been evaluated.

EXPERIMENTAL

Flow Chart for the Preparation of PAC-MnO₂-NC

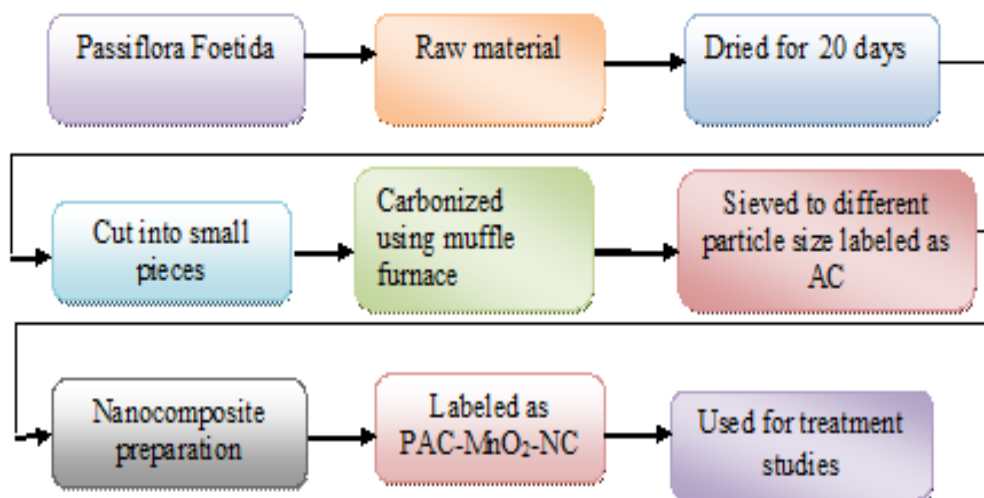


Fig.-1

The Grounding of Activated Carbon

From local area situated at Thindal, Erode District, Tamilnadu, the Passiflorafoetida deposit resources were composed. It is dried for 20 days before it they were cut into small pieces. Lastly, it was full in a steel boat and excited in soften oven. The hotness was raised steadily up to 500⁰C and set aside it for half an hour. The carbonized material was floor well and sieve to diverse subdivision mass. It was stored in a synthetic bottle for auxiliary studies. In this learning particle size of 0.15 to 0.25mm was worn and it was labeled as PAC.

Groundwork of PAC-MnO₂-NC

Activated Carbon (3gm) was permitted to enlarge in 15mL of water-free Alcohol and moved for 2 hours at 25⁰C to get a homogeneous suspension. At the identical instant, the Manganese dioxide (3gm) was detached into water-free Alcohol (15mL). Then the watery Manganese dioxide was bitten by bit added into the deferment of activated Carbon and stimulated for a further 5 hours at 25⁰C. To this, 5mL alcohol and 0.2mL of deionized water was leisurely added. The rousing was sustained for another 5 hours at 25⁰C and the consequential deferment was set aside while sleeping in a void oven for 6 hours at 80⁰C. It was labeled as PAC-MnO₂-NC.

Preparation of Sorbate

Acid Green 25 is purchased from S.d. fine chemicals. Acid Green 25 has molecular formula C₂₈H₂₀N₂Na₂O₈S₂. The dye absorption in supernatant solution was dogged at characteristic wavelength [λ_{max} =622.57nm] by twicegrin UV-visible spectrophotometer [Systronics 2202]. The element configuration of Acid Green is agreed underneath.

EXPERIMENTAL

Batch technique was followed by agitating 50 ml of four dissimilar stain solutions (10, 20, 30 and 40 mgL⁻¹) at their expected pH with 100 mg of PAC-MnO₂-NC in 150 ml stoppered tapering flasks at room heat (30.2°C) in a warmth controlled water soak shaker at 140 rpm. The samples were solitary from the shaker at prearranged occasion intervals and the coloring solution was estranged from the adsorbent by centrifuging at 10,000 rpm for 10 min. The absorbance of the supernatant solution was calculated using UV-VIS spectrophotometer (Cyber Lab, 100) at wavelength 500 nm.

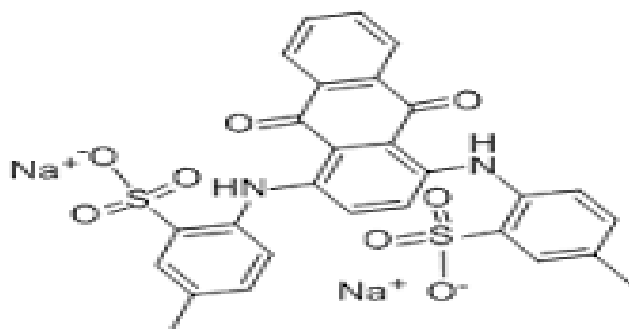


Fig.-2

The quantity of AG25 adsorbed per unit mass was premeditated from the following equation:

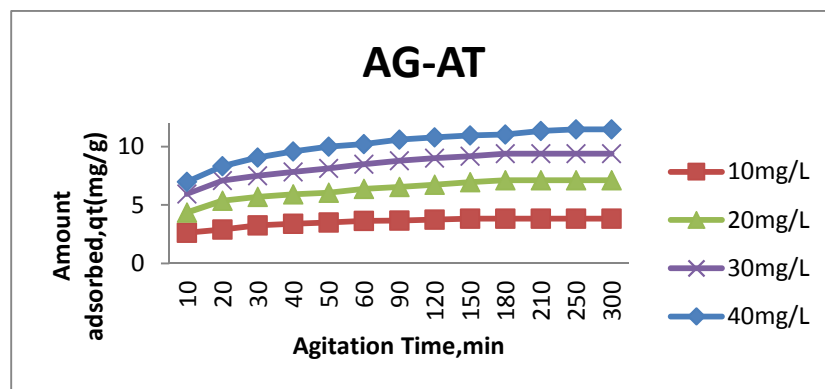
$$q_t = (C_o - C_t / V) / W \quad (1)$$

Where, W is the adsorbent quantity (mg); C_t the absorption of AG25 solution at moment in time t (min); V the quantity of functioning solution (mL); C_o the first concentration of AG25 (mg/L); q_t is the sum of dye adsorbed per unit weight of adsorbent (mg/g). Blank with only the adsorbate in 50 ml of distilled water were conducted concurrently at the parallel situation to report for adsorption in using goblet containers. It originated that no adsorption of AG25 by jugstockade occurred. The investigational parameters considered are initial dye concentration, contact time, pH and temperature and adsorbent dosage. Adsorption kinetics were tested with Elovich models, pseudo-second-order, Intraparticle diffusion model and pseudo-first-order.

RESULTS AND DISCUSSION

Effects of Initial Dye Concentration Vs Agitation Time

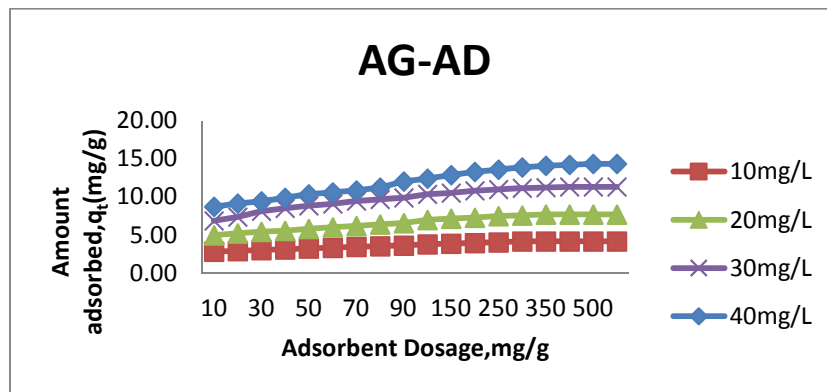
Belongings of initial dye concentration (10, 20, 30 and 40 mg/L) and agitation time on the exclusion of AG are offered in Graph-1. The percent elimination of AG25 enlarged with raise in agitation time and reached stability at 150 min. The percent stain exclusion at stability decreased from 76.73 to 57.35 as the dye absorption was enlarged from 10 to 40 mg/L. It is lucid that the elimination of dye depends on the opening concentration of the dye. The taking away curves are lone, even and nonstop for most to saturation.



Graph-1: Cause of Concentration and Agitation Time of AG25 on Elimination of PAC-MnO₂-NC

Effect of Adsorbent Quantity

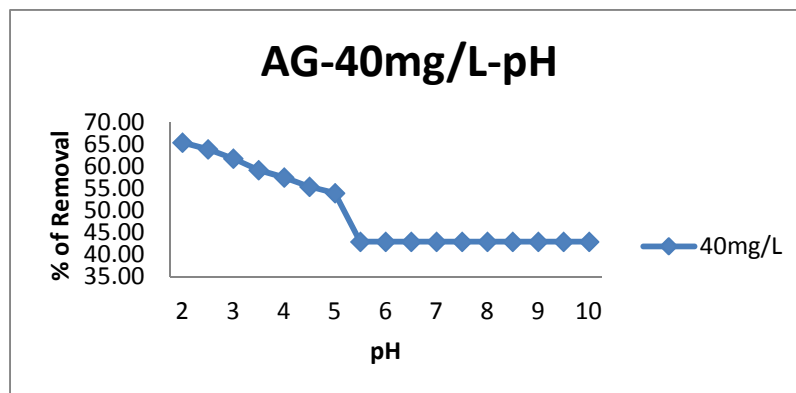
The subtraction of AG25 by PAC-MnO₂-NC at dissimilar adsorbent quantity are existing in Graph-2(10mg to 600mg / 50ml) was experienced for the dye concentration 10, 20, 30 and 40 mg/L. Augment in adsorbent quantity enlarged the percent exclusion of dye which is due to the enlarge in the exterior region of the adsorbent.



Graph-2: Effect of Adsorbent Quantity on Removal of AG25 by PAC-MnO₂-NC

Outcome of pH

The outcome of pH on the exclusion of AG25 by PAC-MnO₂-NC is revealed in Graph-3. Dye adsorption decreases with enlarge of pH from 2 to 5 and no amazing modify thereafter. Low pH nepotism the adsorption, a decrease of pH the plane become more protonated and gain positive charge which makes it easier for the anionic dyes to connect with carbon. Reduced adsorption of AG25at superior pH price is due to the antagonism among the negatively charged hydroxyl ions and anionic dye for the sorption sites.



Graph-3: Cause of pH on Removal of AG25 by PAC-MnO₂-NC

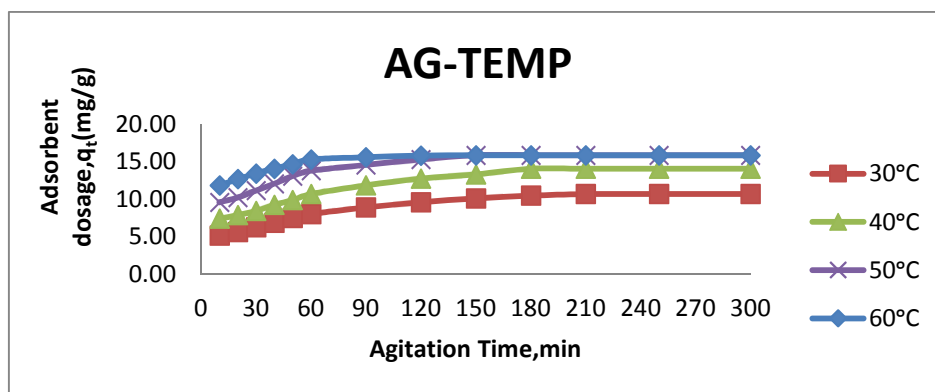
Effect of Hotness

The consequence of temperature of adsorption of AG25 (Graph-4) for absorption 40 mg/L adsorbent was accepted out at 30°, 40°, 50°and 60°C. The percent deletion of colorant enlarged from 20.66 to 79.32. This indicates that enlarge in adsorption with raise in heat perhaps due to a boost in the mobility of the huge dye ions. Besides, increasing hotness may construct a swelling effect inside the interior structure of the adsorbent, piercing the bulky dye molecule further.

Adsorption Kinetics

A learn of adsorption kinetics is enviable as it provides the in turn regarding the method of adsorption, which is significant for good organization of the course. The Elovich adsorption, Intraparticle diffusion,

pseudo-first-order and pseudo-second-order models were used to check dynamical tentative statistics.



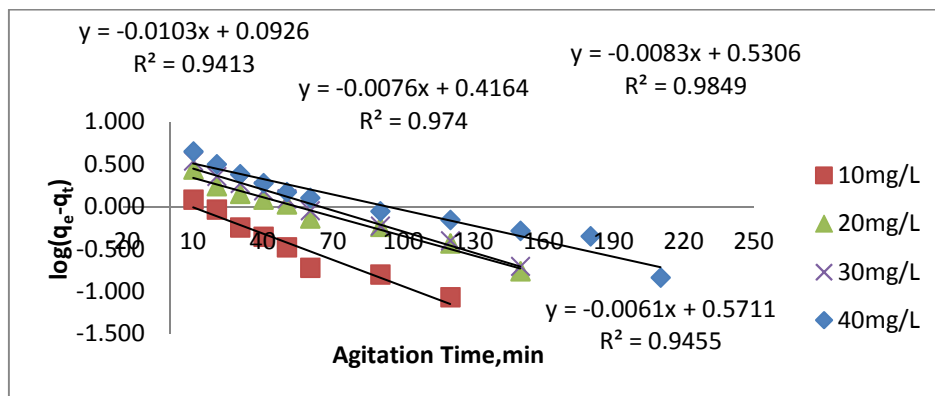
Graph-4: Effect of Heat on Removal of AG25 by PAC-MnO₂-NC

Pseudo Primary Array Representation

Lagergren's linear form of initial order speed equation is as follows¹⁷:

$$\log(q_e - q_t) = \log q_e - k_1 t / 2.203 \tag{2}$$

Where k_1 is the rate constant of first-order adsorption (min^{-1}) and q_e and q_t are the amounts of dye adsorbed on adsorbent at equilibrium and at time t , respectively (mg/g). The slant and interrupt of contriving of $\log(q_e - q_t)$ vs t were worn to conclude k_1 and q_e (Graph-5). These standards are revealed in Table-1. It does not robust for pseudo initial array kinetics.



Graph-5: Plot of Pseudo Initial Array Kinetics at Dissimilar Concentrations

Table-1: Pseudo Initial Array Kinetic Parameters for the Adsorption of AG25 by PAC-MnO₂-NC at different concentrations

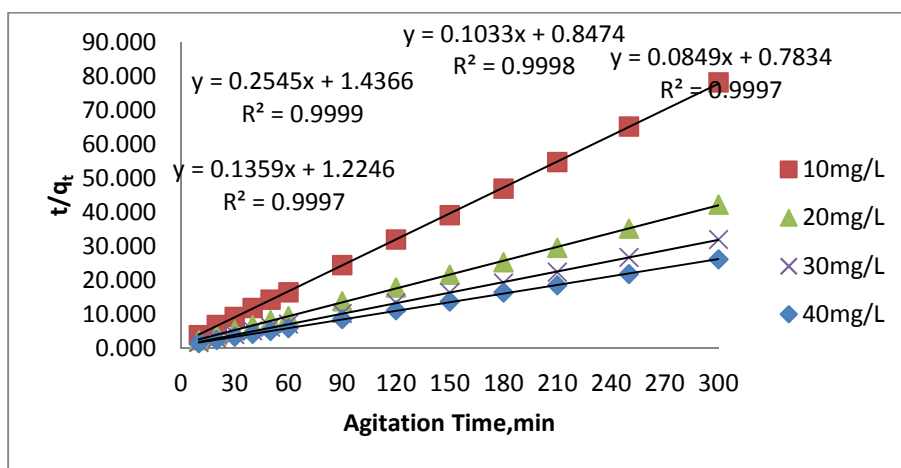
Primary of dye (mg/L)	$q_{e, \text{expt.}}$	Pseudo Opening-Array Kinetics		
		$q_e \text{ cal. (mg/g)}$	$K_1 \text{ (mg min}^{-1}\text{)}$	R^2
10	3.84	1.2359	2.303×10^{-2}	0.941
20	7.11	2.6061	1.612×10^{-2}	0.974
30	9.38	3.3884	1.842×10^{-2}	0.984
40	11.47	3.7239	1.381×10^{-2}	0.945

Pseudo Next Array Representation

Ho¹⁸ as by given the linearised form of the pseudo next tidy representation is:

$$q_t = \frac{k_2 q_e}{k_2 + t} \quad (3)$$

Where q_e is the greatest adsorption capability (mg g^{-1}) and k_2 is the speed stable of Pseudo-subsequent arrange adsorption ($\text{gm}^{-1} \text{min}^{-1}$). The grade of the scheme t/q_t vs t gives the worth of q_e and from interrupt k_2 can be premeditated (Graph- 6). These ideals are exposed in Table 2. It is lucid from the temperament of robust and connection coefficients that the adsorption of AG25 on PAC-MnO₂-NC is superior represented by Pseudo-subsequently kinetics.



Graph-6: Plots of the Pseudo-subsequent Arrange Copy at Dissimilar Concentration

Table-2: Pseudo Subsequent Array Kinetic Parameter for the Adsorption of AG25 by PAC-MnO₂-NC at Diverse Concentration

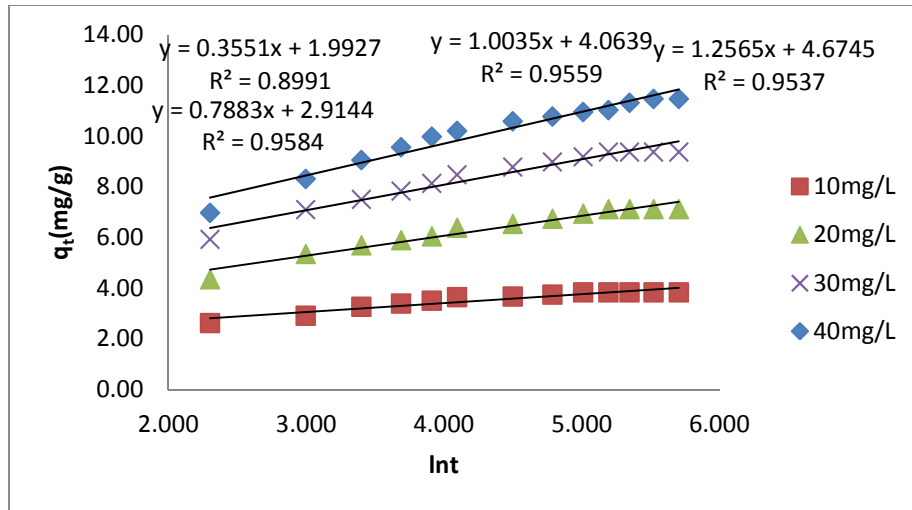
Opening of Dye (mg/L)	q_e expt.	Pseudo Next-array Kinetics		
		q_e cal. (mg/g)	k_2 (mg min^{-1})	R^2
10	3.84	3.9370	4.4927×10^{-2}	0.999
20	7.11	7.4074	1.4889×10^{-2}	0.999
30	9.38	9.7087	1.2525×10^{-2}	0.999
40	11.47	11.9047	9.011×10^{-3}	0.999

Elovich Kinetic Representation

An easy linearized type of Elovich kinetic equation¹⁹ is offered as follows:

$$q_t = \left(\frac{1}{\alpha\beta} \right) \ln(\alpha\beta) + \left(\frac{1}{\beta} \right) \ln(t) \quad (4)$$

Where, β is the desorption constant (g/mg) and α is the initial adsorption rate (mg/g/ min) through any one research. A scheme of q_t versus $\ln(t)$ with a straight streak, as predictable, with a slant of $(1/\beta)$ and a seize of $(1/\alpha\beta) \ln(\alpha\beta)$ can be intended in Graph-7. The elovich sculpt parameters connection coefficient R^2 , α and β are summarized in Table-3. Commencing the table the correlation coefficient (R^2), initial adsorption rate (α) and desorption constant (β) are calculated. The association coefficient is (R^2) is less than that of Pseudo-second order model.



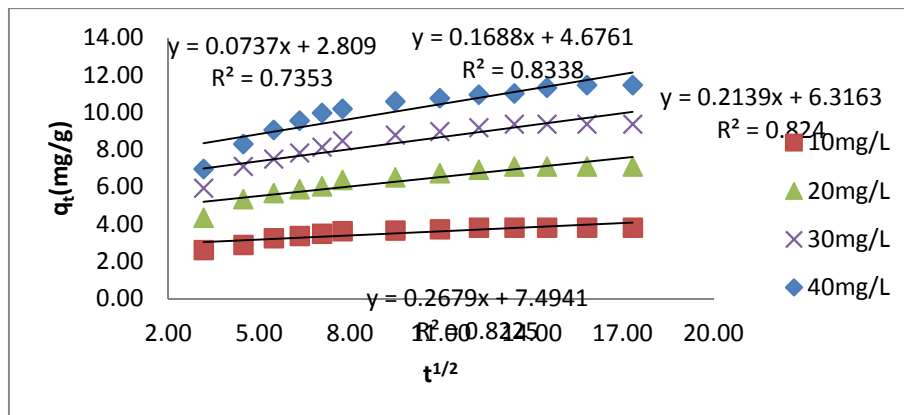
Graph-7: Elovich Kinetic Representation of AG25 by PAC-MnO₂-NC

Intraparticle Dissemination Replica

The intra particle dissemination replicas used here refers to the speculation planned by²⁰ the following equation for the speed stable:

$$q_t = k_{id}t^{0.5} + C \tag{5}$$

Where C is constant and K_{id} is the intraparticle diffusion rate constant (mg/g min^{-1/2}). If that speed restrictive read is intraparticle diffusion, the graphical depiction of adsorbed dye q_t versus $t^{0.5}$ acquires straight shape transient from side to side the source and the grade gives the intraparticle diffusion speed constant k_{id} and correlation coefficient (R^2) is indicated in Graph- 8.



Graph-8: Intraparticle Dissemination Replica Kinetic Model of AG25 by PAC-MnO₂-NC

The correlation coefficients R^2 and intra-particle parameters K_{id} , C are summarized in Table 3. From these statistics buy set value point out that the procession is not transient through the source, as a result, a few another method that may impinge on the adsorption. The association coefficient (R^2) value is less than that of Pseudo next tidy replica.

Thermodynamic Structure

Thermodynamic structure resembling ΔH° and ΔS° were evaluated using Van't Hoff's equation:

$$\ln K_c = \Delta S^\circ/R - \Delta H^\circ/RT \tag{6}$$

Where ΔH° and ΔS° , are the standard enthalpy and entropy changes of adsorption and K_c is the Langmuir equilibrium constant respectively and their principles are designed from the grade and interrupt correspondingly of the linear conspire of $\ln K_c V_s / T$. The free energy change for the adsorption process ΔG° (kJ/mol) is derived in equation-7. The morals of this parameter were premeditated using equation (6&7) at different early concentration are shown in Table-4.

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (7)$$

Table-3: Elovich and Intraparticle Dissemination Replica of AG25 by PAC-MnO₂-NC

Preliminary Dye Concentration (mg /L)	Elovich Replica			Intraparticle Diffusion Sculpt		
	α	β	R ²	K id	C	R ²
10	43.5234	2.8169	0.899	0.073	2.809	0.735
20	31.8042	1.2690	0.958	0.168	4.676	0.833
30	57.2713	0.9970	0.955	0.213	6.316	0.824
40	51.8782	0.7961	0.953	0.267	7.494	0.822

Table-4: Thermodynamic Configuration for the Adsorption of AG25 by PAC-MnO₂-NC

ΔG° (kJ/mol)				ΔS° (J/mol/K)	ΔH° (kJ/mol)
303K	313K	323K	333K	34.2204	34.2204
-34.9314	-36.0854	-37.2394	-38.3934		

The adsorption statistics indicate that ΔG° were negative at all temperatures. The negative ΔG° indicate the viability of the route and the impulsive nature of adsorption of AG25 by PAC-MnO₂-NC. The positive value of ΔH° was further confirmed the endothermic and chemisorptive nature of the adsorption process. The positive ΔS° show augmented randomness at the solid-solution interface during the adsorption of AG25 dye by PAC-MnO₂-NC. The ΔG° value raises with enlarging in temperature is the enlarge in the enhancement of the adsorption capacity of adsorbent may be due to an increase or swelling of pore size and/or activation of the adsorbent surface.

Desorption Study

After activated carbon is flooded with dye molecules, different solvents could be used to redevelop the activated carbon to reinstate its dye adsorptive potential²¹. Desorption with Sodium Hydroxide exposed that the rejuvenation of adsorbent was agreeable, which confirm the chemisorptive nature of adsorption.

CONCLUSION

The current research illustrates that PAC-MnO₂-NC able to be used as an adsorbent for removal of Acid Green 25. The quantity of dye adsorbed varied with adsorbent dose, p^H, temperature and initial concentration. Adsorption kinetics are extraordinarily significant in sequence for adsorption course plan. Compared with the pseudo-first order, Elovich, Intraparticle diffusion model, the pseudo-second-order kinetic model was established to fit the dye adsorption kinetic statistics more properly. Even though a lot of diverse adsorbents are tried to eliminate dyes from wastewaters, activated carbon from a different source is tranquil the mainly far and wide worn adsorbent for color exclusion. From the thermodynamic data the positive value of ΔH° was further confirmed the endothermic and chemisorptive nature of adsorption process.

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