International Journal of Environmental Chemistry
2022; 6(2): 36-41
http://www.sciencepublishinggroup.com/j/ijec
doi: 10.11648/j.ijec.20220602.11
ISSN: 2640-1452 (Print); ISSN: 2640-1460 (Online)

Application of Date Stones on the Process of Removing Erythrosine Dye from Industrial Effluents

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To cite this article:

Mausul Umar, Haliru Aivada Kadir, Amina Doho, Yoro Mela, Muhammad Garba, Auwal Aliyu. Application of Date Stones on the Process of Removing Erythrosine Dye from Industrial Effluents. *International Journal of Environmental Chemistry*. Vol. 6, No. 2, 2022, pp. 36-41. doi: 10.11648/j.ijec.20220602.11

Received: July 4, 2022; **Accepted**: August 17, 2022; **Published**: August 31, 2022

Abstract: The date stones were obtained from the market place and the feasibility of utilizing low-cost carbonized date stones for the removal of erythrosine dye from an aqueous media was carefully conducted under laboratory restricted conditions. Experimental parameters such as temperature, pH, dosage, and concentration were painstakingly maintained. Outcomes show the efficient removal of the contaminant by the substrate CDS (Carbonized date stones), Kinetics models "pseudo-first and pseudo second order was applied. Afterwards, the Langmuir and Freundlich adsorption isotherms were utilized to identify the adsorption mechanisms. The mechanism of this adsorption process displayed Langmuir adsorption isotherm which is a monolayer with R^2 value of 0.9780 which is higher than that of Freundlich with R^2 value of 0.8933. Also, the research work showed that the adhered and suitable kinetic model for the removal of erythrosine dye using carbonized date stones was pseudo second order due to the adsorption capacity of the dye at equilibrium q_e was high at the value of 1.8900 to 8.3689 in pseudo second order compared to pseudo-first order with 7.4567.

Keywords: Erythrosine Dye, Date Stones, Adsorption

1. Introduction

The existence of organic micro pollutants and inorganic substances in the waters has much interesting attention of the international scientific community, favouring new research, oriented to class and to measure the toxicological potentialities of an extremely great number of organic chemicals and inorganic substances. Industrial discharges are the main sources of water contamination, may cause serious environmental consequences for ecosystems to all taxonomic groups (algae, bacteria, fish, birds, mammals) [1].

Many synthetic dyes are used in so many industrial sectors such as dyeing of textiles, papers, leather, food, cosmetics industries and pharmaceutical products [2, 3]. Textile industries cause pollution of water which are harmful to the environment, such as certain carcinogenic azo dyes, they require physicochemical techniques to degrade them [4]. Various techniques such as physico-chemical and biological have been developed and tested on water filled with dyes. These techniques include adsorption [5], coagulation-flocculation [6], ion exchange [7], membrane filtration [8], Fenton reagent [9], photo-catalysis of hydrogen peroxide [10], photolysis of hydrogen peroxide and ozonation [11], biological treatment [12]. Activated carbon is widely used for the treatment of wastewater due to internal surface which makes them ideal for the removal of soluble substances from water [13]. The agricultural solid waste as an abundant and cheap material widely used as raw adsorbent or converted into activated carbon by a physical activation process such as pistachio shells [14], almond shells [15], rattan sawdust [16], cotton stalk [17], orange peel and oil-palm shell [18], powdered peanut hull [19], bagasse [20], Sugarcane [21], Peach stones [22]. Glucose, cellulose and hazelnut shells [23]. The agri-food industries generate an important amount of date stones that are usually considered as waste. This work aims to produce activated carbon as of date stones as a waste agriculture for use in the removal of dye from water, particularly for the removal of textile industry effluents [24].

1.1. Erythrosine Dye

It is an organoiodine compound especially a derivative of fluorine. It is cherry pink synthetic and disodium salt of 2,4,5,7-tetraiodofluorescein with maximum absorbance at 530nm in an aqueous solution. It is used for food colouring [25].

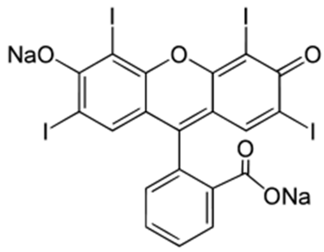

Figure 1. *Structure of Erythrosine dye.*

Chemical formular: $C_{20}H_6I_4Na_2O_5$
Molar mass: 879.86g/mol

1.2. Health Risk of Erythrosine Dye

The presences of erythrosine in aqueous solutions and food have become a problem due to the health risk of causing thyroid issues in humans. Erythrosine dye is used as a food colorant in cherries and in the coating of some tablets for example so high consumption of it has the risk of causing thyroid problem in the body. Erythrosine contains high level of bound iodine, although there is evidence that the bioavailability of the iodine is relatively low [32].

1.3. Date Stones

These are by-product of date stoning, either for the pitted dates or the seeds that are removed from date fruits which are obtained from environmental or industrial wastes during the manufacture of date paste in food industries [33, 34].

Figure 2. *Picture of date seeds/stones.*

1.4. Activated Carbon

Activated carbons are carbonaceous adsorbents with a highly crystalline for and high internal pore structure.

A wide variety of activated carbon products are available depending upon the starting raw material and activation technique. Activated carbons are used to recover organic solvents, purify CO_2 from fermentation processes, purification of drinking water, amine and glycol treating, decolorizing of water and various other chemical and petrochemical processes. [26].

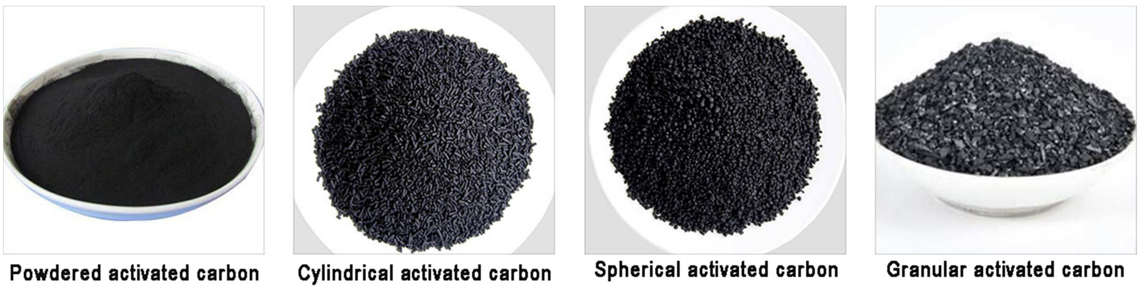

Figure 3. *Activated carbon.*

The widely considered adsorbent materials are the activated carbon prepared from different sources to suit a wide variety of conditions [24, 26]. Uses of coconut shell and wood rice husk carbon and rubber wood saw dust have been reported [26]. The advantage of activated carbon is because of its high surface area (500 to 1,500 m^2/g) [27]. It is widely prepared indifferent sizes and shapes. The adsorption capacity reported for few commercially available activated carbon include: F-400 [28], SHT and GA-3 [29]. Adsorption has several advantages like low price and easy operation over other conventional methods. However, the high adsorption capacity depends on its pH (low pH) and salinity (low salinity) which is not usually suited for removal of erythrosine from an aqueous solution. Moreover several activated carbons do not directly suit to remove erythrosine dye under different physicochemical conditions and needs to be chemically activated to enhance its adsorption capacity [30, 31].

2. Method/Procedure

2.1. Preparation of Erythrosine Dye Solution

Erythrosine stock solution of 500mg/L was prepared by adding 0.5g of the erythrosine dye in 1L of deionized water and dilute solutions of different concentrations (20, 40, 60, 80, 100, 300mg/L) were prepared by utilizing (2ml, 4ml, 6ml, 8ml, 10ml and 30ml) from the stock solution and serially added into 100ml of distilled water. The calibration curve below:

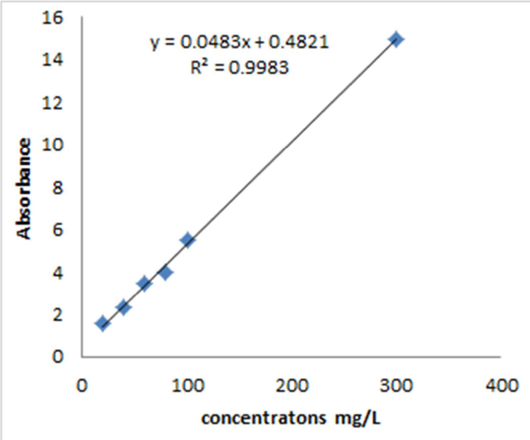

Figure 4. *Calibration curve of erythrosine dye.*

2.2. Sample Pre-treatment/Carbonization of Date Stones

The date stones subjected to thorough washing with tape water followed by treating it with distilled water and was dried. After drying, 100g of date stones was placed in a maffle furnace using a crucible and carbonized at 400°C for a period of 1 hour 20 minutes (heating at a rate of 20°C per 10mins up to 400°C). And reheated for another 20mins to have optimum carbonization and finally crushed and sieved with 500um sieve. Afterwards the powdered CDS treated with ethanol and distilled water and also the weight of treated CDS was measured to determine the yield. Finally the sample was stored and labelled.

2.3. Adsorption Studies

0.5g of adsorbent was added in 100ml of dye solution with concentration of 200mg/L in 250ml conical flask and agitated at speed of 150rpm for a period of 24hrs. After shaking, it was settle for 20mins and 15ml was taken from the solution and placed in special container. The experiment was continued for another 20mins until we arrived at 120mins while pH7 was maintained. Finally the five samples subjected to AAS analysis to determine the amount of dye absorbed at equilibrium q_e and the removal efficiency of carbonized date stones (CDS) which was calculated using the Equations below:

$$q_e = (c_i - c_e)\frac{v}{w}$$

$$\% \text{ Removal} = \left(\frac{(c_i - c_e}{c_i}\right) \times 100$$

C_i: initial dye concentration (mgL^{-1});
C_f: final dye concentration (mgL^{-1});
V: volume of dye (L);
W: mass of CDS (g).

3. Results and Discussion

3.1. Effect of Temperature

0.5 g of adsorbent was added to 100ml of adsorbate with 40 mg/L, and the mixture was agitated for 3 h at 150 rpm at various temperatures (25, 35 and 55°C). Subsequently, each sample was subjected to AAS analysis and the figures below show that the removal of erythrosine dye increases with a decrease in temperature, hence representing the possibility of achieving optimal removal of the contaminant by the carbonized date stone at a low temperature [35].

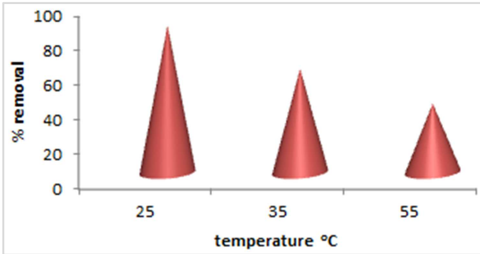

Figure 5. *Effect of temperature.*

3.2. Effect of Contact Time

The adsorption study was conducted by varying the time from 20 to 120 minutes in order to study the adsorption capacity of the adsorbent. From the figure 6 below showed that the removal of dye with carbonized date stones decreases with increase in time which started from 20minutes and decreased with time at 120 minutes [36].

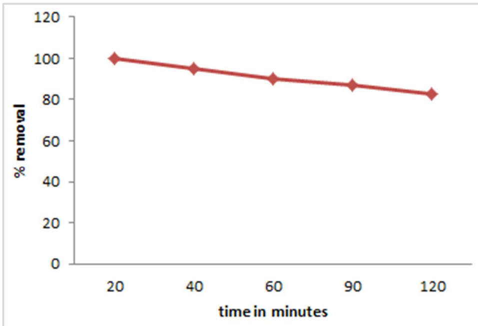

Figure 6. *Effect of contact time.*

3.3. Effect of Dosage

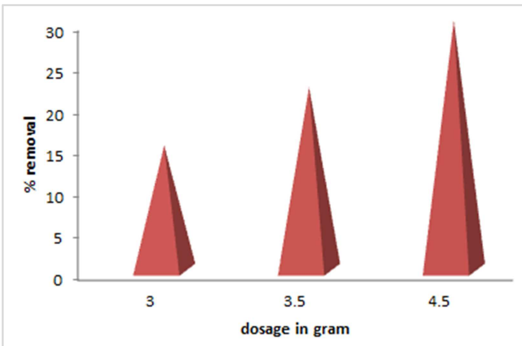

Figure 7. *Effect of dosage.*

3g, 3.5g, and 4.5g of adsorbent were added in to three containers containing 100ml with 300mg/l of dye solution and then agitated with a magnetic stirrer at 150rpm for 3hours and finally 20ml from each undergo AAS analysis to investigate the percentage removal of adsorbate from the result. Considering the figure 7 above, it showed that the removal of dye using carbonized date stones was optimum at 0.05g and therefore the removal of dye attributed with increase in dosage of the adsorbent.

3.4. Adsorption Isotherms Models

The adsorption isotherm of erythrosine dye onto carbonized date stones was better studied under one of the selected temperatures of 25°C and initial solution pH of 7. The adsorption isotherms that were used are Langmuir and Fruindlich adsorption isotherm to evaluate the adsorption capacity of the dye. Application of the isotherm equation to adsorption data was based on comparison of the correlation coefficients (R^2) values of both Isotherm. The Langmuir and Freundlich isotherms and the adsorption parameters obtained from plots were tabulated in table 1. From the table 1, the R^2 values for Langmuir and Freundlich are 0.9780 and 0.8933 respectively, this represent a monolayer adsorption process that conforms to Langmuir isotherm.

Table 1. *Adsorption Isotherms.*

Isotherm	Parameter				
Langmuir	T(K)	q_m (mgg^{-1})	KL (Lmg^{-1})	R_L	R^2
	298	9.09	0.793	0.0126	0.9780
Freundlich	T(K)	K_f(mg/l)(L/mg$^{1/n}$)		1/n	R^2
	298	2.3		0.0299	0.8933

The kinetic models that were applied on this work are pseudo first and pseudo second order and via result obtained showed that the mechanism of the adsorption, highest level of adsorption and adsorption efficiency of erythrosine dye followed pseudo second order due to highest value of correlative coefficient R^2 which was 0.9090. Also adsorption capacity of the dye at equilibrium q_e was high with the value of 1.8900 to 8.3689 in pseudo second order compared to pseudo first order with 7.4567.

Table 2. *Kinetic models.*

model	Parameter				
Pseudo first order	T(K)	$q_{e,cal}$ *(mg/g)*	$q_{e,exp}$ *(mg/g)*	K_1 *(1/min)*	R^2
	298	0.5290	7.4567	0.1344	0.8300
Pseudo second order	T(K)	$q_{e,cal}$ *(mg/g)*	$q_{e,exp}$ *(mg/g)*	K_2 *(1/min)*	R^2
	298	1.8900	8.3689	0.012	0.9090

4. Conclusion

The following results were determined after completion of this research work;

1) Optimum removal of the dye occurred at pH 7.
2) The ability of CDS in removing the dye from solution increased initially but reduces as temperature increased.
3) Optimum dosage used for this study was 0.5g and removal efficiency of CDS increases as dosage increased.
4) Adsorption equilibrium was well fitted to experimental data using the Langmuir isotherm due to high value of correlative coefficient R^2 (0.9780) which shows monolayer adsorption on the sorption sites of CDS.
5) 1/n and R_L values supported favorable adsorption of erythrosine by CDS.

Therefore the research work on the removal of erythrosine dye from aqueous solution using carbonized date stone was achieved at optimum removal because adsorption process is a suitable method for removal of dyes due to its easy in design, low cost, simplicity of operation, and not sensitive to toxic substances. And also date stones activated carbon is a good adsorbent due its good absorbing properties such as large size and attractive surface, high porosity of particle.

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