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Application Of Optimize The Process Variables Using A Novel Adsorbent As *Epicarp Of Ricinus Communis*- Adsorption Studies On The Removal Of Reactive Dyes In Single And Multi System

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ABSTRACT

The purpose of this research is to obtain optimal processing conditions for activated carbon from epicarp of ricinus communis by chemical activation with H_3PO_4 using response surface methodology of the activated carbons produced were characterized by carbon yield (%), SEM-Edax, XRD, and Fourier transform infrared spectroscopy. In order to optimize the preparation conditions of the activated carbon (AC), Taguchi experimental design method was used. The models were able to predict well the values of the responses when the optimum variable parameters were validated as proven by the generally acceptable values of the residual percentages. Direct characterization of the pores using the SEM was found to be a good technique to actually see the pores and get actual measurements. The activation process was performed at the microwave input power of 100W for 4 min. The adsorption behavior was examined using Reactive dyes single, binary, tertiary, quartary system as adsorbate. Removal of these dyes from aqueous solution using Phosphorous ricinus communis (PRC) has been investigated. This study was performed to investigate adsorption of single and multin reactive dyes aqueous solutions onto PRC. The constants parameters obtained from single (RY-15). The extent of adsorption capacity of the binary and ternary reactive dyes tested on PRC was low (64.86-41.38%) as compared to single metal ions. The equilibrium data of the adsorption was well fitted to the Langmuir isotherm. The adsorption process follows the pseudo-second-order kinetic model. It was shown that the equilibrium experimental data for reactive dye adsorption could be well described by the Freundlich model, but for disperse dye the Langmuir model could be better. Based on the well correlated adsorption isotherm, an adsorption process design model was developed for the design of a two-stage batch adsorber to predict the minimum amount of adsorbent to achieve a specified percentage of dye removal at a given volume of wastewater effluents. The adsorption process design analysis indicated that compared with the singlestage batch adsorption, the two-stage process could significantly save adsorbent to meet the higher demands of dye removal efficiency

Keywords: Ricinus Comminus; Adsorption of reactive dyes; single and multi system, Kinetics

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INTRODUCTION

Waste effluent from the textile industry can be particularly problematic due to the presence of colour in the final effluent. This colour on entering the waterways is highly visible and thus undesirable. Conventional treatment facilities are often unable to remove certain forms of colour, particularly arising from reactive dyes due to their high solubility and low biodegradability. The failure of conventional physicochemical methods as a technique for treating reactive dyewaste could be overcome by adsorption. Hence, adsorption is recommended as a viable means for reactive dye removal.[1].

Dyeing and finishing of textile fabrics are generally performed in water based media. This process has environmental problems including water pollution due to discharge of various chemical additives[2-3] . Reactive dyes are mainly dyes for cellulose fabrics. However, the fixation of the reactive dyes on cellulose fabrics is lower and a lot of unfixed dyes may be lost to the effluent during dyeing processes. Removing pollutant from wastewater has grown with rapid industrialization [4-6].

Various physicochemical and biological techniques can be employed to remove dyes from wastewaters. They include the membrane coagulation/flocculation [7], ion exchange [8] advanced oxidation (chlorination, ozonation) [9], decolourisation and metabolism of the commercially used Remazol dye by a strain of *P. Chrysosporium* [10] and biological treatment (bacterial and fungal biosorption), biodegradation in aerobic or anaerobic conditions [11]. In comparison with other techniques adsorption is superior in simplicity of design, initial cost, ease of operation and insensitivity to toxic substances. Adsorption is one of the most effective physical processes for colour removal. This technique uses a large number of suitable adsorbents as activated carbon[12-13].

Consequently, the high cost of the activated carbon, coupled with the problems associated with regeneration, has necessitated the search for alternate adsorbents. Therefore, there is a need to produce activated carbon from cheaper and readily available materials, which can be used economically on a large scale. Hence, this study was undertaken to address the problems associated with multi component adsorption from aqueous solutions. This is essential for accurate design of adsorption systems as the effect of multicomponent interactions in the process effluent may cause deterioration in the adsorption capacity of activated carbon for dyestuffs.

MATERIALS AND METHODS

Preparation of the epicarp of *Ricinus communis* adsorbent (PRC)

The epicarp of *Ricinus communis* was used as the raw material for the preparation of activated carbon. It was obtained from an agricultural farm in Coimbatore District, Tamilnadu, India. It was air-dried and powdered in a grinder. Powdered epicarp of *Ricinus communis* samples with mass of 6g was mixed with 30mL of H_3PO_4 to vary concentration in the range of 30-60% by volume. The slurry was kept at room temperature for various time spans in the range of 16-28 h to ensure the access of the H_3PO_4 to the *Ricinus communis*. After mixing the slurry was placed in a microwave oven at 100 W for 4 min. After a certain

microwave heating power and microwave radiation time, the samples were washed sequentially with 0.5 M NaOH, hot water and cold water until the pH of the washing solution reached 6 -7, filtered and finally dried at 105°C
 The yield of the carbon samples was estimated according to

$$Y = \left(\frac{M}{M_0}\right) X100 \tag{1}$$

Where M is the weight of activated carbon and M₀ is the weight of dried epicarp of *Ricinus communis*.

Optimization of activated carbon preparation conditions

In order to optimize the preparation conditions of the activated carbon (AC), Taguchi experimental design method was used. An L₁₆ orthogonal array with four operational parameters each in four levels was used to evaluate the corresponding optimal vales. These variables and their levels are summarized in Table 1. The complete design matrix of the experiments and the obtained results are shown in Table 2. Iodine is considered as probe molecules for assessing the adsorption capacity of adsorbents for solutes of molecular sizes less than 10 Å [14]. Iodine number was normally listed as specification parameter for commercial activated carbons. Therefore, the responses were iodine number (Y₁, mg/g) and activated carbon yield (Y₂, %).

Table 1: Design and levels

Independent variable	symbol	Range and levels			
		1	2	3	4
Impregnation time(h)	A	16	20	24	28
Radiation time (min)	B	10	8	6	4
Concentration of H3PO4 (vol %)	C	30	40	50	60
Radiation power(W)	D	200	400	600	800

Table 2 Experimental design matrix and results.

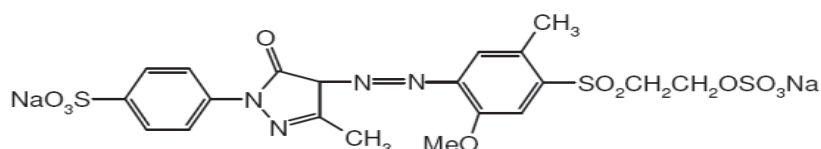
Runs	Variables				Responses(Y)	
	A	B	C	D	Iodine number (y ₁ ,mg/g)	Yield of the AC (y ₂ , %)
1	1	1	1	1	833.74	60.21
2	2	1	1	1	755.56	73.07
3	3	1	1	1	717.39	40.02
4	4	1	1	1	659.23	39.4
5	1	1	1	1	833.74	60.21
6	1	2	1	1	484.725	54.34

7	1	3	1	1	562.281	54.59
8	1	4	1	1	698.004	78.45
9	1	1	1	1	833.74	60.21
10	1	1	2	1	814.338	56.25
11	1	1	3	1	601.059	77.75
12	1	1	4	1	639.337	71.9
13	1	1	1	1	833.74	60.21
14	1	1	1	2	639.837	61.1
15	1	1	1	3	562.281	44.4
16	1	1	1	4	562.281	58.3

Scanning electron microscope SEM- Edax analysis was performed to study the textural structure of adsorbent before and after the activation process. While surface functional groups of PRC before and after the activation process were detected by Fourier transform infrared (FTIR) spectroscopy (FTIR-2000, PerkinElmer) by scanning in the range of 4000–400 cm^{-1} . The FTIR analysis was carried out on by Shimadzu spec, DST lab, Karpagam University. The structures of these samples were checked by the powder XRD technology with Cu Ka radiation at room temperature, using a Rigaku diffractometer (MXP-AHP18) for 2h .

Preparation of dye solution

Reactive yellow (RY), Reactive Green (RG), Reactive Red (RR), Reactive Block (RB) dyes were purchased from sd fine – chem. Limited, Mumbai. These dyes are based on vinyl sulphone reactive group, which have negative charges in aqueous solutions. Deionized water was used to prepared all the reagents and solutions. The stock solution was prepared by dissolving accurately weighed dye in distilled water to a concentration of 500 mg/L of Reactive yellow, Reactive Green, Reactive Red, Reactive Block dye studied. The experimental solution was obtained by diluting the dye stock solution in accurate proportions to different initial concentrations. The analysis of single, binary, tertiary, quartary were spectrophotometrically estimated by monitoring the absorbance at 420nm, 598nm using UV-vis spectrophotometer(shimadzu). It was found the supernatant from the activated carbon did not exhibit any absorbance at this wavelength and also that the calibration curve was very reproducible and linear over the concentration range used in this work.



Reactive yellow 15

Molecular Formula: $\text{C}_{20}\text{H}_{20}\text{N}_4\text{Na}_2\text{O}_{11}\text{S}_3$

Molecular Weight: 634.57

$\lambda_{\text{max}} = 420\text{nm}$

Determination of Ph

About 10 g of the material was weighed and taken in a 500 mL beaker. 300 ml of freshly boiled and cooled water, whose pH was adjusted 7.0, was added and heated to boiling. After 10 minutes, the solution was filtered and the first 20 mL of the filtrate was rejected. The remaining filtrate was cooled and the pH was determined using a Deluxe pH Meter, Model 101E.

Conductivity

About 1 g of the material was placed in 250 mL conical flask. 100 mL distilled water was added and agitated for 1 hour and conductivity was measured using a Digital Conductivity Meter, Model 611.

Adsorption equilibrium studies

Batch adsorption experiments were carried out in a rotary shaker at 160 rpm using 250 mL shaking flasks at room temperature. The adsorbent PRC(0.2 g, 0.6 g and 1 g) were thoroughly mixed with 50 mL of the dye solution. The isotherm studies were performed by varying the initial dye concentrations from 25 mgL⁻¹ to 200 mgL⁻¹ at optimum pH adjusted before the addition of the adsorbent. After shaking the flasks for equilibrium time, the reaction mixture was analyzed for residual dye concentration. All the experiments were duplicated and only the mean values are reported, the maximum deviation observed was less than ± 4 %.

The amount of dye adsorbed at equilibrium onto carbon, q_e (mg/g), was calculated by the following mass balance relationship:

$$q_e = \frac{(C_o - C_e)V}{W} \quad (2)$$

Where C_o and C_e are the initial and equilibrium concentrations (mgL⁻¹) of the adsorbate, V is the volume (L) of the solution and W is the weight (g) of the adsorbent used.

Kinetics studies

The kinetic studies were carried out by taking 50 mL of dye solution in 250 ml shaking flasks and treated with 0.2 g of adsorbent were shaken at room temperature. Samples of 1.0 mL were collected from the duplicate flasks at required time intervals viz. 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140 and 150 minutes and were centrifuged for 5 minutes. The clear solutions were analyzed for residual dye concentration in the solutions.

Desorption studies

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the dye. After adsorption, the adsorbate - loaded adsorbents were separated from the solution by centrifugation and the supernatant was drained out. The dye

loaded adsorbent was given a gentle wash with double - distilled water to remove the unadsorbed dye if present. The dye loaded sample were agitated with distilled water by adjusting the initial pH values with 0.1M HCl or 0.1 M NaOH to from a series of pH from 2 to 9. The desorbed dye in the solution was separated by centrifugation and analyzed as before. The percentage of desorption was calculated.

RESULT AND DISCUSSION

Optimization of AC preparation

Main factors

According to the L_{16} array designed by Taguchi method, 16 different AC samples were prepared. Iodine number and yield of each sample were determined and shown in Table 2 describes that both radiation time and concentration of H_3PO_4 were significant factors for the yield of AC, and shows that not all factors were significant impact factors affected the iodine number of AC.

Effect of independent variable on AC preparation

Effects of Impregnation Time

The results presented in Fig (1a) and Fig (1b), impregnation time (parameter A) had little influence on the yield, But has strong influence on Iodine number. The action of H_3PO_4 on the lignocelulosic material could be expected as the following mechanism. During impregnation stage the acid attacked the cellular structure of epicarp of *Ricinus communis*, forming cleavage to the linkages between the lignin and cellulose. It was followed by recombination reactions, where large structural units and strong cross linked solids were formed. This acid worked, principally, in early stage during impregnation and might be extended to have a slight effect in the carbonization stage [15].

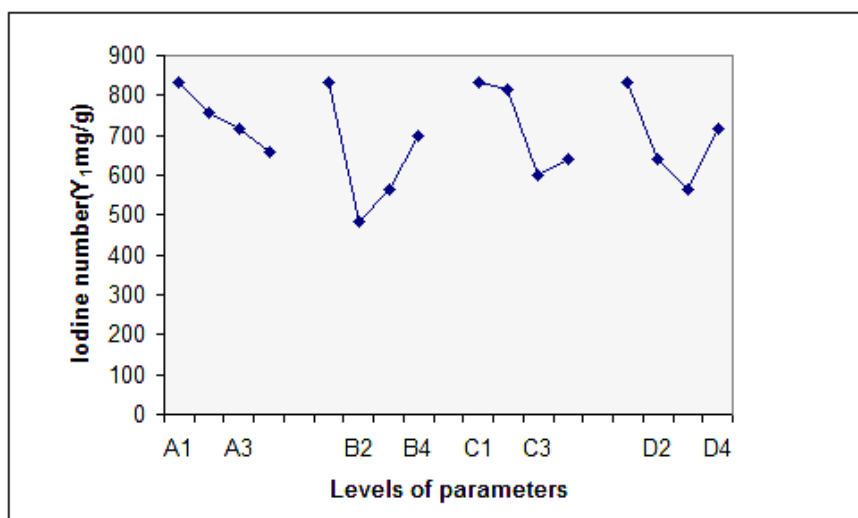


Fig. 1a. The effect of operational parameters on response of the prepared AC samples ((A) Impregnation time, (B) Radiation time, (C) concentration of H_3PO_4 and (D) Radiation Power.

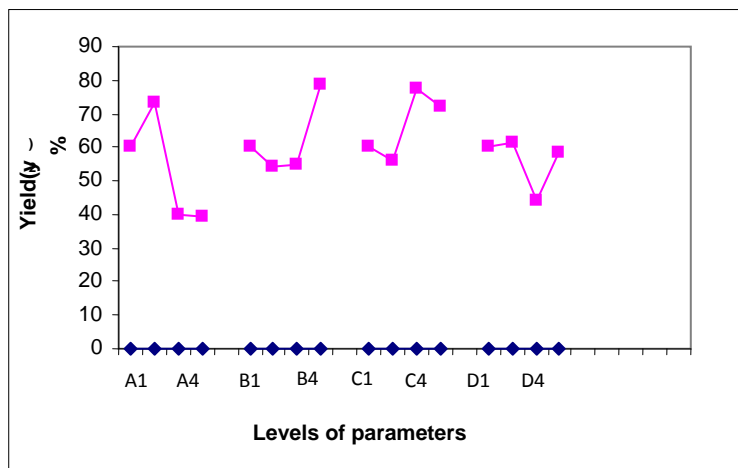


Fig. 1b. The effect of operational parameters on response of the prepared AC samples ((A) Impregnation time, (B) Radiation time, (C) concentration of H_3PO_4 and (D) Radiation Power.

Effects of radiation time

As shown in Fig(1a) and Fig (1b), the adsorption ability of the AC increased gradually lengthening activation time (parameter B) up to 8 min. while it decreased as excessive extension of activation time up to 10min. There was similar tendency of carbon yield. It was also found by Li et al. when they prepared the AC from tobacco stems using microwave radiation [16]. The improvement of activation degree depended on the microwave radiation time, more and more active sites and pores were formed on the surface of samples. Therefore, the adsorption capacity of AC would be increased along with the prolongation of microwave radiation time. However, the pores of carbon would be burnt off by microwave heating. When microwave radiation time reached a certain value, which would lower the iodine number and the yield of AC.

Effect of Concentration of H_3PO_4

The dosage of the activating agent is another factor that has significance on the activation process. It is proposed that phosphoric acid has two important functions: it promotes the pyrolytic decomposition of the initial material and the formation of the cross linked structure. The yield and iodine numbers of the prepared samples were increased by exceeding the phosphoric acid concentration up to 50% by volume and then decreased to 60% by volume. The observed reduction in the sample due to the excess H_3PO_4 content could be attributed to the possible formation of phosphates via interaction with the inorganic present under pyrolysis action, which may block some of the pores present [17]. These salts would be leached out by 0.5M NaOH in the end. This assumption will be confirmed later by FT-IR spectra through the appearing phosphate band.

Effect of radiation power

Fig (1a and 1b) shows that both the yield and the adsorption ability of AC samples were increased, enhancing radiation power (parameter D) up to 200W. One possible reason

is that pore structure on the surface of AC was fully developed at the power up to 200 W. The yield and adsorption ability of the AC reduced when radiation power increased up to 400 W. A small quantity of carbon was possibly burnt out and pore structure on its surface destroyed under over full energy. Similar results have been obtained by other researchers[16].

Optimized Conditions

In the production of commercial activated carbon, relatively high product yield and adsorption capacity were expected. Therefore, more attention should be paid to improve the carbon yield and enhance its adsorption capacity for economical viability. However, it was difficult to optimize both these responses under the same condition, for the different interest in different region. Therefore, in order to compromise the two responses, two experimental conditions with the highest desirability were selected to verify. The optimum conditions were radiation power of 100 W, radiation times of 4 min, concentration of H_3PO_4 of 30 % by volume and impregnation time of 16 h.

Characterisation of Phosphoric acid activated *Ricinus communis* sample (PRC)

XRD

The smaller the particle sizes of a porous carbon, the greater the rate of diffusion and adsorption. Intraparticle diffusion is reduced as the particle size reduces, because of the shorter mass transfer zone, causing a faster rate of adsorption. Since we have prepared our carbon in a powdered form so it has a great efficiency of removal of colour.

X- ray Diffraction Studies of the carbon prepared from the Epicarp of *Ricinus communis* were the preparation of phosphorous activated ricinus communis (PRC) before and after adsorption of PRC carried out using XRD. The XRD pictures taken before and after adsorption are shown in fig .3 It is evident from the figure that there is no appreciable change in the spectra. This may be due to the fact that adsorption did not alter the chemical nature of the surface of the adsorbent i.e. the adsorption is physical in nature.

The before and after adsorption of activated carbon were exhibited two peaks at around $2\theta =$ before PRC 22.2° and 27.6° and after PRC 22.1° and 29.1° which correspond to the peak of graphite [18]. At the same time, it exhibits noise of the powder XRD signals. This reveals a predominantly amorphous structure of carbon. In this result, it can be explained that the pyrolytic reaction of organic compounds consists of the breaking of chemical bonds. These compounds form typical graphitic layers and stacks of planes during carbonization stacks of planes during carbonization [19].

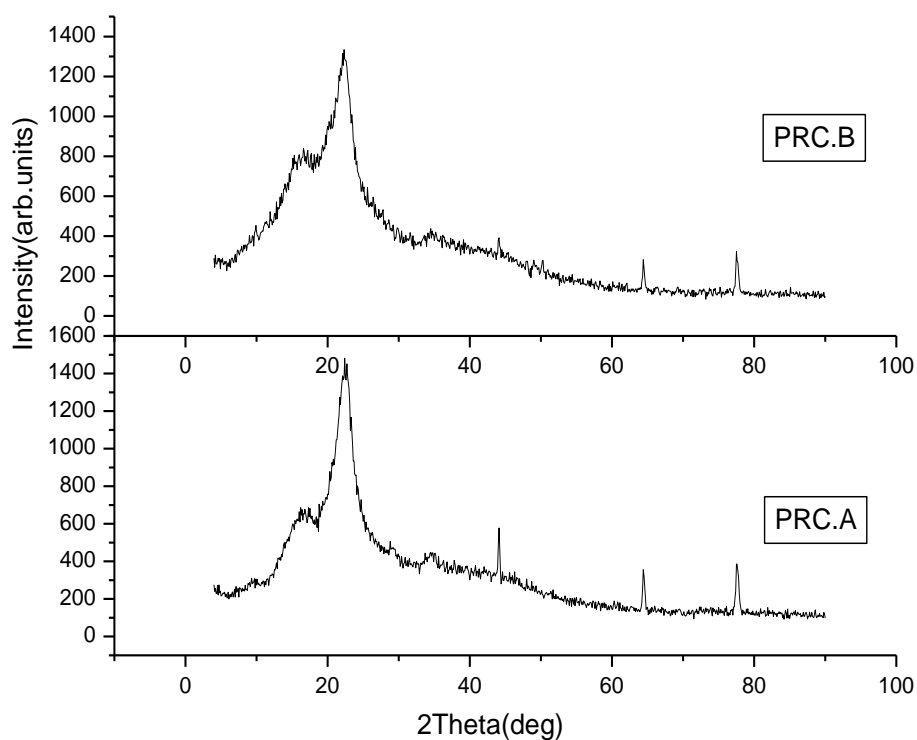
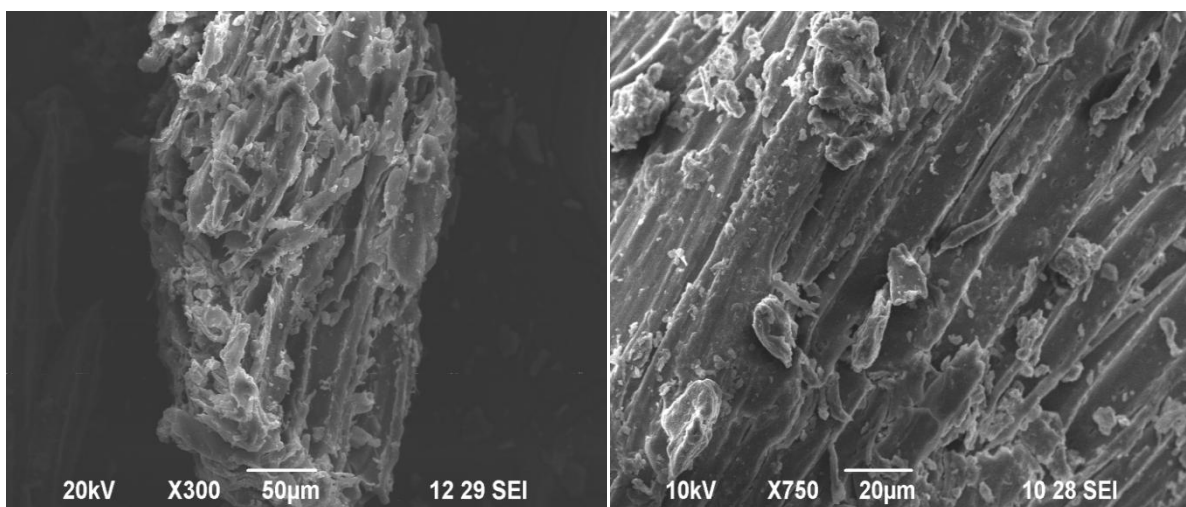
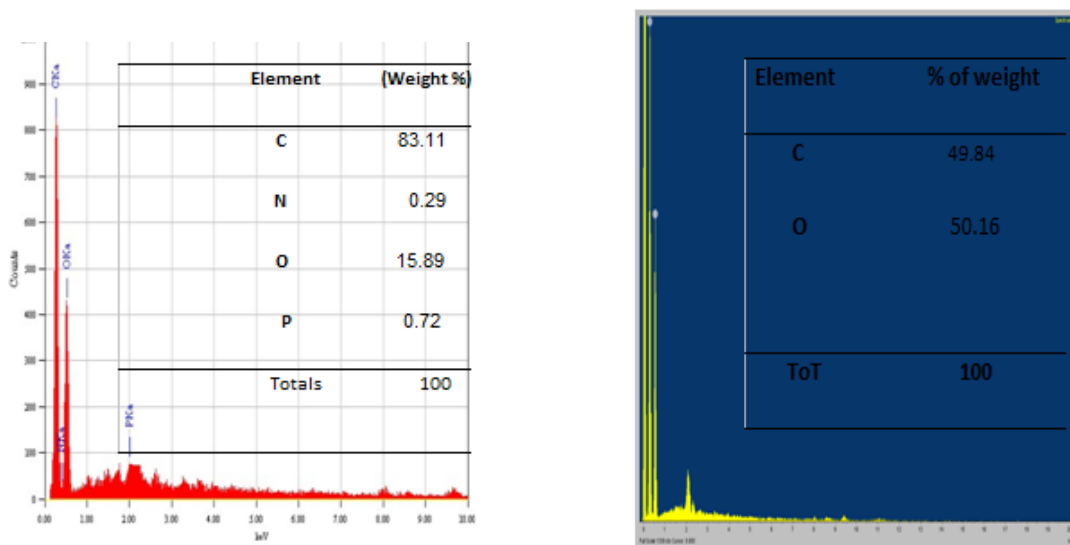


Figure 1.X-ray diffraction studies of before and after adsorption onto PRC

Scanning electron microscopic (SEM)- Edax studies

Scanning electron microscopy was used to study the surface morphology and the pore size of the samples. Samples of before and after adsorption of PRC were subjected to SEM studies and SEM micrograph (Fig.) shows many orderly and developed pores. It is clear that the adsorbent has considerable number of heterogeneous pores where there is a good possibility for dye to be trapped and adsorbed. Similar trends were reported in adsorption of methylene blue onto pumpkin seed hull [20]

The surface morphology Fig of PRC before and after adsorption was examined by means of scanning electron microscopy (SEM, LEO 435 VP model) at an accelerating voltage of 40 kV. As it is known, SEM is one of the most widely used surface characterization method. PRC has heterogeneous surface and micro-pores smaller than 5 μm as seen from its SEM micrographs. It can be seen from the micrographs that the external surface of the activated carbon is full of cavities compared with after adsorption PRC, and the pores were different sizes and different shapes.



Before adsorption onto the PRC

after adsorption onto the PRC

Figure 2. Sem/Edax analysis

The morphologies of both before and after adsorption of PRC are characterized by means of SEM and Edex elemental analysis. The results of Edax analysis shown in Fig confirm Before PRC four major elements, i.e., carbon, oxygen, nitrogen and phosphorous. While dye loaded After PRC shows without presence of Nitrogen, phosphorous and presence of oxygen and carbon presumably due to its influence on the surface properties of the adsorbent and the dissociation of the adsorbate molecule [21].

Infrared spectroscopy

FT-IR spectra were recorded over the wave number range 500–4000 cm^{-1} for both FTIR spectra of PRC before and after adsorption were shown in Figure(3).

Before adsorption of PRC which are followed by fixation of carbon and other species, some changes can be observed such as presence of a very broad band centered at 3406.29 cm^{-1} , which was assigned to the O-H stretching vibration of the hydroxyl functional groups including hydrogen bonding. The intense band at about 2927.94 cm^{-1} for the precursor was attributed to the C-H stretching vibration [22]. The peak at 1639.49 cm^{-1} was characteristics of the C=O stretching vibration of lactonic and carbonyl groups[23-24](Moreno-Castilla et al., 2000; Abdel- Nasser et al;2003). The peaks occurring at 1396.46 cm^{-1} , 1185.00 cm^{-1} were all ascribed to oxygen functionalities such as highly conjugated C-O stretching, C-O stretching in carboxylic groups, and carboxylate moieties[25-26]. Mean while, the surface chemistry of PRC difference from the RRC the band at around 987.56 cm^{-1} was characteristic to P=O was proposed to be condensed phosphates bond to carbon lattice via C-O-P bonding[27]

After adsorption of dye loaded PRC were 3356.14, 2906.73, 16412, 1058.9. The wide band at 3430 cm^{-1} shown in the spectrum of PRC is attributed to stretching vibration of hydroxyl group of PRC. This band was shifted to 3424 cm^{-1} when after adsorption of PRC 3356.14 cm^{-1} was adsorbed. It may indicate a hydrogen bond between before and after adsorption OH groups of PRC.

Batch mode adsorption studies

A comparative study of adsorption single binary, tertiary and quaternary system onto were carried out by using PRC as adsorbents. The results of dye removal were shown in Table 3. The experiments were performed by agitating 0.2 g of each adsorbent in 50 mL of 100 mg/L dye solution at 160 rpm for 2 hours. The PRC showed good adsorption behaviour towards dye solution, where the % dye removal was 79.91 in single systems, However, removal of Reactive Yellow dye solution was favourable by PRC where in single and binary system. The hydroxyl groups of the natural adsorbent help in the binding of the cationic dye molecules.

Table 3. Comparative study of Reactive dyes adsorption by PRC

Adsorbate	% Dye Removal
Single (RY)	79.91
Binary (RY+RG)	64.86
Tertiary (RY+RG+RR)	58.33
Quaternary (RY+RG+RR+RB)	41.38

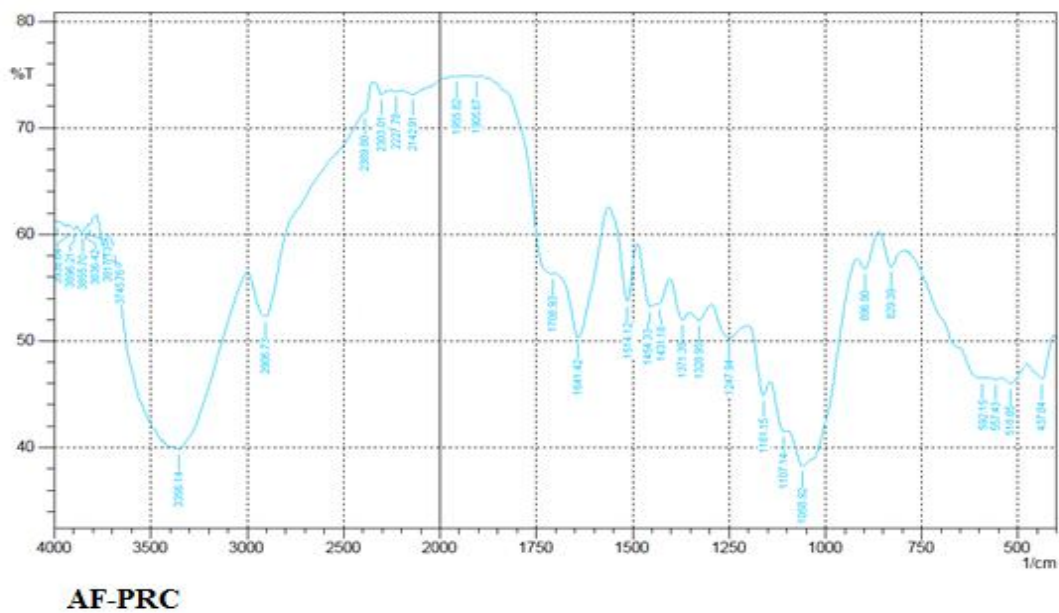
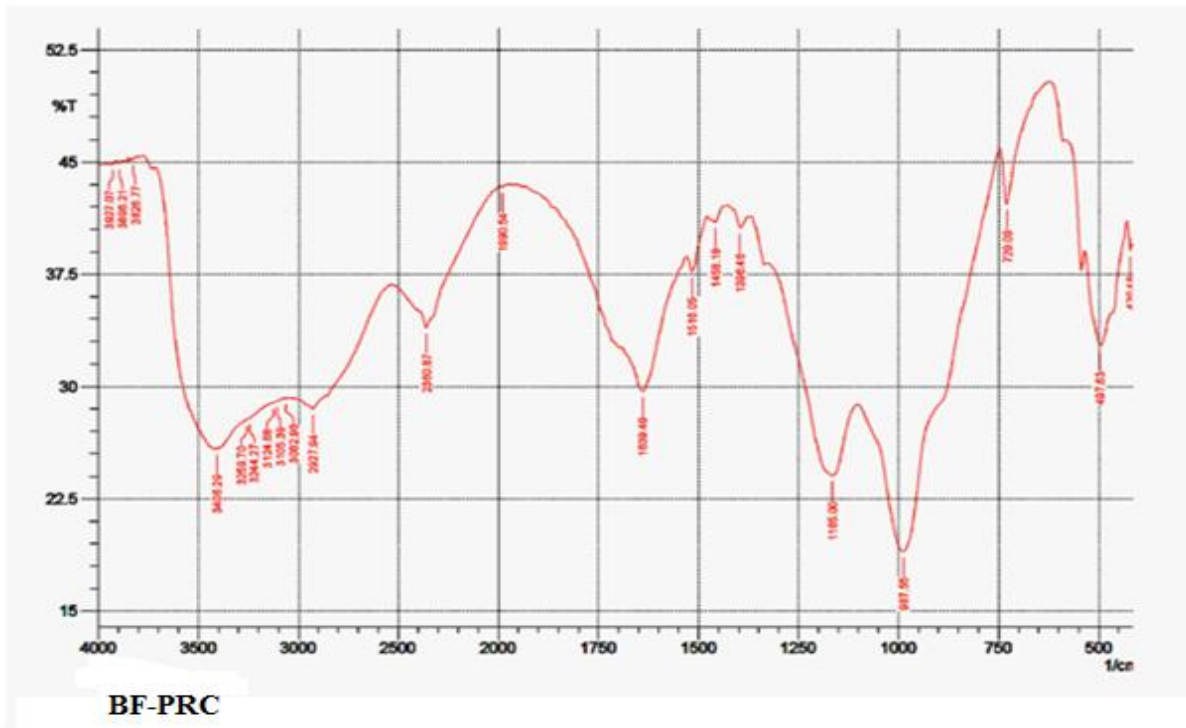


Figure.3 FT-IR spectrum of PRC before and after adsorption Reactive yellow-15

Effect of pH on dye adsorption

The effect of initial pH of dye solution on the percentage removal of Reactive Yellow-15 single and different mixture of reactive dyes were studied by varying the initial pH(2-10pH) under the 100ppm solution agitation at 160 rpm speed constant process parameters. The results are shown in Fig..The dye adsorbed by PRC was higher at lower pH. The

optimum pH was attained at pH of one 3 pH. Similar observations have been reported for the adsorption of Reactive yellow 15 dyes onto Wheat husk [28]. As the pH of the solution increased the dye adsorbed decreased considerably. The same behavior was observed by many authors[29-30]. which exhibited a positive surface charge in water. In the acidic pH range of 2-3, the positive surface charge would increase leading to the attraction of the negatively charged functional groups on the Reactive dye. As a consequence of these experiments, a pH value of 3 was used in all subsequent adsorption tests for all system.

The result also show that carbon affinity was still higher for Reactive yellow in single system and followed by binary system (RY+RG), tertiary system(RY+RG+RB), quartnary (RY+RG+RB+RR). This effect was also reported in a study of mixture of reactive dyes. The adsorption capacity of the individual dye from any mixture was lower than adsorption from single component system for all dyes studied[31].

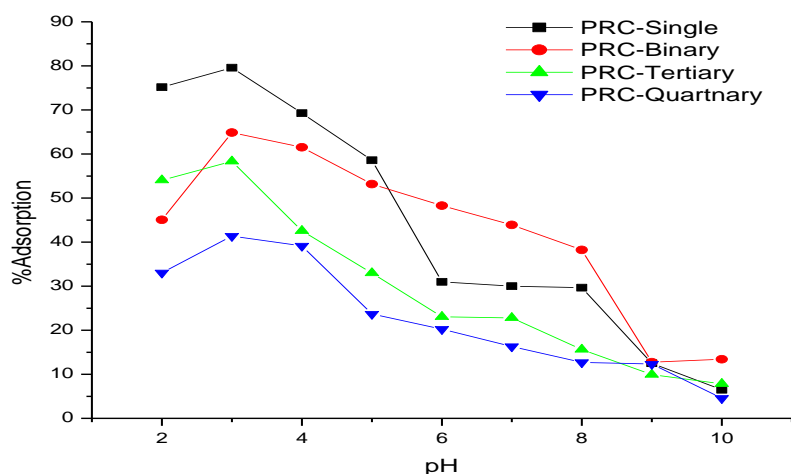


Figure 4. Effect of pH on the removal of reactive dyes (single,binary, tertiary, quartnart system) onto the PRC

Effect of Dye concentration and contact time on dye adsorption:

The effect of contact time for adsorption process was carried out to determine the equilibrium point. The study was carried out at four different temperatures, pH and concentration. It was found for all the set of experiments, Effects of contact time and dye concentration on adsorption of Reactive Yellow 15 by the epicarp of *Ricinus communis* as adsorbent are shown in Fig. The extent of dye adsorption increased both as the initial dye concentration decreased and also as the contact time increased. the adsorption was rapid up to 20 min and latter on became slow, and finally the systems reached equilibrium around 150 min. Henceforth the maximum time of adsorption was restricted up to 150 min. The equilibrium was attained in 150min for single system . A contact time of 150 min was used in subsequent adsorption tests. Equilibrium adsorption was attained within 150min for single system.

Effect of adsorbent dose

The adsorption of CV and RH B was studied by changing the quantity of

adsorbent (0.2,0.4,0.6,0.8 and 1 g) in the test solutions while keeping the initial dyes concentration 100 mgL^{-1} . The effect of adsorbent dose was observed by keeping the optimum pH at equilibrium times (Fig. 6) for each adsorption process. It was observed that the percentage of adsorption increases with increase in adsorbent dose. At equilibrium time the percentage of adsorption increases from single, binary, tertiary and Quartnary system. Maximum dye removal was achieved within 10 – 50 minutes after which dye concentration in the reaction solution was almost constant. Increase in the adsorption with adsorbent dose can be attributed to increased adsorbent surface area and availability of more adsorption sites, while the unit adsorbed of dye decreased with increase in adsorbent dose [32-33]. It was observed that the percentage of adsorption increases with increase in adsorbent dose. At equilibrium time the percentage of adsorption increases from 79.45 % - 84.78 % (PRC-Single), 64.49-72.89 (PRC-Binary), 58.77-62.86% (PRC-Tertiary) and 41.28-51.27% (PRC-Quartnary) for an increase in adsorbent dose from 0.2 g to 1 g in Reactive Yellow -15 single and Different system onto PRC.

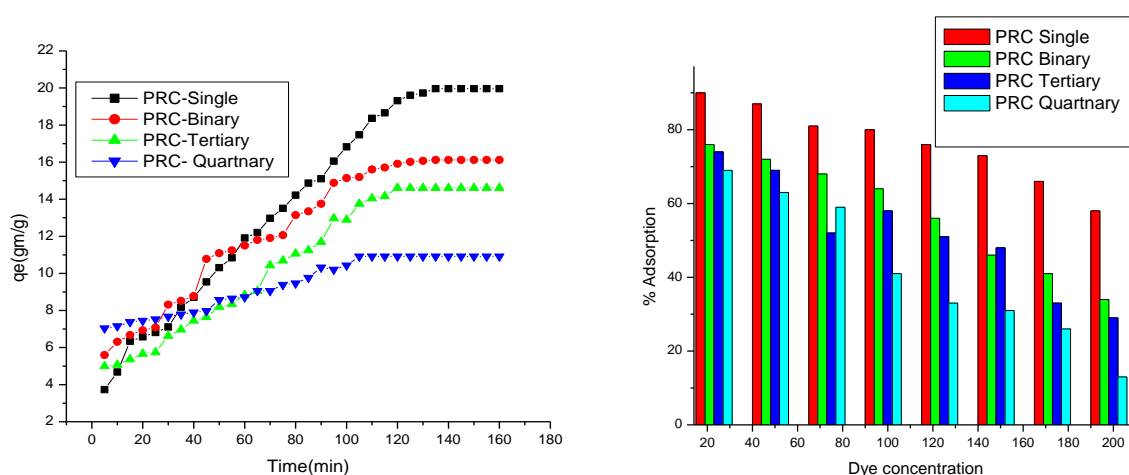


Figure.5 2 Effect of Dye concentration and contact time on removal of reactive dyes (single,binary, tertiary, quartnart system) onto the PRC

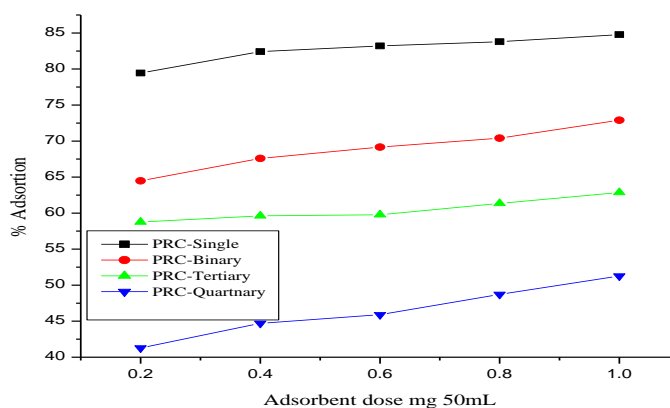


Figure 6. Effect of adsorbent dose on removal of reactive dyes (single,binary, tertiary, quartnart system) onto the PRC

Adsorption isotherm

Adsorption isotherms describe qualitative information on the nature of the solute-surface interaction as well as the specific relation between the concentration of adsorbate and its degree of accumulation onto adsorbent surface at constant temperature. Adsorption isotherms are critical in optimizing the use of adsorbents, and the analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purposes [34]. Four models were tested to describe the adsorption experimental results: the Langmuir model, the Freundlich model, Temkin, and Dubinin-Radushkevich (D-R).

Langmuir isotherm and Freundlich

In this work, Langmuir and Freundlich isotherm models were used to describe the relationship between the amount of dye adsorbed and its equilibrium concentration in solution for single, binary, tertiary, quaternary [(RY), (RY+RG), (RY+RG+RR), (RY+RG+RR+RB)] for 2 h. The Langmuir equation is probably the best known and most widely applied adsorption isotherm. It is represented as follows [35]. The linear form of the Langmuir isotherm model can be represented by using the equation

$$\frac{C_e}{q_e} = \frac{1}{K_a Q_m} + \left(\frac{1}{Q_m} \times C_e\right) \quad (3)$$

In eq.(3) C_e and q_e are as defined before in eq(2), Q_m is a constant and reflects a complete monolayer (mg g^{-1}); K_a is adsorption equilibrium constant (L mg^{-1}) that is related to the apparent energy of sorption.

The Freundlich equation [11] is an empirical equation employed to describe heterogeneous systems, characterized by the heterogeneity factor $1/n$, describes reversible adsorption, and is not restricted to the formation of the monolayer. The well known logarithmic form Freundlich isotherm is given by the following equation.

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

where, C_e = equilibrium concentration (mg L^{-1}), q_e ; amount adsorbed per unit weight of carbon (mg g^{-1}). The empirical Freundlich equation based on adsorption into a heterogeneous surface given as

$$q_e = K_f C_e^{1/n} \quad (5)$$

where K_f and n are the Freundlich constants for the system, which are indicators for the system, which are indicators of adsorption capacity and intensity respectively [36].

The fitness of adsorption data to these isotherm equations were checked by carrying out correlation analysis between the values of (i) $1/q$ and $1/C_e$, (ii) $\log q$ and $\log C_e$ for Single, binary, tertiary, and Quartnary of adsorption on to PRC. The adsorption isotherm parameters (constants) along with the r^2 values (correlation coefficients) are given in Table 4. As can be seen from the isotherms and b regression coefficients, the fitness with Langmuir isotherm model is better than Freundlich ($r = 0.993$). The Langmuir parameters, i.e., q_m and b , increased in sigle system but the competitive adsorption of binary tertiary and quartnary system, the results showed that that the adsorption of an individual dye decreased in the presence of a second or a n number dyes. It can be concluded that temperature can increase the kinetic energy of the dye molecules and, hence, enhanced the mobility of the dye ions. This indicates the applicability of the adsorption isotherm and monolayer coverage on the adsorbent surface

Table 4. Equilibrium model constants for adsorption of RY onto single, binary, tertiary and quartnary system of PRC

Reactive Dyes+adsorbent	Isotherm model					
	Langmuir			Freundlich		
	Q_m (mgg ⁻¹)	b (Lmg ⁻¹)	R^2	$1/n$	K_f (mgg ⁻¹)	R^2
SINGLE	35.71	0.0198	0.9930	1.962	1.0626	0.9550
BINARY	17.86	0.1081	0.9670	2.083	1.1409	0.8560
TERTIARY	16.39	0.0883	0.9540	2.118	1.2273	0.8070
QUARTNARY	8.21	0.1041	0.867	1.028	1.2483	0.615

Temkin and D-R isotherm

The Temkin adsorption isotherm was used to evaluate the adsorption potentials of reactive dyes RY based single, binary, tertiary and quartnary and onto PRC from the aqueous solution. The Temkin and Pyzhey [37] considered the effects of some indirect adsorbate or adsorbate interactions on adsorption isotherms and suggested that because of these interactions the heat of adsorption of all the molecules in the layer would decrease linearly with coverage. The derivation of the Tempkin isotherm assumes that the fall in the heat of adsorption is linear rather than logarithmic, as implied in the Freundlich equation.

$$q_e = \frac{RT}{b} \ln(AC_e) \tag{6}$$

The Temkin isotherm Eq. (10) can be simplified to the following equation:

$$q_e = \beta \ln \alpha + \beta \ln C_e \quad (7)$$

$$\text{Where, } \beta = (RT)/b \quad (8)$$

The correlation coefficients R^2 obtained from Temkin model were comparable to that obtained for Langmuir and Freundlich equations, which explains the applicability of Temkin model to the adsorption of reactive dyes and onto PRC. The R^2 values were greater than 0.9710 for RY single dye concentrations. The theoretical isotherm curves are compared with the corresponding experimental data. The experimental equilibrium curves shows that the Temkin model cannot describe the adsorption isotherms.

The Dubinin – Radushkevich (D-R) isotherm

The D-R isotherm was also applied to estimate the porosity apparent free energy and the characteristics of adsorption[38]. It can be used to describe adsorption on both homogenous and heterogeneous surfaces, it does not assume a constant adsorption potential[39]. The D-R equation can be defined by the following equation.

$$\ln q_e = \ln Q_m - K \varepsilon^2 \quad (9)$$

Where K is a constant related to the adsorption energy, Q_m the theoretical saturation capacity, ε the Polanyi potential, calculated from Eq. (15).

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (10)$$

Where C_e is the equilibrium concentration of dye (molL^{-1}), R gas constant ($8.314 \text{Jmol}^{-1} \text{K}^{-1}$) and T is the temperature (K). By plotting $\ln q_e$ versus ε^2 , it is possible to determine the value of K from the slope and the value of Q_m (mgg^{-1}) from the intercept. The mean free energy E (kJmol^{-1}) of sorption can be defined as the free energy change when one mole of ion is transferred from infinity in solution to the surface of the solid was estimated by using K values as expressed in the following equation.

$$E = \frac{1}{\sqrt{2K}} \quad (11)$$

Table 5. Equilibrium model constants for adsorption of RY onto single, binary, tertiary and quartnary system of PRC

Reactive Dyes+ adsorbent	Isotherm model							
	Temkin				Dubinin-Radushkevich			
	α (Lg ⁻¹)	β (mgL ⁻¹)	b	R ²	Q _m (m _g g ⁻¹)	K (x10 ⁻⁵ mol ² kJ ⁻²)	E(kJmol ⁻¹)	R ²
SINGLE	5.006	0.131	19039	0.971	33.78	2.686	0.2633	0.697
BINARY	5.5608	0.214	11655	0.901	32.04	1.611	0.4389	0.842
TERTIARY	4.0988	0.202	12347	0.693	31.82	1.480	0.4777	0.778
QUARTNAR	2.7751	0.234	10659	0.370	31.64	1.501	0.4711	0.642

Adsorption Kinetics

The kinetic adsorption data can be processed to understand the dynamics of the adsorption reactions in terms of the order of the rate constant. Since the kinetics parameters provide important information for designing and modeling the adsorption process. It is important to point out that the initial RY concentrations employed during the kinetic studies of single, binary, tertiary, quartnary onto PRC were studied. Most biosorption processes take place by a multi step mechanism comprising of transport processes such as diffusion in the bulk of the liquid phase, diffusion across the liquid film surrounding the solid particles, diffusion in the liquid filled micro pores and meso pores as well as chemical reactions[40]. The kinetic data were analyzed using four different kinetic models: pseudo-first order, pseudo-second order, Elovich and intra particle diffusion.

Pseudo – first - order equation

The adsorption kinetic data were described by the Lagergren pseudo-first-order model [41], which is the earliest known equation describing the adsorption rate based on the adsorption capacity. The differential equation is generally expresses a follows:

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \tag{21}$$

Where q_e and q_t are the adsorption capacity at equilibrium and at time t , respectively (mg g^{-1}), k_1 is the rate constant of pseudo – first - order adsorption (L min^{-1}). Integrating Eq. (21) for the boundary conditions $t = 0 - t$ and $q_t = 0 - q_t$ gives

$$\log\left(\frac{q_e}{q_e - q_t}\right) = \frac{K_1}{2.303} t \quad (12)$$

Eq. (22) can be rearranged to obtain the following linear form:

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303} t \quad (13)$$

The pseudo – first - order equation fits well for the first minutes and thereafter the data deviate from theory. Thus, the model represents the initial stages where rapid adsorption occurs well but cannot be applied for the entire adsorption process. Furthermore, the correlation coefficient R^2 is relatively low for most adsorption data Table 6. Besides, the experimental q_e values, did not agree with the calculated values obtained from the linear plots. It suggest that the kinetics of Reactive dye single and mixture all reactive dyes adsorption onto PRC did not follow the pseudo – first - order kinetic model and hence not a diffusion - controlled phenomena.

Pseudo – second - order equation

The adsorption kinetics may be described by the pseudo – second order model [40]. The differential form of the pseudo-second order equation is generally given as follows:

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \quad (14)$$

Where k_2 (g (mg min)^{-1}) is the second - order rate constant of adsorption. Integrating Eq. (24) for the boundary conditions $q_t = 0 - q_t$ at $t = 0 - t$ is simplified as can be rearranged and linearized to obtain:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} (t) \quad (15)$$

The second - order rate constants were used to calculate the initial sorption rate, given by the following equation:

$$h = K_2 q_e^2 \quad (16)$$

The data for the pseudo – second - order kinetic model for different initial concentration of Reactive dye single and mixture onto PRC . The plot of t/q_t versus time is a

straight line as shown in Fig. 14. If the second - order kinetics is applicable, then the plot of t/q_t versus t should show a linear relationship. The K_2 values and equilibrium capacity (q_e) values determined from the slopes and intercepts of the plot are presented in Table () along with the corresponding correlation coefficients. This procedure is more likely to predict the behavior over the whole range of adsorption. The linear plot shows a good agreement between the experimental and calculated q_e values at different initial concentrations of single ,Binary, tertiary,and quartnary system PRC as adsorbents .

The corresponding correlation coefficient (R^2) values for the pseudo – second - order kinetic model were greater than 0.982 –single ,binary-0.917, tertiary-0.868, Quartnary 0.870 for all reactive dye concentration, indicating the applicability of the pseudo – second - order kinetic model to describe the adsorption process of reactive dye single, binary, tertiary, and quartnary system onto PRC. This led to believe that the pseudo – second - order kinetic model provided good correlation for the bioadsorption. The higher R^2 values confirm that the adsorption process of reactive dyes follow a pseudo - second - order kinetic model. Similar trends were observed by [42].

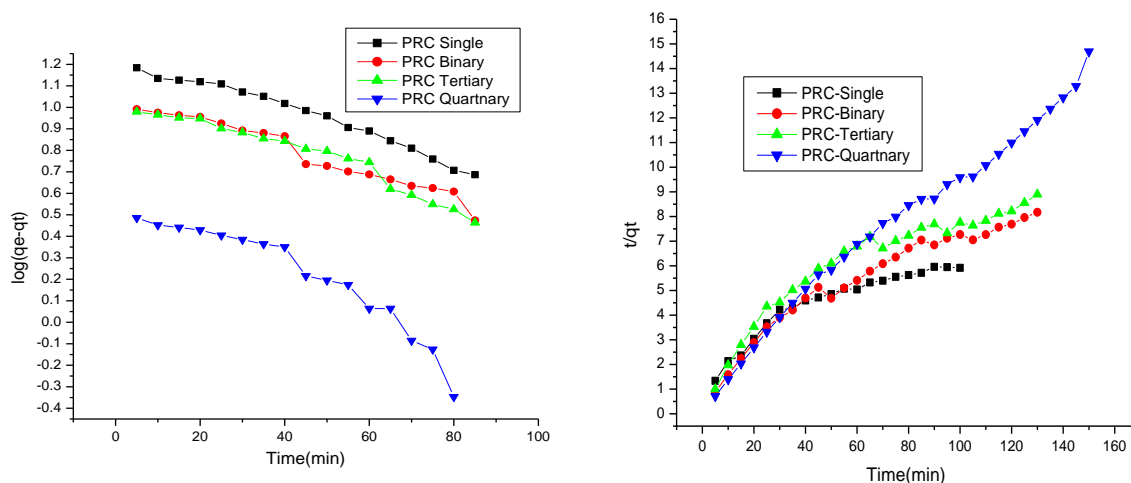


Figure 7. Pseudo – first and second - order for the removal of reactive dyes (single,binary, tertiary, quartnart system) onto the PRC

Table 6. Equilibrium model constants for adsorption of RY onto single, binary, tertiary and quartary system of PRC

PRC-ADSORBENT				
	$K_1 \text{ min}^{-1}$	$q_{e(\text{cal})}$	$q_{e(\text{exp})}$	R^2
Pseudo-first-order				
Single	0.2303	4.2080	19.9645	0.7861
Binary	0.2136	3.4903	16.1191	0.8187
Tertiary	12.6803	1.8441	14.6051	0.9962
Quartary	0.0267	1.8795	10.2113	0.8960
Pseudo-second-order				
	$K_2 (\text{gmg}^{-1}\text{min}^{-1})$	$q_{e(\text{cal})}\text{mg/g}$	$q_{e(\text{exp})}\text{mg/g}$	R^2
Single	4.21×10^{-3}	23.2558	19.9645	0.9820
Binary	5.1×10^{-3}	20.4082	16.1191	0.9172
Tertiary	8.96×10^{-3}	20.0000	14.6051	0.8681
Quartary	5.24×10^{-3}	12.0480	10.2113	0.8704

Elovich equation

The Elovich equation is another rate equation based on the adsorption capacity generally expressed as following[43].

$$\frac{dq_t}{dt} = B_E \exp(-A_E q_t) \tag{17}$$

Where B_E is the initial adsorption rate ($\text{mg} (\text{g min})^{-1}$) and A_E is the de-sorption constant (g mg^{-1}) during any experiment. It is simplified by assuming $A_E B_E t \gg t$ and by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ Eq. (27) becomes:

$$q_t = \frac{1}{A_E} \ln(B_E A_E) + \frac{1}{A_E} \ln(t) \tag{18}$$

The reactive dyes adsorption onto PRC in Single system fits the Elovich model, compare to the another Binary, tertiary, quartnary system a plot of q_t versus $\ln(t)$ should yield a linear relationship with a slope of $(1/A_E)$ and an intercept of $(1/A_E) \ln(A_E B_E)$. Thus, the constants can be obtained from the slope and the intercept are shown in Table7. The parameter $1/A_E$ is related to the number of sites available for adsorption while $(1/A_E) \ln(A_E B_E)$ is the adsorption quantity when $\ln t$ is equal to zero; ie, the adsorption quantity when t is 1 min. This value is helpful in understanding the adsorption behavior of the first step.[44].

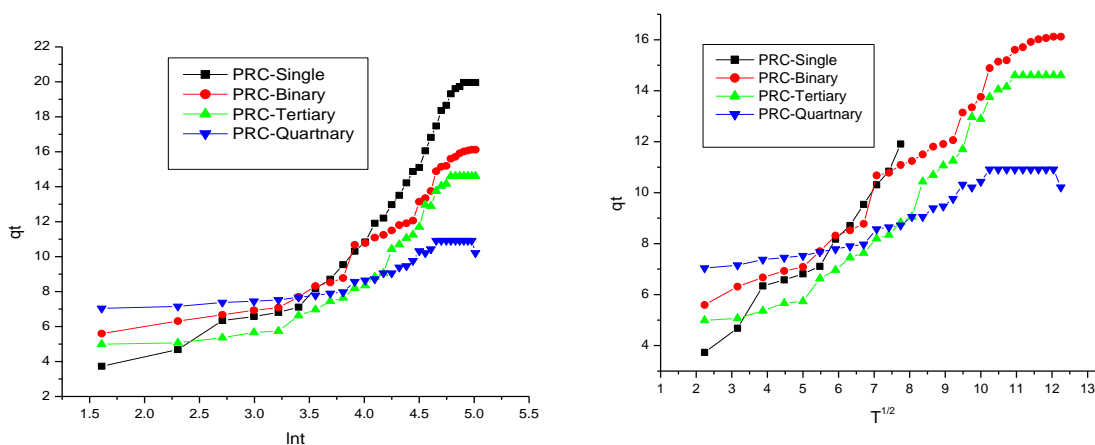


Figure 7. Elovich and intra particle diffusion for the removal of reactive dyes (single,binary, tertiary, quartnary system) onto the PRC

Table 7. Equilibrium model constants for adsorption of RY onto single,binary, tertiary and quartnary system of PRC

Elovich kinetic model	A_E	B_E	R^2
Single	0.1707	5.4380	0.886
Binary	0.2597	2.2428	0.881
Tertiary	0.2622	2.8959	0.846
Quartnary	0.6604	2.6198	0.834

Intraparticle diffusion	K_{dif}	C	R^2
Single	0.795	1.720	0.919
Binary	1.129	1.609	0.974
Tertiary	1.221	0.299	0.956
Quartnary	0.481	0.481	0.927

Intraparticle diffusion:

The kinetic studies help in predicting the progress of adsorption, but the determination of the adsorption mechanism is also important for design purpose. In a solid liquid adsorption process, the transfer of the adsorbate is controlled by either boundary layer diffusion (external mass transfer) or intra - particle diffusion (mass transfer through the pores), or by both. It is generally accepted that the adsorption dynamics consists of three consecutive steps:

- Transport of adsorbate molecules from the bulk solution to external surface of the adsorbent by diffusion through the liquid boundary layer.
- Diffusion of the adsorbate from the external surface and into the pores of the adsorbent.
- Adsorption of the adsorbate on the active sites on the internal surface of the pores.

The last step, adsorption is usually very rapid in comparison to the first two steps. Therefore, the overall rate of adsorption is controlled by either film or intra - particle diffusion, or a combination of both[45]. Many studies have shown that the boundary layer diffusion is the rate controlling step in system characterized by dilute concentrations of adsorbate, poor mixing, and small particle size of adsorbent. Whereas the intra - particle diffusion controls the rate of adsorption systems characterized by high concentrations of adsorbate, good mixing and big particle size of adsorbent [46]. Also it has been noticed in many studies that boundary layer diffusion is dominant during the initial adsorbate uptake, and then gradually the adsorption rate becomes controlled by intra - particle diffusion after the adsorbent's external surface is loaded with the adsorbate.

The adsorbate species are most probably transported from the bulk of the solution into the solid phase through intra - particle diffusion/transport process, which is often the rate - limiting step in many adsorption processes, especially in a rapidly stirred batch reactor [47]. Since the Reactive yellow 15 single and mixture of dyes are probably transported from its aqueous solution to the PRC by intra - particle diffusion, so the intra - particle diffusion is

another kinetic model should be used to study the rate of Reactive yellow -15 single and mixture of dyes adsorption onto PRC. The possibility of intra - particle diffusion was explored by using the intra - particle diffusion model. When the diffusion (internal surface and pore diffusion) of dye molecule inside the adsorbent is the rate-limiting step, then adsorption data can be presented by the following equation:

$$q_t = K_{dif} t^{1/2} + C \tag{19}$$

Where C (mg g⁻¹) is the intercept and K_{dif} is the intra - particle diffusion rate constant (in mg g⁻¹ min^{-1/2}). The data for the plot of intra - particle diffusion model is presented in Table. The values of q_t were found to be linearly correlated with values of t^{1/2} the intercept C and rate constant K_{dif} directly evaluated from the slope of the regression line. The values of intercept C provide information about the thickness of the boundary layer, the resistance to the external mass transfer increase as the intercept increase. The most commonly used technique for identifying the mechanism involved in the sorption process is by fitting the experimental data in an intra - particle diffusion plot. Previous studies[48-49] by various researchers showed that the plot of q_t versus t^{1/2} represents multi linearity, which characterize the two or more steps involved in the sorption process. According to the intra - particle diffusion model, a linear plot indicates a rate controlled by intra-particle diffusion.

The intra - particle diffusion rate constant, K_{dif}, is determined from the slope of the linear regression line while the intercept is proportional to the boundary layer thickness (or resistance). The K_{dif}, values given in Table were in the range of Single and mixture system of reactive yellow-15 onto the PRC. and it increase and decrease with initial dye concentration.

Desorption studies

To make the adsorbent economically competitive, the prepared composite should be reused for n no of cycle. Reactive yellow C.I 15 first time removal onto PRC. Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the dye. The effect of various reagents used for desorption were studied. The results with water, Sodium hydroxide , 0.1M Hydrochloric acid are presented in the Table Desorption increases with increase in the acidity of the desorbing medium. This could be due to the increased solubility of reactive yellow in acidic medium.

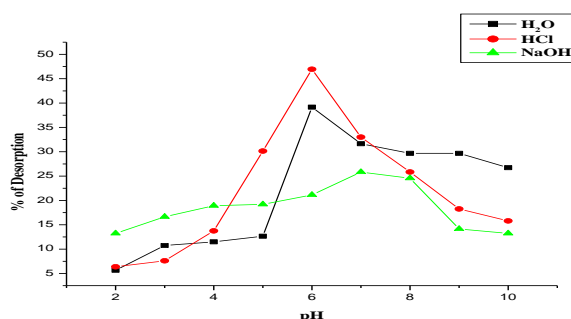


Table 8. Desorption of Reactive Yellow-15 onto PRC

Various adsorbate	H ₂ O	NaOH	HCl
% of desorption	36.17	25.83	46.93

Desorption study for removal of reactive dye onto PRC

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the dye. If the adsorbed dyes can be desorbed using neutral pH water, then the attachment of the dye of the adsorbent is by weak bonds. If sulphuric acid or alkaline water desorb the dye then the adsorption is by ion exchange. If Inorganic acids, like hydrochloric acid can desorb the dye, then the dye has held by the adsorbent through chemisorption. The effect of various reagents used for desorption studies indicate that hydrochloric acid is a better reagent for desorption, because we could get more than 47.46% removal of adsorbed dye. The reversibility of adsorbed dye in mineral acid or base is in agreement with the pH dependent results obtained.

CONCLUSION

This study investigated the equilibrium and kinetic study of the dynamics of the adsorption of single and mixture of reactive dyes on the chemically cross linked onto PRC. The multi system of the reactive dyes (single, binary, tertiary, and quaternary) system onto the phosphoric assisted epicarp of ricinus communis as a low cost adsorbent used for this study. The surface morphology activated carbon very good nature. The from the result showed that the single system(RY) was compared to the other system of binary and tertiary and quaternary. The Langmuir fitted for the single system Q_m 35.71 . The results demonstrate that adsorption mechanisms in the system of Reactive dyes AC onto PRC follow a pseudo- second order kinetics with a significant contribution of kinetics study.

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