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RESEARCH PAPER

Highly Surface Activated Phosphoric Acid Clove Leaf Agro Waste Micro/Nano Bio Sorbent: Characterization, Regeneration, Equilibrium Isotherm of Safranin T

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ABSTRACT

In this study, the efficiency of activated carbon prepared from pineapple skin (ACPS) in removing safranin T (ST) dye from aqueous solution was examined. ACPS was prepared through phosphoric acid chemical activation processes (ACPS-H_3PO_4) and at a temperature of 300 °C foe 2 hr. The results obtained from the preparation process indicate that the prepared ACPS-H_3PO_4 has high surface properties and porosity for use as a highly efficient absorbent material. The prepared surface was characterized by techniques XRD, FESEM, EDX and TEM. The maximum efficiency (84.84%) and absorption (168.73 mg/g) of ACPS-H_3PO_4 for ST dye removal was achieved under the following conditions: ACPS-H_3PO_4 dose = 0.05 g/L, CT dye concentration = 100 mg/L, pH = 7, equlibruim time = 60 min, temperature = 25°C. It was found that the isotherm data matched the Freundlich isotherm with high accuracy values. The much higher adsorption capacity of ACPS-H_3PO_4 for the dye (168.73 mg/g) compared to other previously used sorbents with excellent regeneration level (five cycles) depicts the superior performance of ACPS-H_3PO_4 in adsorption systems.

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INTRODUCTION

Treatment of liquid waste resulting from most industries, especially the textile industry, is considered. It addressed an important global environmental issue. Liquid waste resulting from textile dyes has a clear impact on many hazardous environmental problems on neighboring receiving water bodies due to the presence of toxic dyes, their accumulation in the water, and the dark color remaining in the water. There are many treatment processes that have been applied in the disposal of liquid waste, and the most dangerous are Dyes from wastewater [1]. Removing textile dyes from wastewater using the adsorption process is considered a promising technique for disposing of liquid waste using activated carbon, which is considered very effective, but its cost is high. Such adsorbents have stimulated the search for new, low-cost alternatives and adsorbents [2-6]. Recently, several researchers have attempted to use inexpensive alternative adsorbents to replace the more expensive, commercially available activated carbon. Alternatives include: natural sorbents, bio sorbents, industrial and agricultural wastes, and experimental by-products. It has been used very widely recently to remove dyes from aqueous solutions [7-9]

Safranin T(ST), which is a positively charged

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dye (+ve), is a cationic dye that is soluble in water, as shown in the Fig. 1. It is considered one of the dangerous and toxic dyes that cause genetic mutations. It has appeared as a controversial substance in aquaculture and is used as an ectoparasiticide and fungicide due to its effectiveness and less cost. It is a conventional dye used in most industries for materials such as wood, wool, silk, leather and paper [10, 11]. However, its intense color causes an obvious danger in water, especially bodies of water, because it is not biodegradable, which raises concerns about. The environment, especially aquatic organisms, because of the dangerous environmental problems they cause and making their confiscation difficult. It is extremely harmful, carcinogenic, and also harmful to animal cells. It causes allergies, nausea, and skin infections [12].

MATERIALS AND METHODS

Preparation of stander Solution of ST dye

A 500 mg/L of ST dye stander solution was produced via measuring 0.5 g of the adsorbate and dissolving in 500 ml distilled water. To prepare appropriate concentrations of ST dye the adsorbate utilized for batch tests, it was achieved via diluting the stander solution utilizing distilled water.

Adsorption Isotherm

The batch adsorption method was utilized to study the adsorption behavior of ST dye onto ACPS-H_3PO_4.A known amount of adsorbent (0.05 g) in 100 mL of solution having 100 mg/L solution

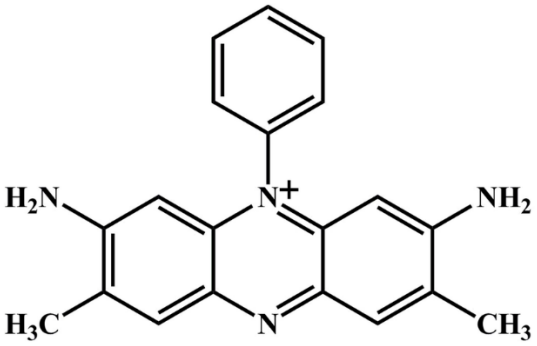

Fig. 1. Chemical stretcher of Safranin T(ST) dye

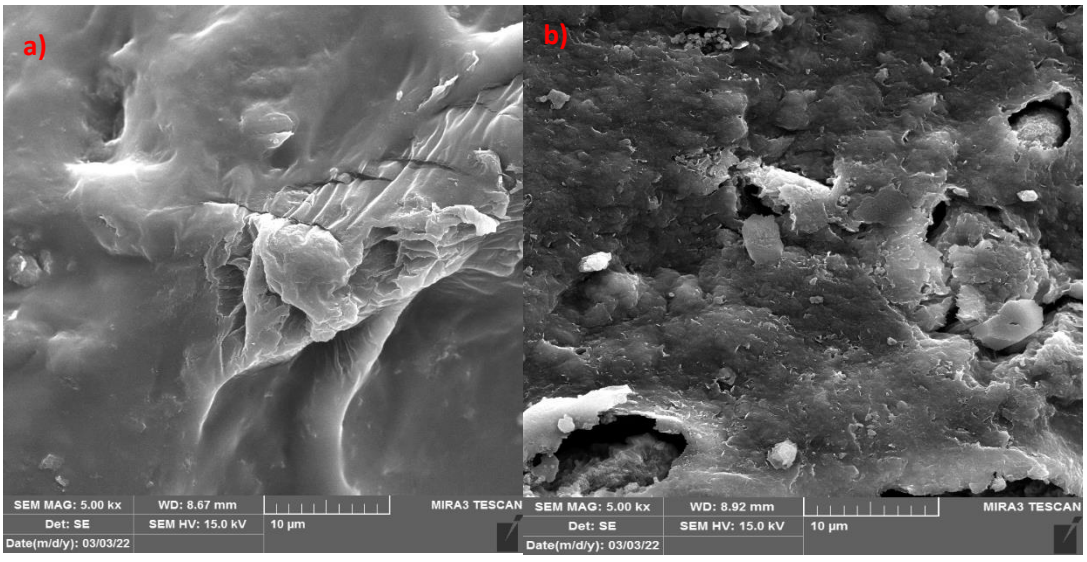

Fig. 2. FESEM image a) before adsorption, b) after adsorption

of ST dye. The reaction mixture was shaker water bath for 1 hr. and then separated in centrifuged for 15 min. The remaining pollutants concentration in the resultant supernatant was estimated utilizing the proposed system. The adsorption efficiency (Qe) and removal percentage (E%) adsorption was calculate in Eq. 1 and 2.

$$Qe\left(\frac{mg}{g}\right) = \frac{(Co-Ce)Vml}{M\ gm} \quad (1)$$

$$E = \frac{Co-Ce}{Co} \times 100 \quad (2)$$

Preparation of pineapple Skin-PS as activated carbon

Waste samples (pineapple Skin-PS) were collected and the pineapple pulp was removed manually. Wash it with distilled water more than once to get rid of any remaining pulp stuck to the peels. The peels were dried at room temperature for three days and later crushed into smaller particles. It is treated physically with phosphoric acid(H_3PO_4) for 2hour with stirring, then washed with distilled water more than once to get rid of the acid residue. After that, it is dried in an oven at a temperature of 70 °C. Finally, it is burned at a temperature of (300 °C) for 2hour to obtain activated carbon (ACPS-H_3PO_4). They were then ground using a laboratory blender and the resulting powders were sieved to a nominal size of 212 µm and used in all experiments.

RESULTS AND DISCUSSION

FESEM

The Fig. 2a shows the morphology of the prepared surface, its ability and high adsorption efficiency. The surface efficiency depends on the method of preparing activated carbon. The surface contained cloud-like clusters in a wavy shape, indicating that the surface is heterogeneous and irregular and contains several active sites. Also, the presence of Small white balls resulting from the process of activation with acid. As the whole (Fig. 2b) shows, the surface prepared after the process of adsorption of the dye on the surface, and most of the active sites were filled, and the surface became regular with few ripples. As can be seen, the surface became dark as a result of the adsorption of the dye on the surface, and this is evidence of the success of the adsorption process [13, 14].

The surface morphology of ACPS-H_3PO_4 was studied using surface morphological analysis TEM; It was clear from Fig. 3 that the cloud was more available and a new geometry was created on the surface of the ACPS-H_3PO_4. This may be attributed to the role of the phosphoric acid activation process, where the architecture-like structure is formed and there are irregular wormhole-like pores in the molecules, which indicates the presence of porous structure. The average current size was found to be 0.6nm, 100 nm [15, 16].

X-ray diffraction (XRD) spectra were used to study the structural properties, represented by composition, crystalline size, and spacing between

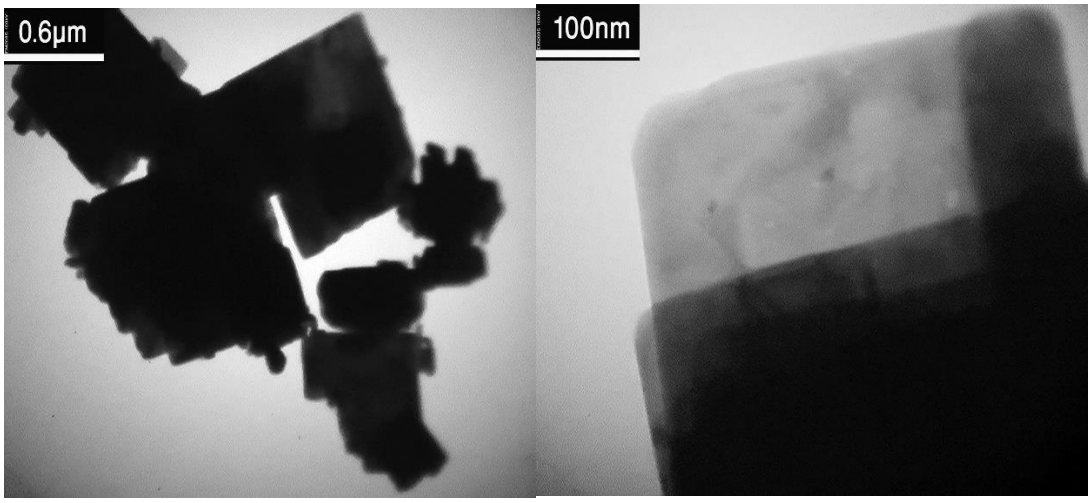

Fig. 3. TEM image of ACPS-H_3PO_4

crystalline planes, of the prepared ACPS-H_3PO_4 in its solid state using single light of wavelength 1.5104 A^0 from a (Cu-Kα) source within the angular range 2θ (5-80) degree, the XRD patterns for the ACPS-H_3PO_4 were observed, the broad peak at 20.109° indicates that the hydrogel composites are semi crystalline, with a significant proportion of amorphous material [11, 17, 18], as show in Fig. 4.

Effect of initial dye concentration

Fig. 5 shows the effect of dye concentration on the adsorption efficiency (Qe mg/g) and removal percentage (R %) at different initial dye concentrations of (10-100mg/L) under constant experimental conditions. The graph shows that the amount of absorbed dye varies with the initial dye concentration and increases with increasing the initial dye concentration, in While the removal rate decreases with increasing dye concentration. The initial concentration of the dye increases the number of collisions between the dye and the ACPS-H_3PO_4, which enhances the adsorption process. It was found that the effect of the dye concentration (the best concentration used on the ACPS-H_3PO_4 is important for the dye used, as

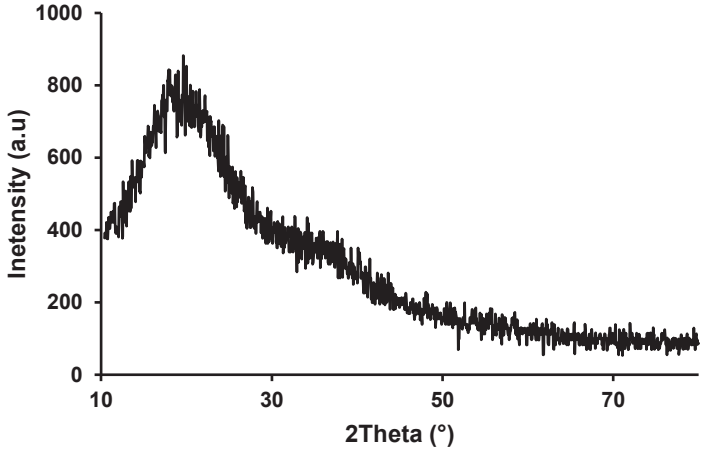

Fig. 4. X-ray diffraction (XRD) spectra of ACPS-H_3PO_4

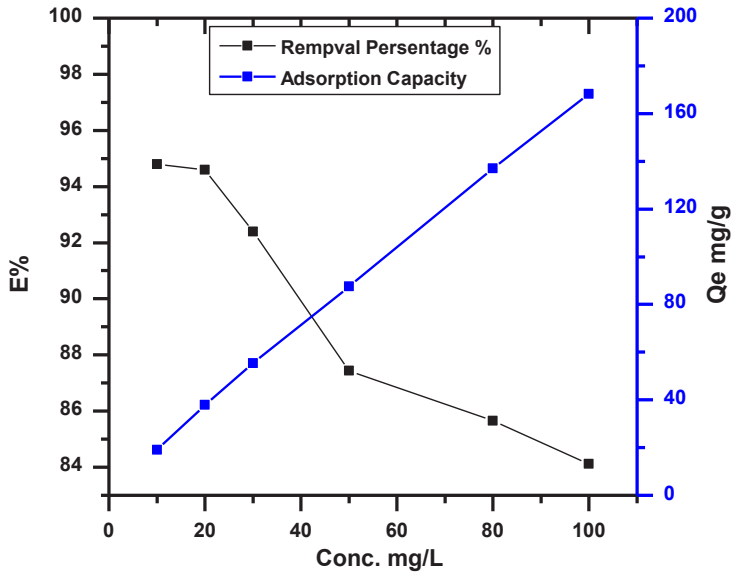

Fig. 5. Effect of ST dye concertation on to removal percentage by ACPS-H_3PO_4. Temperature = 25°C, weight 0.05 g and t 60 min).

it gives the adsorption efficiency (18.11-168.34 mg/g) and the removal percentage (48.55-49.55 %) [5, 19, 20].

Effect of ACPS-H_3PO_4 dosage

The effect of ACPS-H_3PO_4 dosage on the percentage of ST dye adsorbed from aqueous solutions showed that increasing the dosage of ACPS-H_3PO_4 stably improved the removal potential of ST dye. As shown in Fig. 6, increasing the weight of ACPS-H3PO4 from 0.01 g to 0.1 g is followed by an increase in the absorption percentage from 46.44% to 98.44 % for the ST dye. Increasing the weight of ACPS-H_3PO_4 reduced the adsorption

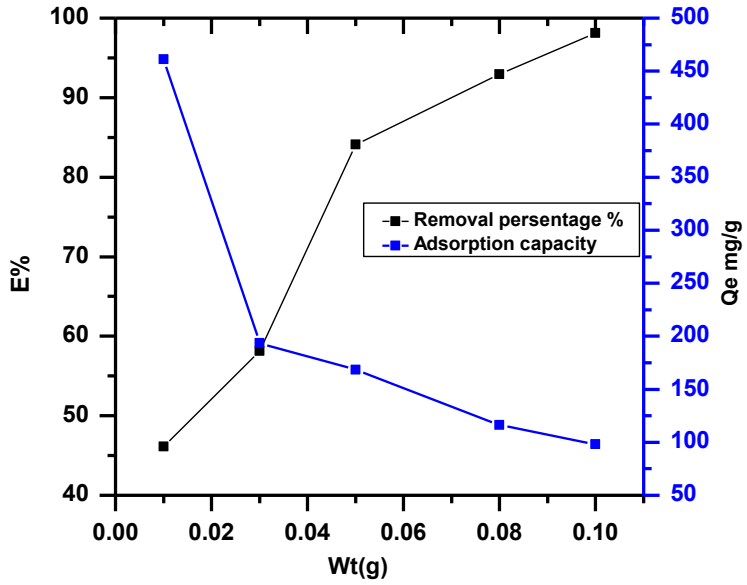

Fig. 6. Effect of weight of ACPS-H_3PO_4 onto adsorption capacity and removal percentage ST dye, Temperature = 25°C, con. 30 mg. L^{-1}, and t 60 min).

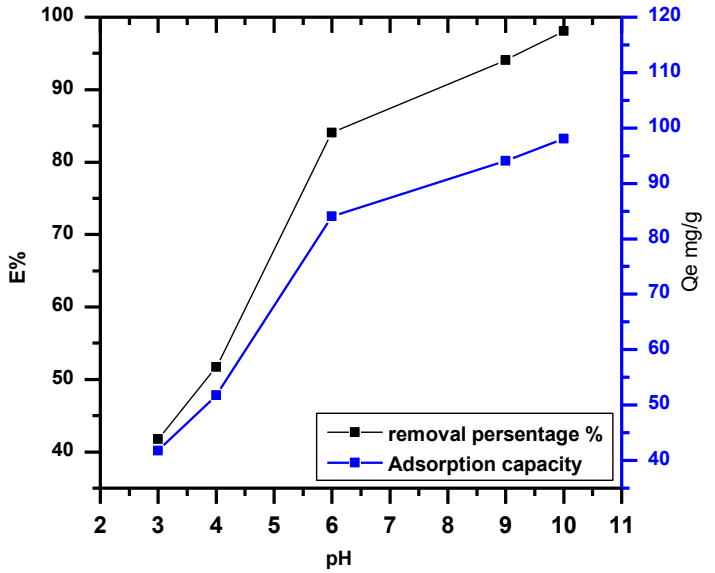

Fig.7. Effect of solution pH onto removal ST dye by ACPS-H_3PO_4

capacity of the same dye series from 498.44 to 98.76 mg/g. This may be because increasing the volume of adsorbent produced a larger surface area or more adsorption sites for the dye. The additional increase in the amount of ACPS-H3PO4 used from 0.08 g to 0.1 g had no effect on the percentage of ST dye removed [21-23].

Effect of solution pH

The pH is one of the basic important factors that must be taken into consideration when conducting the adsorption experiment, depending on the type of dye used and also on the surface charge. Fig. 6 displays the effect of basic solution pH ranging from about 3 to 10 on the dye removal ability of ACPS-H_3PO_4. At the operational conditions of the study (100 mg/L) dye adsorbed on 0.05 g of ACPS-H_3PO_4, equilibrium time of 1hr. and shaking rate of (120 rpm) the equilibrium adsorption efficiency was lowest at pH 3 (41.23 mg/g) [8, 24, 25]. The maximum dye absorption limit was achieved at pH 10 (98.63 mg/g) as show in Fig. 7.

Adsorption isotherms

The isotherm considers an important factor for resolve adsorption ways. In truth, adsorption isotherms can detect adsorbent-adsorbate interactions. Two models isotherm found; of the equilibrium adsorption models, like Freundlich isotherm multilayer and Langmuir isotherm monolayer adsorption isotherms apply to solid-liquid adsorption methods [26].

$$Qe = \frac{Qm\ KL\ Ce}{1+KL\ Ce} \quad (3)$$

According to the isotherm Langmuir (Eq. (5)), adsorption happens on a homo-geneous surface

Table 1. Freundlich and Langmuir isotherm parameter Cu(II) on to ACPS-H_3PO_4

Isotherm	parameter	ACPS-H_3PO_4
Freundlich	K_F	31.44
	1/n	0.6019
	R^2	0.9987
Langmuir	q_m (mg/g)	179.06
	K_L(L/mg)	0.33
	R^2	0.9611

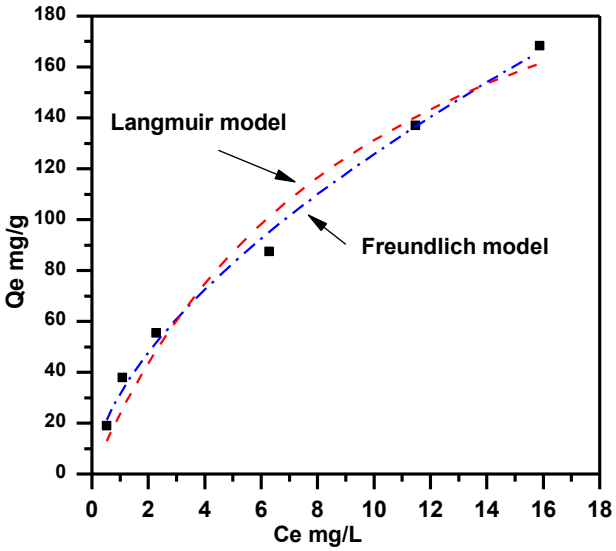

Fig. 8. Adsorption models nonlinear fit of adsorption ST dye on to ACPS-H_3PO_4, Temperature = 25°C, con. 100 mg. L^{-1}, weight 0.05 g and t 60 min).

Table 2. Adsorption-desorption cycles of ACPS-H_3PO_4

NO. OF CYCLES	E%
0	84.33
1	82.16
2	77.733
3	70.778
4	67.87

through mono-layer coverage. The isotherm Freundlich (Eq. (4) is a multilayer adsorption on hetero-geneous surface analytical model.

Where Qe (mg. g^{-1}) and Ce(mgL^{-1}) are the sums of adsorbed ST adsorption capacity and unit mass of sorbent and, respectively, the concentration of ST in solution at equilibrium. Qm is the maximum adsorption of the adsorbed ST per unit of the surface to form a full mono layer on the surface-bound at high Ce (mgg^{-1}), and KL (Lmg^{-1}) is a Langmuir constant related to the affinity of the adsorbent's binding sites on the surface.

$$Qe = K_f\, Ce^{1/n} \quad (4)$$

While K_f (L/mg) is the constant Freundlich, and 1/n is the hetero-geneity parameter

Fig. 7 appear a plot of qe vs Ce where 1/n and Kf are set from the slope and intercept of the nonlinear retreating function. As seen, good regression correlation coefficient was show by the isotherm Freundlich (R= 0.9987). This tick that the Freundlich isotherm was so appropriate for characterizing the sorption of dye on ACPS-H_3PO_4 compared to Langmuir isotherm (R=0.9611), at 25 ^oC result show in Fig. 8, the studied factor of the two isotherms clarify in Table 1 [3, 27, 28].

Regeneration and reactivation

Adsorption-desorption cycles were applied to study the ACPS-H_3PO_4 reusability. Adsorbent recovery is a crucial step in the usage of adsorption since it helps to demonstrate adsorbent happening again. As result, both the commercial value of the adsorption way and the recovery method of the adsorbed material will considerably rise. A NaOH 0.1 N, HCl 0.1 N, and H_2O were applied to study the adsorbed ST dye desorption performance from the ACPS-H_3PO_4 [11]. The performance reactivation of ACPS-H_3PO_4 was studied to imperfect its feasibility for industrial use. The adsorbent utilized in Table 2, compared adsorption performance of ACPS-H_3PO_4 in this work and other activated carbon on the high capability to remove different dyes.

CONCLUSION

We prepared activated carbon from pineapple peels by activating it with phosphoric acid, which produces a low-cost surface with high efficiency in removal ST dye. Several characterization techniques revealed the successful prepara tion of activated carbon. The nonlinear approach was used to model the adsorption isotherms and equilibrium of ST dye adsorption at different process parameters. The high activity of ST dye removal attributed to the abundance of surface active aggregates which increases the adsorption capacity, and leads to efficiencies higher than 84.99%. The maximum removal efficiency of 98.33% was obtained at pH 10. Activated carbon can reportedly be used for four successive cycles of adsorption and desorption, according to studies on surface recycling and regeneration. In short, an absorbent material was prepared from activated carbon with a high ability to regenerate, excellent properties, and a high adsorption capacity.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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