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ADSORPTION OF VAT DYE FROM AQUEOUS SOLUTION USING AGRICULTURAL SOLID WASTE (ASW) AFTER UV LAMB IRRADIATION WITH TiO_2: ISOTHERM AND KINETIC STUDIES

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ABSTRACT

Studies were conducted using soaking process of agricultural solid waste (ASW) like coconut coir pith, bagasse pith, watermelon peel (watermelon shell) and banana pith on the colour removal of vat red R1 (VR1) dye from its aqueous solution and also applied photocatalysis using metal as a TiO_2 *to degrade dyes. The performance of adsorption was examined by studying the effects of various parameters like initial dye concentration, pH, contact time and adsorbent dose. The results indicated that the dye uptake from water was concentration dependent and increased with increase of initial concentration of dye and remained nearly constant after 180 minutes, the equilibrium time and the initial concentration of 5 mg/l was observed a maximum dye adsorption. The results were also analyzed using the Langmuir and Freundlich models. The study confirmed that the adsorbents prepared from ASW with* TiO_2 *as a function of irradiation of UV light can be used to treat textile waste containing this dye.*

Keywords: Agricultural Solid Waste (ASW), Langmuir and Freundlich isotherm models Photocatalysis, vat red R1

I INTRODUCTION

Dyes are synthetic aromatic water soluble and dispersible organic compounds, which cause coloration of natural water bodies when released into the environment [1]. Hence, the removal of synthetic organic dyestuff from waste effluents becomes environmentally important [2]. Many methods used to remove dyes from wastewaters such as coagulation and membrane separation process, electrochemical, chemical oxidation, reverse osmosis and aerobic and anaerobic microbial degradation, but these methods have many restrictions, and therefore not successful for removing the color completely from wastewater [3]. Advanced oxidation processes have proved to be one of the other most effective treatments for wastewater that are difficult to be treated biologically. These are successfully used to decompose many toxic and bio-resistant organic pollutants in aqueous solution to acceptable levels, without producing additional hazardous by-products or sludge which requires further handling. TiO_2 is the most extensively studied material for photocatalysts because of its strong oxidizing power, low toxicity, and long-term photostability [4].

The present work intends to study the influence of the soaking process of the coconut coir pith, bagasse pith, watermelon peel (watermelon shell) and banana pith on the colour removal of vat red R1 (VR1) dye. The agricultural solid waste residue alone is not capable to destroy vat dyes. Some authors have applied UV light using metals as a TiO_2 to degrade dyes [5]. Although colour removals by Agricultural Solid Waste (ASW) combine with advanced oxidation method of TiO_2 on UV irradiation treatments to achieve good colour removal of vat red R1 (VR1). Initial dye concentrations, adsorption capacity, adsorption isotherms and adsorption kinetics were also investigated.

II MATERIALS AND METHODS

2.1. Adsorbate used for the Work

Vat Red R1 (VR1) is indigo type dye was used in the present work. Stock solution was prepared by dissolving 1.0 g of VR1 in 1L distilled water (distilled water containing mixture of sodium hydrosulphite and sodium hydroxide) without further purification. The test solutions were prepared by diluting stock solution to the desired concentrations (1mg/l to 5mg/l).

2.2. Adsorbent used for the Work

Agricultural Solid Waste (ASW) residue like coconut coir pith, bagasse pith, watermelon peel (watermelone shell) and banana pith were obtained from local farm and were subjected to repeatedly washing with water to remove dust and soluble impurities. They were cut into small pieces and washed again thoroughly with distilled water and dried overnight at 60^0C and grinding into powder. After grinding the waste residue was sieved using 250 mesh sieve and stored in air tied container for further use.

2.3. Experimental Procedure

Stock solution of dye at different concentrations (1 – 5 mg/L) were prepared from vat red R1 ($VR_{1).}$ The adsorption process was conducted by adding 0.5g of ASW to 50ml dye solution at fixed pH value (7.5). The pH was adjusted by adding 1M of sodium hydroxide (NaOH) or 1M of hydrochloric (HCL) solutions. The samples were agitated at 30^0C for 300 min at constant agitation speed of 150rpm. After agitation the solution was mixed with 1g TiO_2. The suspension was stirred using a magnetic stirrer for 2 hours in the dark and later this suspension was illuminated for 1 hour using 125W UV lamp. After I hour reaction time the samples were centrifuged twice prior to monitoring the absorbance of solution from 613nm wavelength using UV/VIS (Helios Zita UV-VIS) spectrophotometer. Before measurement, a calibration curve was obtained by using the standard VR1 solution with known concentrations. A linear relationship between the absorbance of standard solution at 613 nm VR1 concentrations was obtained.

2.4. Adsorption Isotherms

Langmuir and Freundlich isotherm models are applied for the rate of adsorption take place. A basic assumption of the Langmuir theory [6] is that adsorption takes place at specific homogeneous sites within the adsorbent. It is then assumed that once a dye particle occupies a site, no further adsorption can take place at that site. The rate of adsorption to the surface should be proportional to a driving force, which times an area. The driving force is the concentration in the solution, and the area is the amount of bare surface [7]. In 1906, Freundlich [8] studied the sorption of a material onto animal charcoal. He found that if the concentration of solute in the solution at equilibrium, C_{eq}, was raised to the power m, the amount of solute adsorbed being q_e, then C_e^m/q_e was a constant at a given temperature [9]. This fairly satisfactory empirical isotherm can be used for non-ideal sorption. Langmuir isotherm is represented by the following equation:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \qquad (1)$$

q_e Amount of adsorbate adsorbed at equilibrium (mg/g)
q_{max} Maximum monolayer adsorption capacity of the adsorbent (mg/g)
K_L Langmuir adsorption constant related to the adsorption capacity and intensity of adsorption respectively (L/mg)
C_e Equilibrium concentration of adsorbate (mg/L)

If the adsorption obeys Langmuir equation, maximum adsorption capacity and Langmuir constant can be evaluated from the slopes and the intercepts of the plots C_e/q_e versus Ce.

The essential feature of the Langmuir isotherm can be expressed by means of R_L, a dimensionless constant referred to as separation factor or equilibrium parameter R_L is calculated using the following equation[10]

$$R_L = \frac{1}{1 + K_L C_0} \qquad (2)$$

K_L Langmuir adsorption constant related to the adsorption capacity and intensity of adsorption respectively (L/mg)

C_o The highest initial adsorbate concentration (mg/L)

- Unfavorable ($R_L > 1$)

- Linear (R_L =1)
- Favorable (0< R_L <1)
- Irreversible (R_L = 0)

The modelling of experimental results of the adsorption isotherms by the Langmuir equation presents considerable differences according to the mode of exploitation (linearization). It appears that the method of linearization thus intervenes in the estimation of the adsorption isotherms parameters.

The Freundlich model equation is expressed as:

$$q_e = K_F \, C_e^{1/n} \quad (3)$$

Where K_F and n are Freundlich constants, K_F (L/mg) is the adsorption capacity of the sorbent and n giving an indication of how favourable the adsorption process. If the value of exponent n was greater than 1 (n >1) then the adsorption represent favourable adsorption condition [13].

The constants K_F and n, can be determined from the linear form of Freundlich isotherm equation from the graph of $\ln q_e$ against $\ln C_e$ as expressed from the following equation:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)$$

In general, as the K_F value increases the adsorption capacity of adsorbent will also increase .

2.5. Adsorption Kinetics

The prediction of adsorption rate gives important information for designing batch adsorption systems. Information on the kinetics of solute uptake is required for selecting optimum operating conditions for full-scale batch process [11]. The kinetics of the adsorption data was analyzed using two kinetic models, pseudo-first order and pseudo-second order. These models correlate solute uptake, which are important in predicting the reactor volume.

The linear form of pseudo-first-order model was described by Lagergren [12]as:

$$\frac{dq_t}{d_t} = K_1 (q_e - q_t) \quad (5)$$

Where q_e and q_t are the amounts of dye adsorbed at equilibrium and at time t (mg/g), respectively, and k_1 is the pseudo-first-order rate constant (min^{-1}).

Pseudo-second order model

A pseudo-second order model proposed by Ho and McKay [13] can be expressed as,

$$\frac{dq_t}{d_t} = K_2 (q_e - q)^2 \quad (6)$$

If second order kinetics is applicable, the plot of t/q_e versus time should give a linear relationship from which the constants q_e and K_2 can be determined.

Intraparticle Diffusion Model

The intraparticle diffusion model was proposed to identify the adsorption mechanism and to predict the rate controlling step, where intraparticle equation can be expressed as [14].

$$q_t = K_{diff.} t^{1/2} + C \quad (7)$$

Where, C is the intercept and $k_{diff.}$ (mg/g $min^{1/2}$) is the intraparticle diffusion rate constant which can be evaluated from intercept and slope of the plot of qt versus $t^{1/2}$. The large intercept can reflect the great of boundary layer effect. If the plot of q_t versus $t^{1/2}$ is linear and passes through the origin, then intraparticle diffusion is the rate-controlling step.

III EXPERIMENTS AND RESULTS

The experiments were conducted with 50ml of dye solution of desired concentrations, 0.5g of ASW were added and irradiated with UV lamp. ASW added dye solution with TiO_2 photo irradiation and without TiO_2 photo irradiation were also be detected. The amounts of vat red R1 removal per gain of adsorbent at different contact time with various initial dye concentrations are analysed.

3.1. Effect of Contact time and Concentration

The pollutant concentration is very important parameter in wastewater treatment. The influence of initial concentration of the dye solution has been investigated on the photo catalytic degradation of dye after the optimization of pH and catalyst dose. In order to optimize the catalyst dose the initial dye concentrations was varied during the photo catalytic treatment from 1 to 5 mg/l, at constant pH of 7.5 and catalyst (ASW) dose of 0.5 mg/L and 1g of TiO_2. The following treatment techniques are undergone in order to detect maximum adsorption.

3.2. Dye removal using Agricultural Solid Waste

Adsorption of dyes from an vat red R1 (VR1) onto coconut coir pith, bagasse pith, watermelon peel (watermelon shell) and banana pith was measured at given contact times (0 to 300 min) for five different initial dye concentrations at an adsorbent dosage of 0.5g (particle size, 200 µm size). The effect of initial dye concentration on the rate of adsorption is shown in figure 1 to 4. VR1 dye adsorption onto ASW at 30^0C, it was observed that the amount of VR1 (1 – 5 mg/L) was increased from ASW of banana pith from 21.60 to 71.10 mg/g, watermelon peel was ranged from 20.66 to 82.68 mg/g, bagasse pith from 21.66 to 85.09 mg/g and coir pith from 32.66 to 83.08 mg/g. The results indicated that the dye uptake from water was concentration dependent and increased with increase of initial concentration of dye. The equilibrium time was found to be at 180 min and the initial concentration of 5 mg/l was observed a maximum dye adsorption. The dye uptake increased rapidly in the initial stages of contact time, then became almost constant denoting the attainment of equilibrium. This phenomenon might be initially due to the all active sites on the adsorbent surface were vacant and the solution concentration was high. After that period, a few surface active sites were available, so only average low increase in the dye uptake was observed [15].

3.3. Dye removal using TiO_2 with UV irradiation

The experiments were carried out at dye concentrations of VR1 in the range of 1mg/l to 5mg/l for different time intervals up to 300 min at fixed pH (7.5) and constant weight of TiO_2 (1g). The removal of VR1 was showed similar features of the above work containing increased with increase in dye concentration and remained nearly constant after equilibrium time. Photo catalytic degradation capacity at equilibrium for VR1 increased from 21.66 to 70.80 mg/g for 1- 5 mg/l of the dye solution. The equilibrium established within 180 min photocatalysis for all the concentration studies. It is established that removal of dye depends upon the concentration of dye.

3.4 Dye removal using Combination of ASW and TiO_2 with UV irradiation

The Photo catalytic degradation of vat red R1 (VR1) dye has been investigated in aqueous suspension of ASW with TiO_2 as a function of irradiation of UV light. The experiment was carried at fixed ASW dose 0.5mg/l, weight of TiO_2 (1g), agitation time 180 min, concentration 5 mg/l and pH 7.5. It was observed that the adsorption of VR1 on ASW with Photocatalytic degradation capacity of banana pith + TiO_2 was 95.68 mg/g, watermelon peel + TiO_2 showed that 97.68 mg/l, bagasse pith + TiO_2 found that 98.68 mg/g and coir pith + TiO_2 was showed that 99.12 mg/g.

The results indicate that the decomposition rate of both dyes strongly depends on the initial dye concentration. The efficiency of degradation capacity of ASW + UV irradiation with TiO_2 was more suitable for comparison of other two type experiments. The maximum adsorption was showed the adsorbent used by photocatalytic degradation with coir pith + TiO_2 at 5 mg/l initial concentration of dye solution at 180 min equilibrium time. The efficiency of photocatalytic degradation of dye increased with increase of the initial dye concentration. As the initial concentration of the dye increased, more dye molecules were adsorbed on the surface on the catalyst, consequently the generation of hydroxyl radicals was reduced since the active sites were occupied by dyes [16]

[17] [18]. An increase of the initial dye concentration results in an increase of the amount of dye adsorbed on the catalyst surface, affecting the catalytic activity of the photocatalyst [19][20].

3.5 Effect of UV-Irradiation Time

Effect of UV-light irradiation time (2 hours intervals) on the photo catalytic degradation of VR1 (5 mg/l) soaked ASW of banana, watermelon, bagasse and coir pith with 1 g of TiO_2. It was observed that 56% of banana pith 32% of watermelon peel 36% of bagasse pith and 65% of coir pith of the dyes were degraded, respectively, after an irradiation time of 30 min. It is also evident that the percentage of decolourization and photo degradation increases with increasing irradiation time. As expected the concentration of 1 g of TiO_2 promoted the highest percentage of degradation for the dye. This concentration degraded 80% of banana pith 84% of watermelon peel 86% of bagasse pith and 88% of coir pith in 45 min. The rate of degradation became slower after 45 minutes. By the end of two hours degradation increased 90%, 86%, 92%, 95% of banana, watermelon, bagasse and coir pith respectively of soaked solutions.

3.6 Effect of TiO_2 Photocatalyst

The catalyst dose is another important parameter which has strong influence on the degradation of dye solution. In order to determine the optimal amount of catalyst concentration, a series of experiments were carried out using different amount of TiO_2 varying from 1g to 5 were combine with 0.5g of banana pith, bagasse pith, watermelone peel and coir pith, at optimized pH of 7.5 with 1 ppm dye solution at 1 hour UV irradiation. The results showed that as the concentration of catalyst TiO_2 increases from .1 to 2 g, the percentage degradation increases from 42% to 95% of banana pith, 30% to 90% of watermelon pith, 58% to 99% of bagasse pith and 38% to 96% subsequent analysis. But increasing the catalyst concentration from 2 to 5 g, the percentage degradation decreases from from 95 % to 73% of banana pith, 90 % to 70 % of watermelon pith, 99 % to 80% of bagasse pith and 96 % to 72% coir pith respectively. The maximum degradation rate has been observed with catalyst dose of 2g.

The lower percentage degradation at lower TiO_2 loading can be attributed to the fact that more light is transmitted through the reactor and the transmitted light is not utilized in the photocatalytic reaction [21]. The enhancement of removal rate at higher catalyst loading is due to the increase in amount of the catalyst weight which increases the number of dye molecules absorbed on the active sites and also due to the increase in the density of particles in the area of illumination.

3.7. Adsorption Isotherms

The adsorption data yielded good fits with Langmuir and Freundlich isotherms in case of each adsorbent. The isotherm plots of Langmuir model presented in figure1. In Langmuir adsorption isotherm shows that the high values of correlation coefficient R^2, Jaynes and Boyd [22] proposed that the adsorption conforms to the Langmuir model when the value of the correlation coefficient R^2 is greater than 0.89, indicating that the isotherms are consistent with Langmuir model. The R^2 values showed that greater than 0.89, indicating that the isotherms are a good agreement between adsorbent and vat red R1 and confirms the monolayer adsorption of vat red R1 on the adsorbent surface. The dimensionless parameter R_L value of banana pith is 0.30, watermelone peel is 0.51, coir pith is 0.22 and bagasse is 0.99, which confirms the favourable uptake of the vat red R1 dye. The values of Freundlich coefficient, 1/n of banana pith, watermelon, coir pith and bagasse pith and 1.69, 1.36, 1.11 and 1.13 respectively, which shows that the value of 1/n was greater than 1 which represents a favourable adsorption condition.

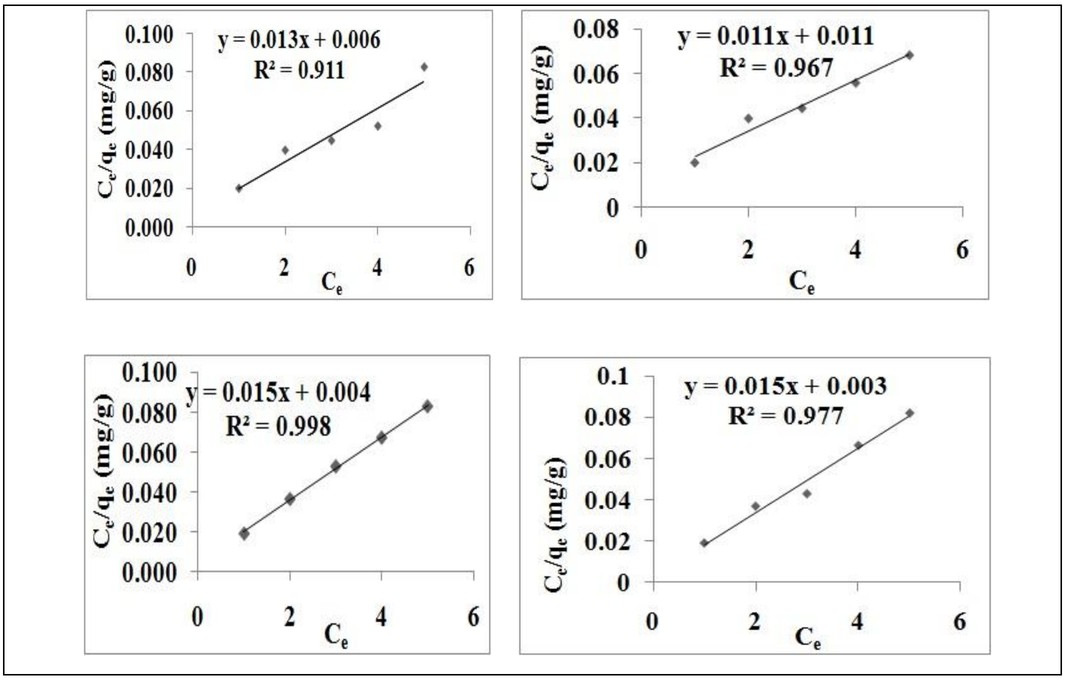

Fig. 1: Langmuir isotherm of Banana pith,Watermelon peel, Coir pith and Bagasse pith.

3.8. Adsorption Kinetics

According to Table.1, the calculated q_e values did not agree with experimental q_e values thus the pseudo-first-order model did not fit well. The correlation coefficients R^2 for the linear plots of pseudo-second-order model arranged between 0.971-0.988 which higher than correlation coefficients R^2 for pseudo-first-order. This indicates that the adsorption kinetic is better represented by the pseudo-second-order model.

In the case of intraparticle diffusion model the large intercept can reflect the great of boundary layer effect. If the plot of q_t versus t^{-1} is linear and passes through the origin, then intraparticle diffusion is the rate-controlling step.

Table 1: Kinetic parameter for the adsorption of dye

Adsorbent	**$q_{e\ exp}$ (mg/g)**	**Psuedo – First order**			**Psuedo - Second order**			**Intraparticle diffusion**	
		$q_{e\ cal}$ (mg/g)	**K_1 (min^{-1})**	**R^2**	**$q_{e\ cal}$ (mg/g)**	**K_2 (mg/g.min)**	**R^2**	**K_{int} (mg/g.min)**	**R^2**
Banana pith	**67.32**	**103**	**2.56**	**0.63**	**43.66**	**1.17**	**0.97**	**0.77**	**0.99**
Watermelon peel	**64.44**	**163.09**	**2.34**	**0.54**	**38.16**	**1.26**	**0.97**	**1.73**	**0.99**
Bagasse pith	**76.54**	**83**	**2.01**	**0.93**	**37.5**	**1.04**	**0.98**	**0.98**	**0.99**
Coir pith	**73.98**	**84**	**2.60**	**0.73**	**70.4**	**0.42**	**0.98**	**2.20**	**0.99**

IV CONCLUSIONS

The results showed that agricultural solid waste combine with Advanced Oxidation process using TiO_2 can be successfully used as an adsorbent for the removal of vat red R1(VR1) from aqueous solution. The equilibrium adsorption is practically achieved in 180 min. Adsorption was influenced by various parameters such as initial concentration, pH, contact time and catalyst dose. The highest removal of VR1 obtained from combination of bagasse pith + TiO_2. The adsoption capacity was increased with increase in agitation time and initial dye concentration and percentage removal was decreased with increase in the initial dye concentration . The effect of UV-light irradiation time on the photocatalytic degradation of VR1, It is also evident that the percentage of decolourization and photo degradation increases with increasing irradiation time. In order to determine the optimal amount of catalyst concentration, a series of experiments were carried out using different amount of $TiO_{2.}$ The maximum degradation rate has been observed with catalyst dose of 2g.

The adsorption parameters for the Langmuir and Freundlich isotherms were determined and the equilibrium data were best described by both two models. The adsorption kinetics can be successfully fitted to pseudo second order kinetic model. The result of the intraparticle diffusion was the rate controlling step. Desorption study reveals that the recovery of the dye from adsorbent is possible.

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