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Evaluation of *Calotropis procera* fruits as a Bioadsorbent for Removing of Acid Red 73 dye from the Aqueous Solutions

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ACID red 73 dye is a colorant dyes is using in many dyeing processes and may causes many harmful effects to aquatic life with lasting effects. So, it must be removed from aquatic environment, one of the most useful methods is the using of plants biomass in its removal. Therefore, **b**oth of raw andacid activated (with HCl) *Calotropis procera* fruits (CPF) was used for the adsorption of Acid red 73 (AR73) dye from an aqueous solution.Various parameters (including dye concentration,contact time, dose, temperature, and pH) were optimized to obtain the maximum adsorption capacity.Surface morphology and surface functional groups of both raw and modified CPF samples were investigated by scanning electron microscope (SEM) and fourier transformation infrared (FTIR). Among the adsorbents, HCl-CPF had more adsorption capacity (65%) than CPF (22.4%) at an initial concentration of 20 mg/L and at 30°C.The thermodynamic parameters, such as the changes in enthalpy (ΔH°), entropy (ΔS°), and Gibbs free energy (ΔG°), showed that the adsorption is exothermic, random and nonspontaneous at high temperatures.

Keywords: Adsorption, Acid Red 73, *Calotropis procer*a fruits, Langmuir isotherm.

Introduction

Deterioration of the natural resources is the major threat to the ecosystem. The development in agriculture, medicine, energy sources, and all chemical industries is necessary to fulfill the needs and demands of the overgrowing human population. One of the most polluting industries is dyes production and its application for many products. The most dyes are inert and nontoxic at the concentration discharged into the receiving water. Dyes are usually stable to photodegradation, biodegradation, and oxidizing agents [1]. Color removal from effluents is a major environmental problem because of difficulty of treating such streams by conventional physicochemical and biological treatment methods [2]. Various physical, chemical and biological methods were used for treating dye wastewater [3]. These methods have some drawbacks such as, being economically unfeasible; incompetent to treat the complex organic dyes and metabolites because of the color fastness; stability and the resistance of dyes to degradation; considerably raising the economic value of the treatments with complex processes [4-7]. By reviewing the available literature, it was found that, the advantages of adsorption when compared to the other available wastewater treatment methods are as follows: requirement of less land area, comparatively lesser sensitivity to daylight variation, less impact of toxic chemicals on the system, flexible design, operation and superior removal of organic contaminants [8,9]. Conventional industries use activated carbon as

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adsorbents for wastewater treatment. Because of its high cost that are in the range of approximately 2.0 to 4.0 US dollar/kg [10], researchers around all the world are in search for an efficient, and readily available and low cost adsorbent [11-18]. Many of them succeeded in their endeavor, and found many of low cost adsorbents. In the last few decades, a lot of researches has been carried out on finding low cost adsorbents and the search is still going on. The major drawbacks of their low cost adsorbents are low adsorption capacity and high adsorbent dosage for complete color removal.

Calotropis procera is a wild growing plant of family '*Asclepiadaceae'* is well known for its medical properties. The dried leaves were used as an expectorant and anti-inflammatory, for the treatment of paralysis, ulcers and rheumatic pains [19]. It grows in most parts of the world in dry, sandy, alkaline soils and warm climate.

The current study objective is to compare the adsorptive effects of raw and acid modified C*alotropis procera* fruits as a new low-cost and effective adsorbent from an agricultural waste to remove acid red 73 dye from aqueous solution.

Material and Methods

Preparation of Adsorbent

Calotropis procera fruits (CPF), Fig. 1 were collected from AL-Mukhwah governorate, AL-Baha, KSA in the summer season. The spongy fruit part of plant was cut and washed by tap water to remove dust and other impurities. The washed fruits then dried in sun light for 7 days and ground to fine powder, and then divided to two parts. One part of the powder is used as it is and another part of CPF is activated by soaking in 1% HCl for 24 h. The acid treated part was washed several times by distilled H_2O tell be neutral, then dried in an oven at 105^{o}C for 3h and used for adsorption study.

Preparation of Adsorbate

The AR73 dye (molecular weight: 656.5 g/mol., λ_{max}: 545 nm, CI 27290, chemical formula C_{22} H_{14} N_4 Na_2 O_7 S_2) was obtained from Merck and used without purifications, their chemical structure is illustrated in Fig. 2. A calculated amount of the dye (500 mg/L) was dissolved separately in 1.0 L of distilled water to prepare stock solutions. For batch study, an aqueous solution of this dye was prepared from stock

(a) Raw CPF (b) Dried CPF (c) Ground CPF

Fig. 1. *Calotropes procera* fruits: (a) raw, (b) dried, and (c) ground .

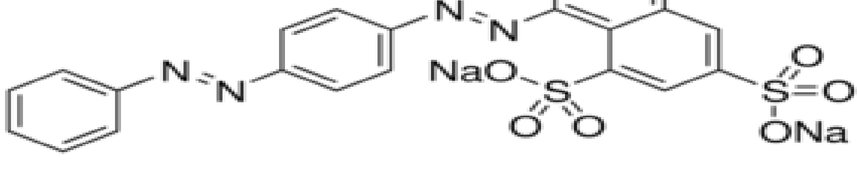


Fig. 2. Chemical structure of acid red 73 dye (AR73).

solutions in distilled water. To adjust the pH, solutions of 1%HCl and 1%NaOH were used.

Characterization of Adsorbent

SEM

The scanning electron microscope (SEM) observation were carried out with, SEM Model Quanta 250 FEG (Field Emission Gun) attached with EDX Unit (Energy Dispersive X-ray Analyses), with accelerating voltage 30 K.V., magnification 14x up to 1000000 and resolution for Gun.1nm). The SEM technique was employed to observe the surface physical morphology of raw and activated CPF.

FTIR

The surface functional groups of the raw and activated CPF were measured by FTIR (Perkin Elmer, model II) where the obtained spectra were recorded in the range 4000-400 cm^{-1} to elucidate the functional groups presenting in adsorbents before and after activation.

Batch Mode Adsorption Experiments

The adsorption experiments were carried out by agitating 0.06 mg adsorbent with 20 mL of dye solutions of 5.0 to 20 mg/Lconcentration at 600 rpm. The mixture was withdrawn at specified intervals, filtered, and unadsorbed supernatant liquid was analyzed for the residual dye concentration using (UV-Vis Spectrophotometer at λ_{max} of 545 nm. The effect of pH was studied by using 1.0 % diluted HCl and NaOH solutions. The effect of temperature was studied at three different temperatures (30, 40 and 50°C). The effects of each parameter (initial dye concentration, pH, agitation time) were evaluated in an experiment by varying that parameter, while other parameters are maintained as constant.

Adsorption Equilibrium Study

Langmuir and Freundlich are two adsorption isotherm models were adapted to fit the data obtained from the study on the effect of the initial dye concentration in order to understand the mechanism of adsorption of AR73 dye onto the adsorbents. The maximum adsorption capacity of the adsorbent could be determined from the adsorption isotherm studies. This analysis provides a clear view of the efficiency of the adsorption of AR73 dye onto the adsorbents and also to estimate the economic viability of the adsorbents for commercial applications.

Langmuir Adsorption Isotherm

The theoretical Langmuir adsorption isotherm is based on three assumptions, namely: Equivalent active sites present on the surface of the adsorbent, and can adsorb minimum one atom; the adsorption of the adsorbate molecules at a given site does not depend on the adsorption of other adsorbate molecules onto theneighboring active sites, and adsorption of the molecules follows a monolayer trend [20, 21]. The Langmuir isotherm model [22] can be expressed as the following equation: (eq. 1):

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (1)$$

Where q_e is the amount of dye adsorbed on the adsorbent at equilibrium (mg/g); C_e is the concentration of dye at equilibrium (mg/L);q_m is the maximal amount of dye adsorbed onto the adsorbents (mg/g). The essential characteristic of the Langmuir isotherm can be evidenced by the dimensionless constant called equilibrium parameter, R_L (2).

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

I

Where K_L is the Langmuir constant of adsorption (L/mg) and C_o is the initial AR73dye concentration. R_L values indicate the type of isotherm to be irreversible ($R_L= 0$), favorable ($0 < R_L< 1$), linear ($R_L= 1$) or unfavorable ($R_L> 1$) [23].

Freundlich Adsorption Isotherm

The assumptions of this model are: adsorption occurs on heterogeneous surfaces with an interface between the adsorbed molecules, and the adsorption energy exponentially decreases, on sustaining the adsorption centers of the given adsorbent.

The Freundlich model equation is conveniently used in the linear form as[24]:

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

A linear form of this expression is :

$$\ln q_e = \ln k_F + 1/n \ln C_e \quad (4)$$

1/n and k_F (mg/g) are empirical Freundlich constants and indicate adsorption capacity and intensity, respectively. Their values were obtained from the intercepts ($\ln k_F$) and slopes (1/n) of linear plots of $\ln q_e$ versus $\ln C_e$.

Theory and Formulation

The percentage of adsorption can be calculated as:

$$R(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (5)$$

Where C_o and C_e are the initial and final concentrations of AR73 dye, before and after contact. The equilibrium adsorption capacities can be expressed as follows:

$$q_e = \frac{V}{W} \times \left(C_0 - C_e\right) \quad (6)$$

Where V and W are the aqueous solution volume and the adsorbent weight, respectively.

Thermodynamics of Adsorption

Thermodynamic parameters provide in-depth information of inherent energetic changes associated with adsorption; therefore, these parameters should be accurately evaluated.

Langmuir isotherm equation was applied to calculate the thermodynamic parameters as follows :

$$\Delta G^{\circ} = -RT \ln K_L \quad (7)$$

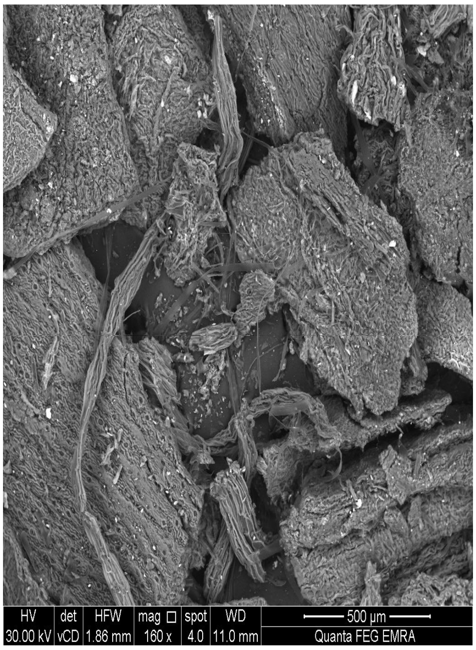
$$\ln K_L = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{R}\frac{1}{T} \quad (8)$$

Where k_L is the Langmuir equilibrium constant, ΔH^o, ΔG^o and ΔS^o are the standard enthalpy, Gibbs free energy and entropy changes of adsorption respectively. Thermodynamic parameters like ΔH^o, ΔS^o and ΔG^o were determined from the slope and intercept of Van't Hoff's plot of ln k_L versus 1/T and the results are given in Table 4.

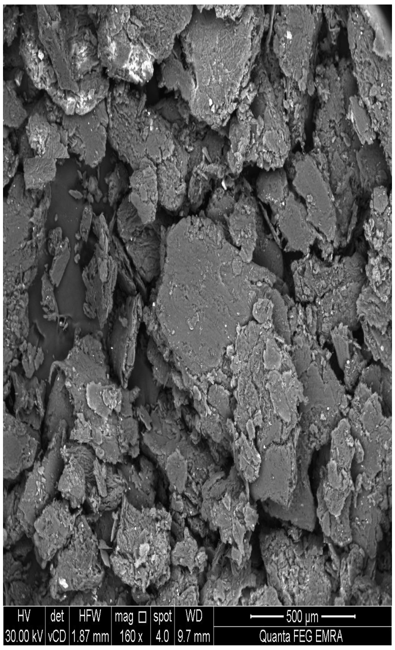
Results and Discussions

SEM Analyses

The SEM images shows the morphology of the absorbent, (CPF and HCl-CPF), in Fig. 3 (a) and (b) respectively. Results of the SEM study showed that, HCl-CPF was porous with well-developed pores. Raw CPF was characterized by a highly oriented structure in the form of filaments filled with material, conferring an anisotropic character to the adsorbent plant. The treatment with acid leading to eliminate of this anisotropy. Hydrochloric acid firstly, cleans the filaments, thereby eliminating *Calotropis procera* fruits anisotropy and leaving empty channels. Then, it reacts with the CPF components, thereby preserving a honeycomb structure. Based on this observation, it is clearly evident that the HCl-CPF has an adequate morphology for AR73 adsorption.



(a): The SEM image of CPF



(b): The SEM image of HCl-CPF

Fig. 3 SEM of raw (a) and acid activated (b) *Calotropesprocera* fruits.

FTIR Analysis

The IR spectra of raw and acid modified CPF are shown in (Fig. 4a and 4b). Fig. 4a exhibited broad bands at 3433.60 cm^{-1}, due to the stretching of OH groups. A greater number of OH groups on the glucose units of the cellulose polymers broadened the peak. The absorption bands at 2924.09 and 2862.36 cm^{-1} are due to a contribution from C-H stretching. The peak at 1519.91 to 1635.64 cm^{-1} was assigned to the C=O bonds, while the band at 1429.96 cm^{-1} and 1319.14 cm^{-1} are assigned to $–CH_2$ scissoring and –OH bending vibration, respectively. The strong band observed at 1103.28 cm^{-1} indicated the stretching of many C-OH and C-O-C bonds. The strong band between 532.35 and 601.79 cm^{-1} shows the presence of the C-X group. The bands in Fig. 4b are the same that of Fig.4a except, the shift of C-X group bands due to HCl effect.

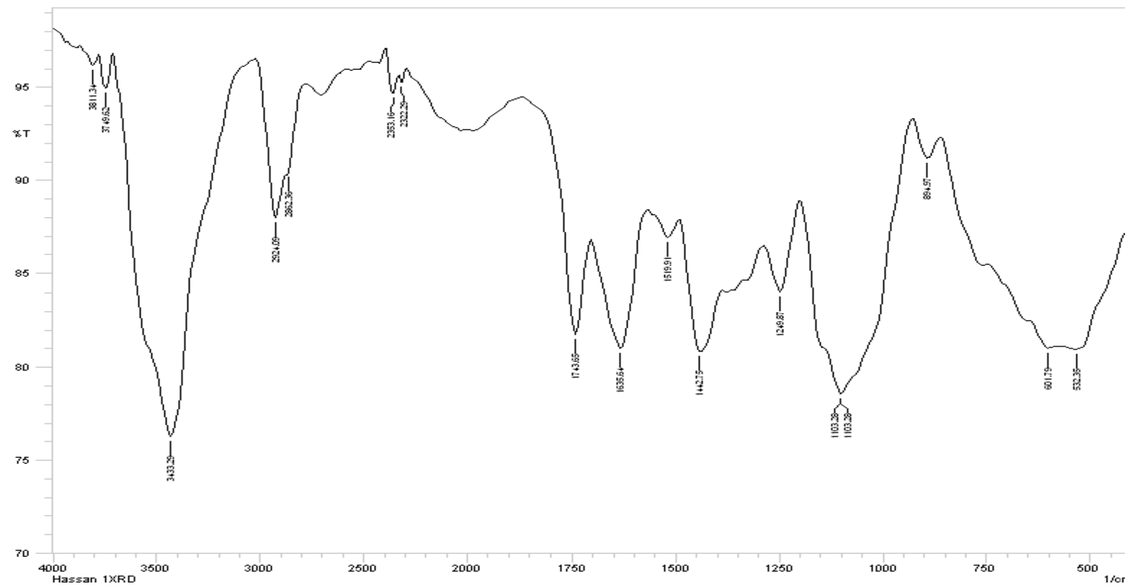


Fig. 4a. The IR spectrum of CPF.

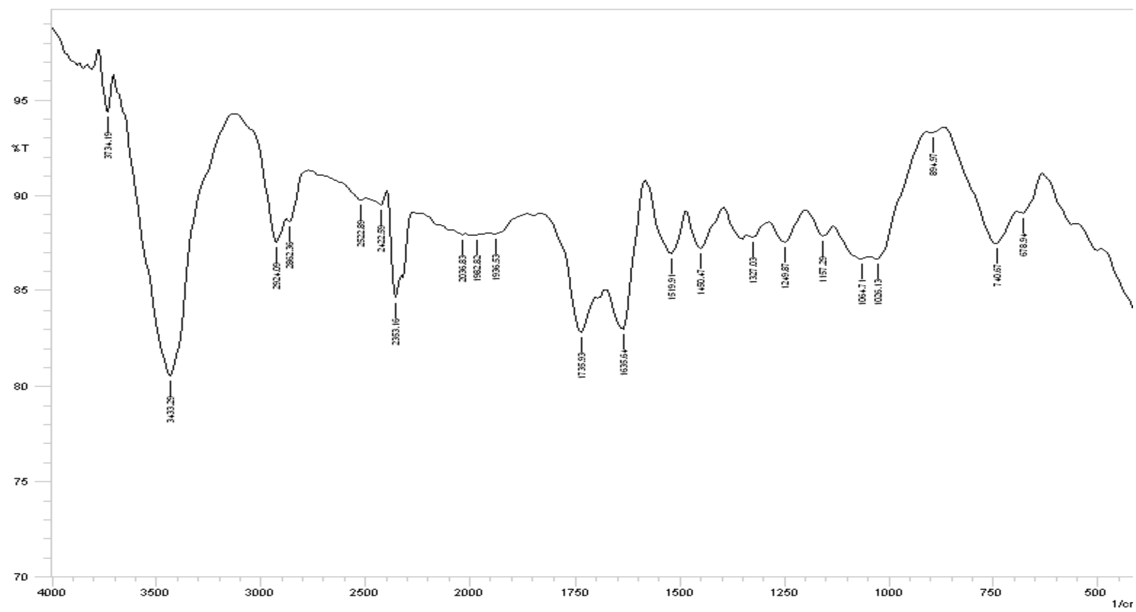


Fig. 4b. The IR spectrum of HCl-CPF.

Effect of pH

The study of pH effect on dyes adsorption seems essential as it could affect the surface charge of adsorbent and molecular structures of the adsorbate [25]. Removal of AR73 solutions was made at a pH ranging between 3 and 11 by CPF and HCl-CPF with a fixed adsorbent mass and temperature. The obtained results are given in Fig.5. The percent removal of AR73 dye on CPF and HCl-CPF surfaces was found to be 93% and 95.5% respectively at pH less than 4.0. At pH 3, positively charged surface sites on the adsorbent favor the adsorption of dye anions due to the electrostatic attraction, so the adsorption capacity in case of HCl-CPF is better than CPF due to excess positive sites arise from acid activation. Lower adsorption capacity noticed gradually of both adsorbent with decrease of pH, due to the presence of OH- ions excess, which competes with the dye anions for the adsorbent active sites. As the pH of the system increases, the number of positively charged sites decreases and the number of negatively charged sites increases [26].

Effect of Adsorbent Mass

The effect of adsorbent dose is the parameter most commonly used to evaluate the adsorption, which was also easily controlled during the adsorption process of waste water treatment. Solution of 20 ml of concentration 20 mg/l was used to test the effect of CPF and HCl-CPF masses. Different doses of both adsorbent (between 1.0 g and 5.0 g) were separately introduced at a fixed temperature and pH. The removal percentages of AR73 as a function of adsorbent mass were illustrated in Fig.6. We noted that an increase in the adsorbent mass from 1.0 g to 5.0 g increased the colour removal from 93% to 94.5% for CPF and from 95% to 95.6% for HCl-CPF, to achieve the best efficiency.Thus, the number of adsorption sites was proportional to the adsorbent amount [27, 28].

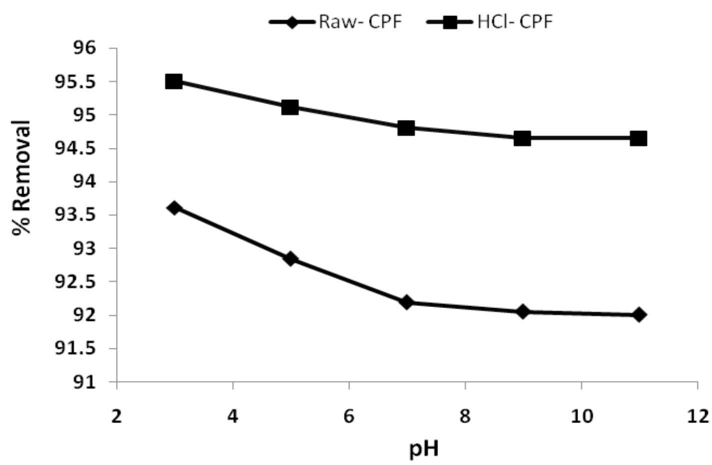


Fig. 5. Effect of system pH on AR73 adsorption by CPF and HCl-CPF.

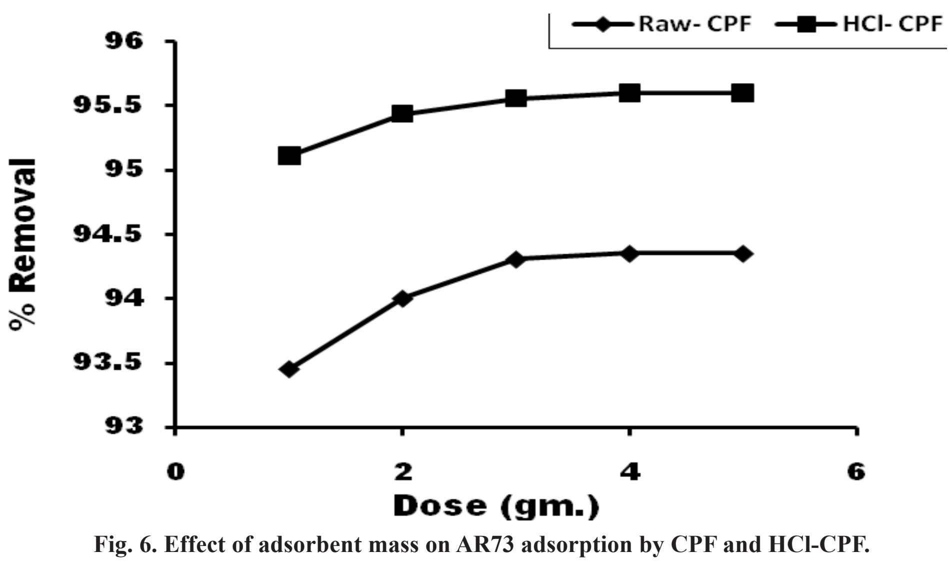


Fig. 6. Effect of adsorbent mass on AR73 adsorption by CPF and HCl-CPF.

Effect of Temperature

Various textile dye effluents are produced at relatively high temperatures. Also, the temperature of the aqueous solution has a driving effect on the adsorption process. Therefore, to distinguish the exothermic or endothermic nature of the adsorption process, the experiments were carried out at different temperatures ranges of 30 to 60°C and the date is displayed in Fig. 7. The data of adsorption of AR73 by CPF and HCl-CPF respectively showed significant high dye removal for both CPF and HCl-CPF at low temperature compared with that adsorbed at high temperature range. The percentage removal of AR73 decreased from 95.0 % to 93.9 % on CPF and 95.52 % to 94.2 % on HCl-CPF respectively on increasing the temperature from 303 to 333°k. This suggests that the adsorption of AR73 dye on given adsorbents is an exothermic process. The percentage removal of the HCl-CPF was also higher compared to that of the ordinary CPF which showed that the HCl-CPF possessed more energy required for adsorption. Other wise, the decrease in adsorption with increasing temperatures suggests weak adsorption interactions between adsorbent surfaces and the dye molecules.

Effect of Initial Concentration

The initial dye concentration was found to play significant roles in the process of removal of dyes from water and wastewater by adsorption at a particular temperature and pH. Concentrations from 5.0 to 20 mg/L at 298 k and pH 3.0 were considered. Fig. 8 shows that the adsorption percentage of CPF & HCl-CPF improved from 78 to 88 % and from 80 to 93.4 % for the CPF and HCl-CPF adsorbents, respectively, when the initial AR73 dye concentration was increased from 5.0 to 15 mg/L. However, HCl-CPF displayed a very high adsorption capacity of 94.5 % at an initial dye concentration of 20 mg/ L (compared to 90 % for CPF), this could be because of the large surface area of HCl-CPF due to activation by acid. The adsorption capacity of AR73 dye on both adsorbent surfaces is increase slightly after dye concentration of 15 mg/L. This attributed to that the more concentrated the solution or effluent, the smaller is the volume of effluent that a given mass of adsorbent can purify. In high concentration range, the fractional adsorption is low [29].

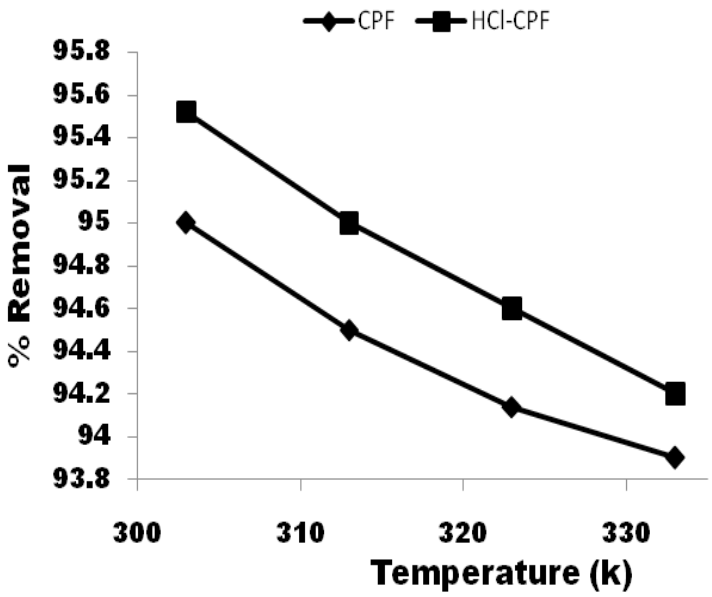


Fig. 7. Effect of temperature on AR73 adsorption by CPF and HCl-CPF.

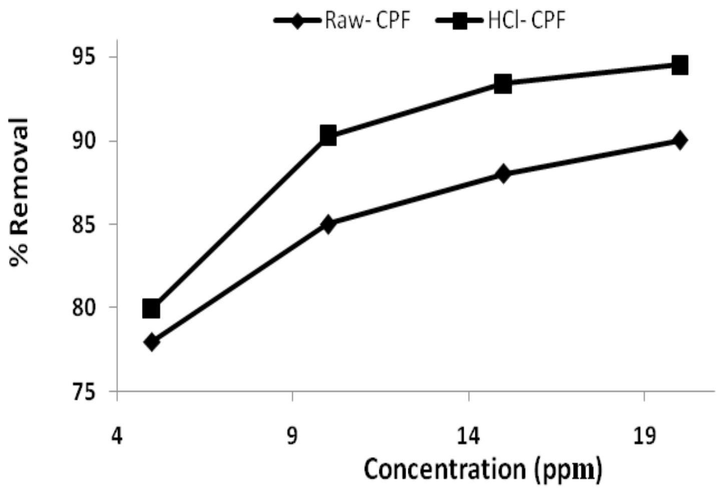


Fig. 8. Effect of concentration on AR73 adsorption by CPF and HCl-CPF.

Effect of Contact Time

The variation of AR73 dye adsorption percentage with contact time on the CPF & HCl-CPF is shown in Fig. 9. It is evident that both the adsorbents are efficient to adsorb AR73 with different efficiencies. It was observed that dye uptake is rapid for the first 15 min and 10 min for CPF & HCl-CPF respectively; thereafter it proceeds at a slower rate and finally attains saturation. The highest dye uptake during few min confirms that dye molecules quickly occupy all of the vacant sites, and the adsorption process is reduced with time [30]. After the aforementioned contact time, no additional dye uptake occurs because the dye molecules compete with each other for adsorption sites and there are fewer available binding sites [31].

Adsorption isotherms

In this study, Langmuir and Freundlich isotherms were investigated. The parameters of both isotherms are presentedin Table (1) which indicates that the equilibrium data for the adsorption processes by CPF and HCl-CPF suitable well with Langmuir and Freundlich adsorption models, respectively. It can be seen in Fig. 10 that the Langmuir plot is a better fit of the experimental data compared to Freundlich plot (Fig.11) for both the adsorbents. The AR73 adsorption capacity on HCl-CPF was 65 mg/g at 25°C, whereas that of CPF was only 22.4 mg/g adsorbent under the same conditions. The magnitude of the exponent 'n' gives an indication of the favorability and K_F the capacity of the adsorbent / adsorbate system. The 'n' values (1.23 for CPF and 1.5 for HCl-CPF) between 1 and 10 indicate beneficial adsorption [32]. Table 2 shows R_L values between zero and one, which indicate favorable adsorption [33].

Thermodynamic Studies

Thermodynamic parameters were determined to further evaluate the temperature effect on the capacity of CPF and HCl-CPF for the adsorption of AR73 dye (Table 2). The values of ΔH and ΔS for the CPF and HCl-CPF adsorbents were calculated as -9.20 kJ/mol and 0.08 kJ/mol, for CPF and -9.44 kJ/mol and 0.09 kJ/mol for HCl-CPF respectively. The negative values of ΔH showed that AR73 adsorption onto both adsorbents were exothermic, while the positive ΔS values confirmed the increased randomness at the solid–solution interface. The ΔG (Gibbs free energy change, kJ/mol) values were negative at all temperatures, which showed that the adsorption of AR73 dye onto CPF and HCl-CPF is spontaneous in the forward direction (Table 2).

Comparison Study of Adsorption of AR73 on Different Adsorbent Surfaces

The adsorption capacities of various adsorbents used for AR73 removal were compared with present study and data showed in Table 3. From the Table 3, it is very clear that the capacities of adsorbents for adsorbing AR73 are in a wide range. It is vary from 1.25 to 728.2 mg/g. The adsorption capacities of CPF and HCl-CPF are very less compared to chitosan. Otherwise, the adsorption capacity of HCl-CPF for AR73 is comparable with chitosan nano particles, Partheniumhy sterophorus L, Magnetic nanoparticles Fe_3O_4, copper diethyldithiocarbamate ($Cu(DDTC)_2$), and HCl-water hyacinth stems (HCl-WHS).

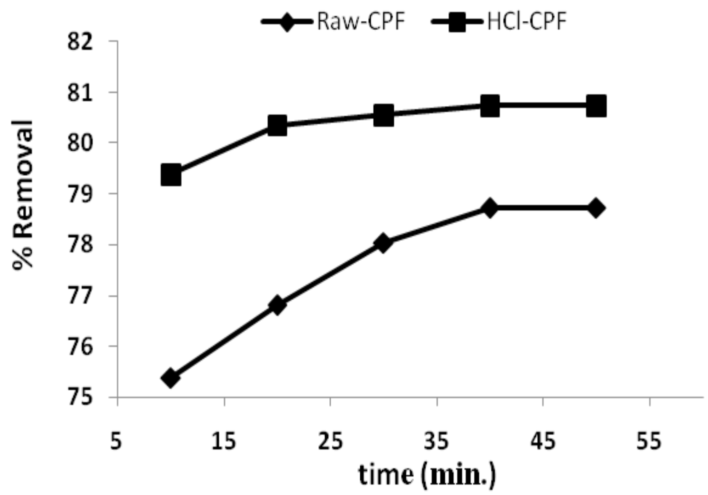


Fig. 9. Effect of contact time on AR73 adsorption by CPF and HCl-CPF.

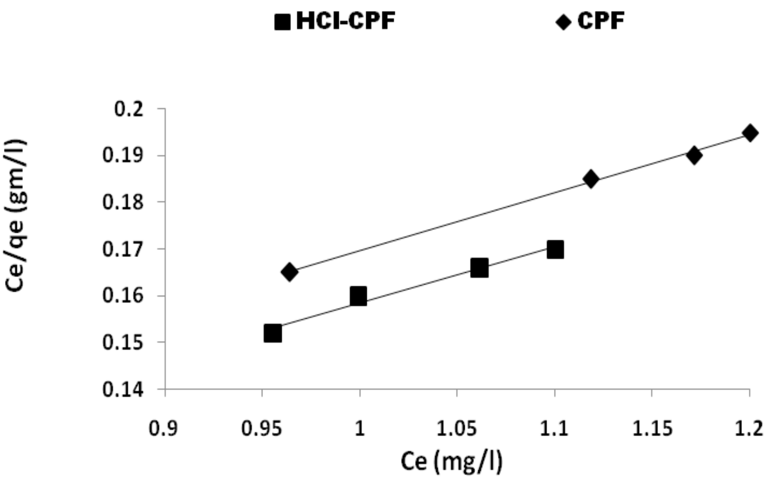


Fig. 10. Langmuir isotherm model of AR73 dye adsorption by CPF and HCl-CPF.

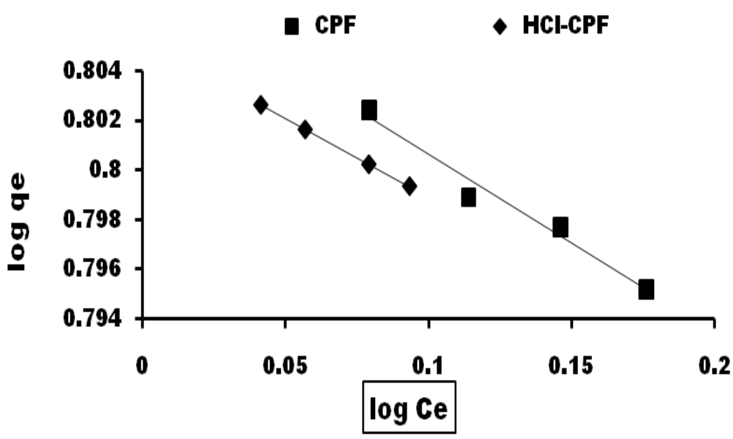


Fig. 11. Freundlichisotherm modelof AR73 dye adsorption by CPF and HCl-CPF.

TABLE 1. Isotherm modelsconstants for the adsorption ofAR73 dye onto CPF and HCl-CPF surfaces.

Adsorbents	Langmuir isotherm constants				Freundlich isotherm constants		
	q_m (mg/g)	b (L/ mg)	R^2	R_L	k_F	n	R^2
CPF	22.4	0.3	0.987	0.12	0.85	1.23	0.972
HCl-CPF	65	0.09	0.998	0.34	1.48	1.5	1

TABLE 2. Thermodynamic parameters for adsorption of AR73 onto CPF and HCl-CPF surfaces.

adsorbents	adsorbate	ΔH° ($KJ.mol^{-1}$)	ΔS° ($KJ.mol^{-1}$)	ΔG° ($KJ.mol^{-1}$)		
				303K	313K	323K
CPF	AR73	-9.206	0.0820	-11.68	-11.73	-11.89
HCl-CPF		-9.441	0.0911	-12.16	-12.34	-12.43

TABLE 3. Comparison of the maximum adsorption capacities of AR73 on various adsorbents based on Langmuir model.

Adsorbents	Adsorption capacities (mg/g)	References
chitosan nano particles	1.25	[33]
Partheniumhysterophorus L	2.86	[29]
Magnetic nanoparticles Fe_3O_4	40.1	[30]
copper diethyldithiocarbamate ($Cu(DDTC)_2$)	42.9	[31]
HCl-water hyacinth stems (HCl-WHS)	50	[34]
CPF &HCl-CPF	22.4 & 65	THIS STUY
chitosan	728.2	[32]

Conclusions

This study was carried out on raw and acid activated fruits of *Calotropis procera* plant and showed that :

1. The *Calotropis procera* friuts, either raw or modified, can be successfully used for the removal of the acid red 73 dye from aqueous solutions.
2. The treatment of raw *Calotropis procera* friuts with HCl modify its composition and behavior. The modified *Calotropis procera* friuts show higher uptake of studied dye as compared with the raw fruits.
4. The changes in the characteristics of the modified *Calotropis procera* friuts were verified by FTIR and SEM.
5. Isotherm studies also confirmed that modified *Calotropis procera* fruits is a suitable adsorbent for effluents treatment, that containing AR73 dye.

References

1. Hashemian S., Forighimoghadam A., Effect of copper doping on CoTiO3 ilmenite type nanoparticles for removal of Congo red from aqueous solution. Chemical Engineering Journal, 235, 299–306 (2014).

2. McKay G., Adsorption of dyestuffs from aqueous solutions with activated carbon 1: equilibrium and batch contact-time studies. Journal of Chemical Technology and Biotechnology, 32 (8), 759–772 (1982).

3. Nigam P., Banat I. M., Singh D., and Marchant R., Microbial process for the decolorization of textile effluent containing azo, diazo and reactive dyes. Process Biochemistry, 31 (5), 435–442 (1996).

4. Dermentzis K., Marmanis D., Valsamidou E., Christoforidis A., Ouzounis K., Electrochemical decolorization treatment of nickel phthalocyanine reactive dye wastewater. Environmental Engineering and Management Journal, 10, 1703-1709 (2011).

5. Forgacs E., Cserhati T., Oros G., Removal of synthetic dyes from wastewaters: a review. Environment International, 30, 953-971 (2004).

6. Tawfik A., Zaki D., Zahran M., Decolorizing of reactive dyes wastewater via down-flow hanging sponge (DHS) system. Environmental Engineering and Management Journal, 16, 39-46 (2017).

7. Zhang F., Yediler A., Liang X., Kettrup A., Effects of dye additives on the ozonation process and oxidation by-products: a comparative study using hydrolyzed CI reactive red 120. Dyes and Pigments, 60, 1-7 (2004).

8. Jaycock M.J., Parfitt G.D., Chemistry of Interfaces, Ellis Horwood, Onichester, 12-13 (1981).

9. Kitinya J., Onyango M., Ochieng A., Removal of multilan red and multi-active blue dyes from aqueous solution by adsorption and oxidation techniques: equilibrium, kinetics and thermodynamic studies. Environmental Engineering and Management Journal, 16, 2731-2743 (2017).

10. Mrudula V, Vijaya T, ChnadraMouli K, Naga Jyothi U, Aishwarya S, Reddy Vasudeva, Novel method for removal of heavy metals by using low cost adsorbents. Indo Am J Pharm Res, 6(5),5472–5480 (2016).

11. Hong S., and Ning C., Adsorption of Cr(VI) on Fe-Ni modified bentonites. Environmental Engineering and Management Journal, 10 (7), 875–879 (2011).

12. Koppelman M. H. and Dillard J. G., "A study of the adsorption of Ni(II) and Cu(II) by clay minerals. Clays and Clay Minerals, 25 (6), 457–462(1977).

13. Hashemian S., Removal of acid red 151 from water by adsorption onto nano-composite MnFe2O4/ kaolin. Main Group Chemistry, 10 (2),105–114 (2011).

14. Hashemian S., MnFe2O4/bentonitenano composite as a novel magnetic material for adsorption of acid red 138. African Journal of Biotechnology, 9 (50), 8667–8671(2010).

15. Hashemian S. and Mirshamsi M., Kinetic and thermodynamic of adsorption of 2-picoline by sawdust from aqueous solution. Journal of Industrial and Engineering Chemistry, 18, 2010–2015 (2012).

16. Hashemian S., Modified sawdust for removal of methyl violet (basic dye) from aqueous solutions. Asian Journal of Chemistry, 21 (5), 3622–3630 (2009).

17. Habib A., Islam N., and Alam A. M. S., Removal of copper from aqueous solution using orange peel, sawdust and bagasse. Pakistan Journal of Analytical and Environmental Chemistry, 8 (2), 21–25(2007).

18. Ofomaja A.E., Kinetic study and sorption mechanism of methylene blue and methyl violet onto mansonia (Mansoniaaltissima) wood sawdust. Chemical Engineering Journal, 143 (1–3), 85–95 (2008).

19. Murti Y., Yogi B., and Pathak D., Pharmacognostic standardization of leaves of Calotropis procera (Ait.) R. Br. (Asclepiadaceae). Int. J. Ayurveda Res., 1, 4(2010).

20. Gupta V. K., I. Ali I., Removal of lead and chromium from wastewater using bagasse fly ash--a sugar industry waste. J. Colloid Interface Sci., 271 (2), 321–328 (2004).

21. Ahalya N., Kanamadi R.D., Ramachandra T.V., Biosorption of chromium (VI) from aqueous solutions by the husk of Bengal gram (Cicerarientinum). J. Biotechnol, 8, 258–264 (2005).

22. Langmuir I., The adsorption of gases on plane surface of glass, mica and platinum. Journal of the American Chemical Society, 40, 1361-1403 (1918).

23. Shawabkeh R. A., Tutunji M. F., Experimental study and modeling of basic dye sorption by diatomaceous clay. Appl. Clay Sci., 24,111–120 (2003).

24. Freundlich H.M.F., Over the adsorption in solution. Journal of Physical Chemistry, 57, 385-470 (1906).
25. Laabd M., Abdelhadi E., Hafsa C., Nouh A., Bazzaoui M., and A. Albourine A., Etude cin´etique et Thermodynamique de l'adsorption des colorants monoazo¨ıquessur la polyaniline. Journal of Materials and Environnemental Science, 6 (4), 1049–1059 (2015).
26. Kavitha D., and Namasivayam C., Experimental and kinetic studies on methylene blue adsorption by coir pith carbon. Bioresource Technology, 98, 14-21 (2007).
27. Tsai W.-T., Hsu H.-C., Su T.-Y., Lin K.-Y., Lin C.-M., and Dai T.-H., adsorption of cationic dye from aqueous solution onto acid-activated andesite. Journal of Hazardous Materials, 147 (3), 1056–1062 (2007).
28. Gupta V. K., Mittal A., and Gajbe V., Adsorption and desorption studies of a water soluble dye, Quinoline Yellow, using waste materials. Journal of Colloid and Interface Science, 284 (1), 89–98 (2005).
29. Khan, T. A., Ali, I., Singh, V. V., and Sharma, S., Utilization of fly ash as low cost adsorbent for the removal of methylene blue, malachite green and Rhodamine B dyes from textile waste water. Journal of Environmental Protection Science, 3, 11-22 (2009).
30. Argun M. E., Gu¨clu¨ D., Karatas M., Adsorption of Reactive Blue 114 dye by using a new adsorbent: Pomelo peel. J IndEng Chem., 20, 1079–1084 (2014).
31. Bulgariu D., Bulgariu L., Equilibrium and kinetics studies of heavy metal ions biosorption on green algae waste biomass. BioresourTechnol, 103,489–493 (2012).
32. Asfour H.M., Fadali O.A., Nassar M.M. and El-Geundi M.S., (1985), Equilibrium Studies on Adsorption of Basic Dyes on Hard Wood. J. Chem. Tech. Biotechnol., 35 (A), 21–27 (1985).
33. Kavitha D., and Namasivayam C., Experimental and kinetic studies on methylene blue adsorption by coir pith carbon. Bioresource Technology, 98, 14-21 (2007).
34. Hassan A., Kinetics and Thermodynamic Study of Acid Red 73 Dye Removal on HCl- Water Hyacinth Stems Biomass. Egypt.J.Chem., 63 , accepted, (2020) (in press).