

Removal of Acid Dye (AR37) by Adsorption onto Potatoes and Egg Husk: A Comparative Study

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Abstract: Adsorption of Acid Red 37 from aqueous solution on potatoes (POH) and egg (EGH) husk have been studied comparatively. The adsorption process is affected by various parameters such, solution pH (2.01- 9.02), initial concentration of dye (10, 15, 25, 50, 75 and 100 mg/l), adsorbent dose (0.2 - 1 g/l) and contact time. As initial pH of dye solution increased, the percentage of the removal increased, reached a maximum pH = 5.3±0.5 and the final solution pH after adsorption decreases. Inhibition of the dye sorption onto raw POH and EGH at low acidic and high basic pH ranges may be attributed to the increase of hydroxyl and hydrogen ions leading to formation of aqua complexes that retards the dye sorption. Therefore, it is suggested that the optimum pH for the removal of AR37 is 5.3±0.5. Adsorption isotherms of the studied dye on adsorbent were determined and compared with the Langmuir, Freundlich and Temkin models. The adsorption capacity (Q_m) obtained from the Langmuir isotherm plot was 23.53 and 20.85 mg /g for POH and EGH respectively at initial pH= 5.3±0.5, initial concentration of dye 50 mg/l and adsorbent dose 1g/l. Adsorption kinetics were verified by pseudo-first order and pseudo-second order models. Results indicated that, two selected adsorbents could be employed as low cost adsorbent for removal of AR37 from aqueous solution. The removal of dye solution by potatoes husk (POH) is found to be more efficiency than egg husk powder (EGH).

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1.Introduction:

Dyes are a type of organic compounds which are used in many industries for coloration purpose such as textile, rubber, paper, plastic, cosmetic etc. The total dye consumption of the textile industry worldwide is more than 107 kg year⁻¹. There are more than 10,000 commercially available dyes with over 7x10⁵ tones of dyestuff produced annually across the world [1]. It is estimated that 2 % of dyes produced annually are discharged in effluent from manufacturing operations. While in the textile industry, it is estimated that 10–15% of the dye is lost during the dyeing process and released with the effluent. Effluents discharged from washing and dyeing processes represent 95% of the total amount of consumed water, namely 200 l /kg fabric [2]. Without appropriate treatment, discharge of dye wastewaters into water bodies can adversely affect aquatic environment by reducing light penetration and photosynthesis, and being hazardous and toxic to aquatic life [3-6]. This led to an intensive search for the best available technology, which can be used for the removal of dyes. Many physical and chemical methods have been carried out for treating dye wastewater, e.g. coagulation/flocculation, chemical oxidation, activated sludge process, are difficult, ineffective or economic disadvantage [3-5, 7-10]. The adsorption process is one of the efficient methods to remove the contaminants from the wastewater. Activated carbon is widely used

due to its effectiveness and versatility, but this method is expensive. Many low-cost adsorbents have been investigated on dye removal, such as fly ash [3, 11-14], bottom ash [6], clay [8], zeolite [6-8], calcine alunite [15], peanut hull [7], rice husk [4], and brown seaweed [10]. Agricultural by-products are considered to be low cost products, which are arbitrarily discarded or burned, resulting in resource loss and environmental pollution. Generally, sorption capacity of crude agricultural by-products is low [16]. These materials are chemically modified in order to enhance their sorption capacities and, by extension, their usefulness in the treatment of wastewater. These materials, in general, possess high sorption capacities towards either positively or negatively charged dye molecules, but not both. However, a mixture of different types of dyes is usually found in the industrial effluent. Hence there is a need to have sorbents capable of removing different types of dyes either singly or simultaneously [17]. The objective of this study was to explore the possibility using egg husk powder EGH and potatoes husk POH for removing anionic dye, Acid Red 37 (AR 37) from aqueous solution. The present study has been undertaken into report in detail the characteristics of (AR37) adsorption in the batch process. Various isotherm models have been studied for their usefulness in correlating the experimental data.

2. Material and Methods

2.1. Preparation of adsorbents

In this study, potatoes husk POH and egg shell EGH were used as adsorbents for the removal of anionic acid dye (AR37). The potatoes were purchased from local agricultural field. Its skin was removed by scratching, and then it was washed several times with distilled water to remove dust and other foreign particles and dried in shadow. It was then grinded to fine powder. Its mesh size was determined (sieved with 0.850 mesh sieve). Egg shells were collected, washed with distilled water and dried in the oven. Then, it was grounded and sieved to 150-200 μm particle size. It was then dried at 105 $^{\circ}\text{C}$ for 24 hours to remove moisture and stored in a closed bottle for later use in adsorption studies.

2.2. Preparation of dye solution (adsorbate)

Lissamine Red B (Acid Red 37) was obtained from Imperial Chemical Industries Company and was used without further purification. Its molecular formula is $\text{C}_{18}\text{H}_{14}\text{N}_4\text{Na}_2\text{O}_8\text{S}_2$ and its color index C.I. 17045. A stock solution of the dye was prepared by dissolving 1 gram of dye in 1000 ml distilled water to make a stock solution of 1000 mg/l. The experimental solution was prepared by diluting definite volume of the stock solution to get the desired concentration. For absorbance measurements a UV-VIS spectrophotometer, JAPAN APEL (PD-303S) was employed using quartz cells of path length 1 cm. The maximum wavelength was measured at 516.38 nm.

2.3. Batch adsorption studies

2.3.1. Adsorption study: effect of adsorbent dosage.

Different dosages of adsorbent were added to working standards. The amount of adsorbent used was 0.2, 0.4, 0.6, 0.8, 1.0, 1.5 and 2.0 g. All these adsorbents, at pH 5.35, were added to 100 ml dye solution of 50 mg/l in a 250 ml conical at room temperature. These samples were placed on rotary shaker. The samples were withdrawn from the shaker after 24 hrs agitating. The solution was separated by filter paper filtration. The concentration of the residual dye solution was determined by UV-VIS spectrophotometer measurements.

2.3.2. Adsorption study: effect of adsorbate initial concentration.

Dye solutions with concentration of 10, 15, 25, 50, 75 and 100 mg/l were prepared. 1.0 g of adsorbent at pH 5.3 ± 0.5 was added to the solutions in a 250 ml conical flask. These were followed by agitating the solution on a rotary shaker. The concentration of the residual dye solution was determined by UV-VIS spectrophotometer measurements.

2.3.3. Adsorption study: effect of initial pH and contact Time.

Adsorption experiments for the removal of dye were conducted in the pH range of 2.01 – 9.02, and contact time from 0- 180. The amount of dye adsorbed per unit mass of the adsorbent was calculated using the following equation:

$$Q_e = (C_o - C_e)V/W \quad (1)$$

Where, C_o and C_e are the initial and equilibrium adsorbate concentrations (mg/ L), respectively, V is the volume of solution (L) and W is the mass of adsorbent (g). The dye removal percentage can be calculated as follows:

$$\% \text{ Removal} = \frac{C_o - C_e}{C_o} 100 \quad (2)$$

Where, C_o and C_e (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. Finally the suitability of the Langmuir, Freundlich and Temkin adsorption isotherm models to the equilibrium data were investigated for dye adsorbate.

3. Results and Discussion

3.1. Effect of the pH

Figure 1 shows the effect of the initial pH of the dye solutions towards the adsorption of AR37 by potatoes and egg husk in dye solutions. The pH value of the solution is an important process-controlling parameter in the adsorption of dye. The initial pH values of the dye solutions affect the surface charge of the adsorbent and thus the adsorption of the charged dye groups on it [15]. In order to evaluate the influence of this parameter on the adsorption, the experiments were carried out at different initial pH values. The pH range was chosen as 2.01 – 9.02. For AR37 dye solutions adsorbate onto POH and EGH adsorbent, mild acidic condition i.e. pH 5.3 shows maximum adsorption (% R = 91.62, 79.75 and $Q_e = 32.80, 28.55$ mg/g for POH and EGH respectively). At strong acidic and basic pH condition i.e. pH 2.01 and pH 9.02, adsorption is least (% R = 49.92, 44.07 and $Q_e = 15.0, 13.20$ mg/g for POH and EGH respectively at pH 2.01) for initial dye concentration of 50 mg/l and contact time 2 hour. However, the mild acidic pH ($\text{pH} 5.3 \pm 0.5$) system showed good adsorption behavior for the AR37 dye solution.

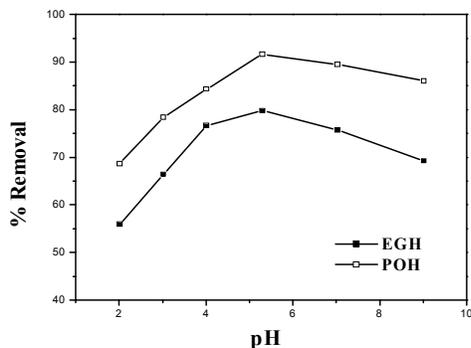


Figure 1: Effect of pH on Adsorption of AR37 Solution by Selected Adsorbents, Adsorbent Dosage 1g/l, Initial Concentrations 50 mg/l and Contact Time 2 hrs.

As the pH of the system decreases, the protonated surface groups facilitate the adsorption of the negatively charged dye. The number of positively charged sites increases resulting in an increase of binding sites for anionic dye molecules AR37 [18]. A lower percentage of the removal of AR37 in basic pH may be due to the presence of excess OH ions competing with the dye anions for the adsorption sites. The electrostatic repulsion between the anionic dye and the negatively charged sites contribute to the decreased uptake of AR37 [18, 19]. Moreover, inhibition of the dye sorption onto raw POH and EGH at low acidic and high basic pH ranges may be attributed to the increase of the hydroxyl and hydrogen ions leading to the formation of aqua complexes. That retards the dye sorption [20]. Therefore, it is suggested that the optimum pH for the removal of AR37 is 5.3 ± 0.5 .

3.2. Effect of initial dye concentration

The experimental results of adsorptions of AR37 dye on the low cost adsorbed potatoes and egg husk at various concentrations (10, 15, 25, 50, 75 and 100 mg/L) are shown in Figure 2.

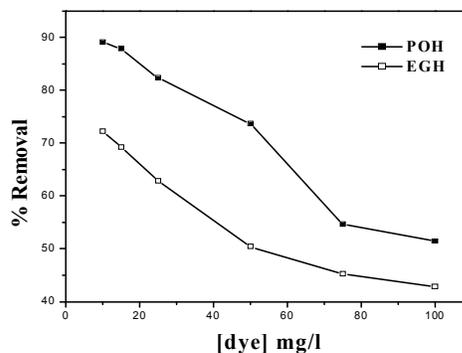


Figure 2: Effect of AR37 Dye Concentration on Adsorption by Selected Adsorbents (P.H. and E.H.) pH= 5.3 ± 0.5 , Adsorbent Dosage 1g/l, Contact Time 60 min.

The results were collected in Table 1, reveals that, the percent of the adsorption decreased with the increase of the initial dye concentration, but the actual amount of dye adsorbed per unit mass of adsorbed increased with the increase of the dye concentration. This means that the adsorption is highly dependent on the initial concentration of the dye. It is because this that at lower concentration, the ratio of the initial number of dye molecules to the available surface area is low; subsequently the fractional adsorption becomes independent of initial concentration. However, at high concentration the available sites of adsorption becomes fewer and hence the percentage removal of dye is dependent upon initial concentration. Also, the results indicate that the adsorption of acid dye onto the surface of adsorbent (POH and EGH) were initially rapid, slowed down later on and finally reached towards equilibrium (Figure 2) indicating saturated adsorption [21-23]. The increased adsorption may be attributed to the increase in surface activity and due to micelle formation or the aggregation of dye molecule in the concentration range studied. Similar results have been also reported by several researchers [21].

Table (1): A comparison of Removal Percentages of Dye (%R) and Amount of Dye Adsorbed per Gram of The Adsorbent (Q_e) at Different Initial Concentrations of AR37 on POH and EGH Adsorbent

[Dye] mg/l	Potatoes husk adsorbent (POH)		Egg husk adsorbent (EGH)	
	% R	Q_e (mg/g)	% R	Q_e (mg/g)
10	82.59	8.30	72.64	5.84
15	80.79	13.25	66.16	10.85
25	74.69	21.10	55.75	15.75
50	64.32	31.10	45.81	22.15
75	55.66	39.85	39.25	28.10
100	46.69	40.85	36.00	31.50

3.3. Effect of contact time

The percentage of the removal increased with the increase of the contact time and reached a constant value. This may be due to the attainment of equilibrium

condition at 80 min of contact time for EGH and 60 min of contact time for POH, which are fixed as the optimum contact time. The effect of contact time is shown in Figure 3.

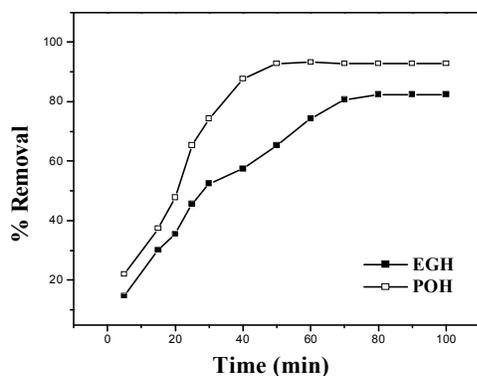


Figure 3: Effect of the Contact Time on Adsorption of AR37 by Selected Adsorbent pH=5.3±0.5, Adsorbent Dosage 1g/l, Initial Concentration 50 mg/l.

At the initial stage, the rate of the removal of AR37 was higher, due to the availability of more than required number of active sites on the surface of adsorbent. The rate of the removal became slower at the later stages of contact time, due to the decreased or lesser number of active sites [24]. Similar results have been reported in literature for the removal of dyes [25], organic acids [26] and metal ions [27] by various adsorbents. Figure 3 reveals that the curves are single, smooth, and continuous, leading to saturation, suggesting the possible monolayer coverage of the dye on the adsorbent surface.

3.4. Effect of dose of adsorbent

The effect of adsorbent dosage on the removal of AR37 at 50 mg/l initial concentration and pH 5.3±0.5 was studied and the results are represented in Figure 4. Dosage study is an important parameter in adsorption studies because it determines the capacity of adsorbent for a given initial concentration of dye solution. The removal of the dye was found to increase with an increase in adsorbent dosage from 0.2-2 g/l. The adsorption equilibria of the dyes were reached at 1 g and the removal of dyes remained almost invariable above this dosage. Therefore, 1 g appears to be the optimum sorbent dosage. Increase in adsorption with increase in adsorbent dosage attributed to the increase of active sites for adsorption of dye molecules with increasing adsorbent dosage. At very low adsorbent concentration, the adsorbent surface becomes saturated with the dye and the residual dye concentration in the solution to large. The data clearly shows that the POH is more effective than EGH for removal of AR37 from aqueous solution.

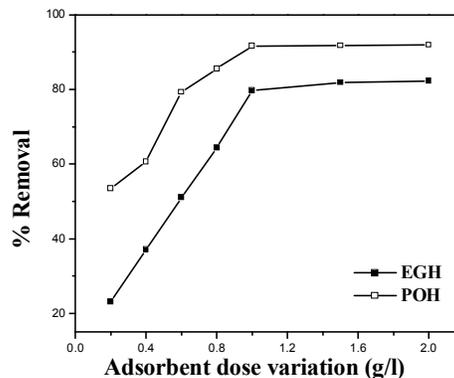


Figure 4: Effect of Adsorbent Dosage on Removal of AR37 by Selected Adsorbents [POH and EGH], at pH=5.3 ± 0.5, Initial Concentration = 50 mg/l, Contact Time 2h.

3.5. Adsorption isotherm at different concentration of adsorbate

The adsorption isotherm of AR37 was analyzed using the Langmuir, Freundlich and Temkin isotherms models.

3.5.1. Langmuir isotherm

The Langmuir equation is based on the assumption that maximum sorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface. The energy of sorption is constant and there is no transmigration of the sorbate in the plane of the surface [28]. The Langmuir type equation is expressed as:

$$1/Q_e = (1/Q_m) + (1/bQ_m) (1/C_e) \quad (3)$$

where C_e is the equilibrium concentration (mg/l), Q_e is the amount adsorbed at equilibrium (mg/g). Q_m and b are Langmuir constants related to adsorption capacity (mg/g) and energy of adsorption capacity (1/mg), respectively. The linear plots of $1/Q_e$ versus $1/C_e$ suggest the applicability of the Langmuir isotherms. The values of Q_m and b were determined from slope and intercepts of the plots. These values are presented in Table 2 and Figures 5, 6. The shape of the Langmuir isotherm was investigated by the dimensionless constant separation term (R_L) to determine high affinity adsorption [18]. R_L was calculated as follows:

$$R_L = 1 / (1 + b C_o) \quad (4)$$

where, C_o is the initial dye concentration (mg/l), R_L indicates the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) (or) unfavorable ($R_L > 1$). In the present investigation, the R_L values for EGH and POH were less than one, showing favorable adsorption.

Table 2: Isotherm Parameters for Adsorption of AR37 onto Selected adsorbents, POH and EGH

Adsorbent	Langmuir model				Freundlich model			Temkin model		
	Q_m	b	R_L	r^2	n	K_f	r^2	B	A	r^2
POH	23.53	0.093	0.860- 0.982	0.999	2.40	26.30	0.973	4.82	1.56	0.992
EGH	20.85	0.27	0.679- 0.949	0.999	2.32	14.59	0.987	5.05	1.24	0.985

3.5.2. Freundlich isotherm

Freundlich isotherm model was chosen to estimate the adsorption intensity of the adsorbate on the adsorbent surface [29]. Linear form of Freundlich model was expressed by:

$$\log Q_e = \log k_f + 1/n \log C_e \quad (5)$$

Where, Q_e is dye concentration in solid at equilibrium (mg/g), C_e is dye concentration in solution at equilibrium (mg/l), k_f is the Freundlich isotherm constant related to adsorption capacity (l/mg) and n is the Freundlich isotherm constant related to adsorption intensity. The linear plot of $\log Q_e$ versus $\log C_e$ for adsorption of AR 37 onto POH and EGH is shown in Figures 7, 8 and the values of n and k_f calculated from the slope and intercept are given in Table 2. The values of n are greater than one indicating the favorable adsorption.

3.5.3. Temkin isotherm

Temkin and Pyzhev [30] considered the effect of the adsorbate interaction on adsorption and proposed the model known as the Temkin isotherm, which can be expressed as:

$$Q_e = (RT/\beta) \ln A + (RT/\beta) \ln C_e \quad (6)$$

Where A and B are Temkin constant, R is the gas constant and T is the absolute temperature. A Plot of Q_e versus $\ln C_e$ can be used to determine the constant A and B , where $(RT/\beta) = B$. The Temkin adsorption isotherm model was chosen to evaluate the adsorption potentials of the adsorbent for adsorbates. The Temkin isotherm plot for AR37 is presented in Figures 9, 10 and Table 2.

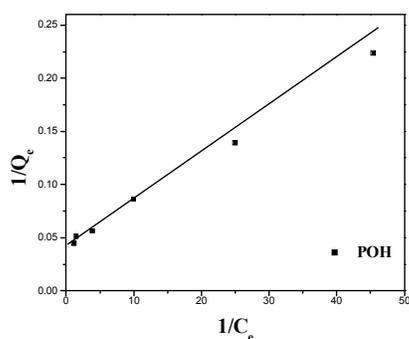


Figure 5: Langmuir Isotherm Plot for Adsorption of AR 37 onto POH

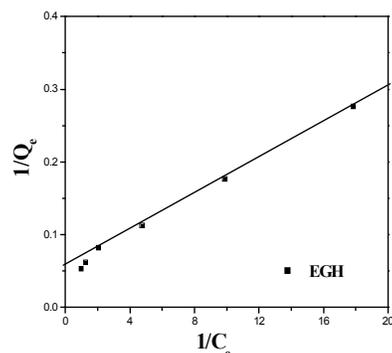


Figure 6: Langmuir Isotherm Plot for Adsorption of AR 37 onto EGH.

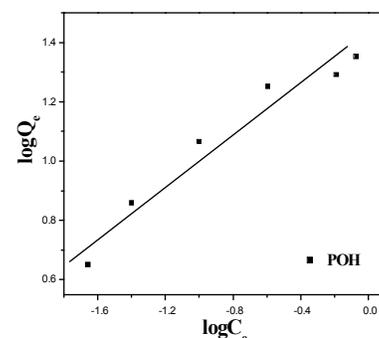


Figure 7: Freundlich Isotherm Plot for Adsorption of AR 37 onto POH.

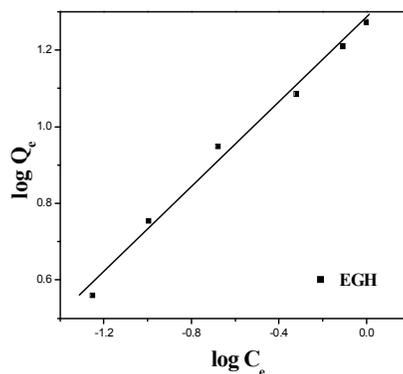


Figure 8: Freundlich Isotherm Plot for Adsorption of AR 37 onto EGH.

For AR 37 dye, adsorption onto both adsorbents confirms the Langmuir, on the correlation coefficients (r^2 values) of the isotherms studied, it was found that Langmuir isotherm was more suitable

isotherm than Freundlich and Temkin isotherms for the experimental data. The Langmuir maximum adsorption capacity of EGH was 20.85 mg/g that is low compared with that of POH (23.53 mg/g) for adsorptive removal of AR 37 dye, this indicates, that the POH adsorbent is more effective than EGH adsorbent in adsorption. The fitness of Langmuir's model indicated the formation of monolayer coverage of the adsorbate on the outer surface of the adsorbent.

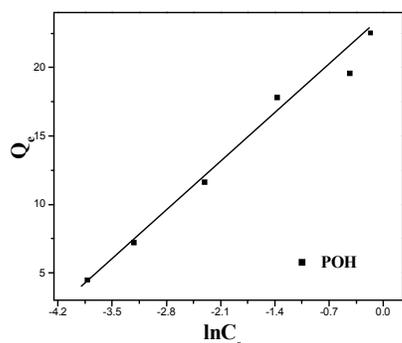


Figure 9: Temkin Isotherm Plot for Adsorption of AR 37 onto POH.

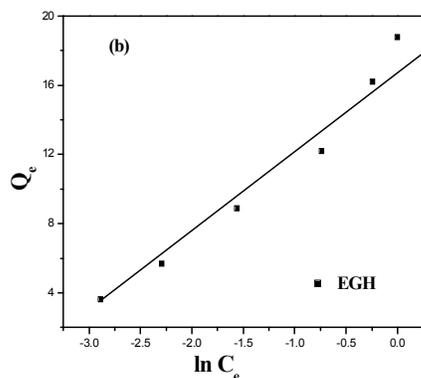


Figure 10 : Temkin Isotherm Plot for Adsorption of AR 37 onto EGH.

3.6. Adsorption kinetics

Table 3: The Kinetics Constants for The Adsorption of AR37 onto POH and EGH, [Initial Concentration of AR37 = 50 mg/l, pH = 5.3±0.5, Dose Adsorbent = 1 g/ l].

Adsorbents	Pseudo-first order kinetics				Pseudo-second order kinetics		
	k_1 (1/min)	Q_e (exp.mg/g)	Q_e (cal.mg/g)	r^2	k_2 (g/mgmin)	Q_e (cal.mg/g)	r^2
POH	0.025	17.80	15.60	0.995	4.23×10^{-3}	15.90	0.971
EGH	0.035	12.18	10.97	0.992	8.35×10^{-3}	12.69	0.989

In order to investigate the mechanism of adsorption, the pseudo-first order and the pseudo-second order kinetic models were used to test dynamical experimental data.

3.6.1. Pseudo-first order kinetic model

This model was suggested for the adsorption of solid/liquid systems [31]. The integrated linear form of the model is as follows:

$$\log(Q_e - Q_t) = \log Q_e - k_1 t / 2.303 \quad (7)$$

a plot of $\log(Q_e - Q_t)$ versus t gives a linear line (Figure 11,12) from which the values of k_1 and Q_e were determined from the slope and intercept respectively. These values are presented in Table 3.

3.6.2. Pseudo-second order kinetic model

The adsorption mechanism is explained by the pseudo – second order kinetic model [32]. The integrated linear form of the model is as follows:

$$t/Q_t = 1/k_2 Q_e^2 + t/Q_e \quad (8)$$

A plot of t/Q_t versus t gives a linear relationship (Figure 13, 14), from which Q_e and k_2 were determined from the slope and the intercept of the plot respectively. These values are presented in Table 3. For all the systems studied, good correlation coefficients were obtained ($r_2 \approx 1$) by fitting the experimental data to pseudo-first order kinetics than that for the pseudo-second order kinetic model. The Q_e values calculated from the pseudo second order model system are in good agreement with the experimental Q_e values. Therefore, the sorption was more favorably by pseudo second order kinetic model, which was based on the assumption that the rate limiting step may be chemisorption involving valences forces through sharing or exchange of electrons between sorbent and sorbate [33].

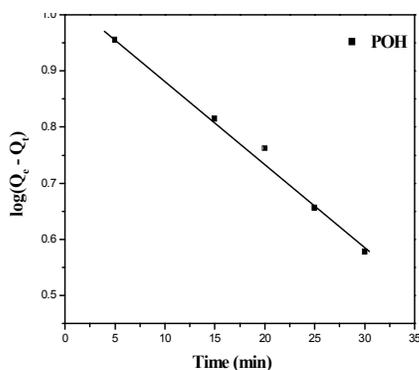


Figure 11: Pseudo-First Order Plot for Adsorption of AR 37 onto POH.

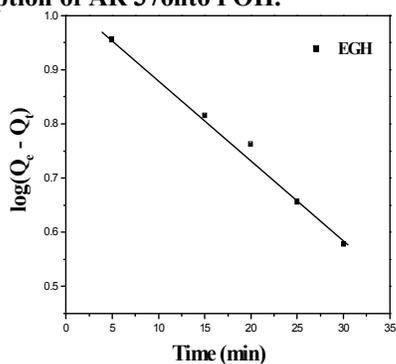


Figure 12: Pseudo-First Order Plot for Adsorption of AR 37 onto EGH.

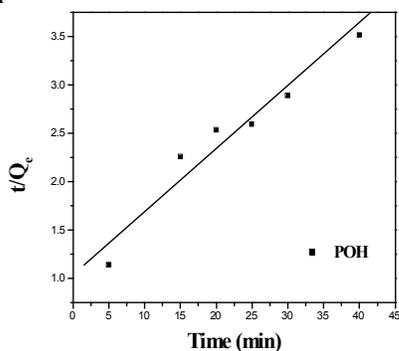


Figure 13: Pseudo-Second Order Plot for Adsorption of AR 37 onto POH.

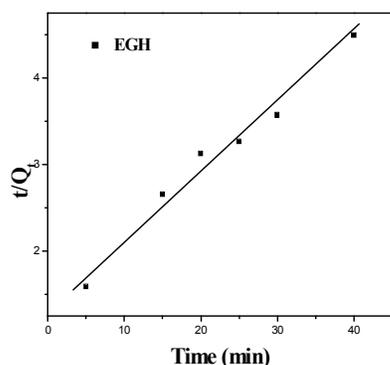


Figure 14: Pseudo-Second Order Plot for Adsorption of AR 37 onto EGH

4. Conclusion

The present study was carried out to compare the adsorption capacity of AR37 dye from aqueous solution using potatoes husk and egg husk powder. The adsorption characteristics of two selected adsorbents have been examined by initial pH, initial concentration, dose adsorbent and contact time. The maximum removal of AR 37 was observed at pH 5.3 ± 0.5 . Percentage removal of dye increased with the decrease in initial concentration and increased with increase in contact time and dose of adsorbent. The equilibrium time for absorption of AR37 from aqueous solutions was achieved within 60 min of POH and 80 min of EGH. The dye removed almost remained invariable above adsorbent dosage 1g/l for two selected adsorbent. The experimental data were better described by pseudo-second order model as evident from correlation coefficient.

The adsorption isotherm studies showed that Langmuir model were found to provide the best fit of the experimental data. The results showed that POH and EGH have been successfully used as low cost adsorbent for the removal of AR37 from aqueous solution. Moreover, POH has adsorption capacity more than EGH for AR37 removal.

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