



## Comparative performance between rice husk and granular activated carbon for the removal of azo tartrazine dye from aqueous solution

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### ABSTRACT

In this study, the batch adsorption process was adopted to remediate azo tartrazine dye from an aqueous solution. The commercial granular activated carbon (GAC) adsorbent and rice husk (RH) as natural adsorbents were employed. The effect of the parameters such as pH (2–12), initial dye concentration (5–50 mg L<sup>-1</sup>), and contact time (10–180 min) was investigated with both adsorbents dose (0.05–0.2 g) of GAC and (0.1–1 g) of RH. The results indicated that the higher removal efficiency was achieved for both adsorbents GAC and RH such as 99.81% with adsorption capacity 3.32 mg g<sup>-1</sup> and 90.45% with an adsorption capacity of 1.24 mg g<sup>-1</sup>, respectively. The optimum parameters were obtained for both adsorbents such as pH 2, initial tartrazine concentration 5 mg L<sup>-1</sup>, contact time 60 min of GAC and 120 min of rice husk, and adsorbent dose 0.1 g of GAC and 0.2 g of RH. The comparison between Langmuir and Freundlich isotherm adsorption models were checked and the data displays that Langmuir isotherm shows a higher correlation coefficient,  $R^2$  (0.99 and 0.98) of RH and GAC respectively. The adsorption kinetics were investigated with pseudo-first-order and pseudo-second-order models and the rates of adsorption were found to confirm the pseudo-second-order kinetics with good correlation  $R^2$  (0.97) of both adsorbents. Thermodynamic results indicating that the adsorption process was an endothermic, spontaneous, and favorable process in nature. The results appeared the removal efficiency of dye by RH was less than those of GAC at the same operating condition.

*Keywords:* Azo tartrazine dye; Rice husk; Environment technology; Adsorption; Natural adsorbent; Wastewater treatment; Granular activated carbon; Environmental pollution; Batch adsorption

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### 1. Introduction

Many industries such as plastics, pharmaceuticals, food, textile, and paper produce huge amounts of polluted wastewater [1]. The common types of organic pollutants present in the aqueous environment are phenols, dyes, pharmaceuticals, biocides, pesticides, compounds, surfactants, and heavy metals [2,3]. As for coloration agents, most dyes are not biodegradable and tend to repress photosynthetic activities in aqueous habitat by prevention

sunlight permeation and limits the oxygenation of water surfaces, significantly causes harm and danger on aqueous fauna and plants. Besides their well-known toxic and carcinogenic effects. In addition, synthetic dyes can generate during the degradation of secondary toxic products that may cause toxicity to live organisms which are harmful to the environment [4,5]. The inappropriate releasing of these effluents into the environment can cause adverse effects on human life and the aqueous ecosystem [6]. Effluents of textile wastewater are very hard to treat

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utilizing conventional processes, due to these processes are cannot efficiently and costly be utilized to remove the wide range of dyes found in wastewater, because of the synthetic origins and complex structures of dyes [7]. Azo dyes are synthetic organic compounds widely utilized in various industrial processes such as paper printing, textile dyeing, pharmaceutical drug manufacture, foods, and toys [8]. This chemical type of dyes, which possess at least one nitrogen-to-nitrogen double bond ( $-N=N-$ ) bearing aromatic rings, approximately 70% of them dominate the worldwide market as shown in Fig. 1 [9].

Tartrazine is a synthetic lemon yellow azo-dye licensed in many countries in the industrial processes of food with the maximum allowed use levels of 50–500 mg kg<sup>-1</sup> food for processing of the different food. Tartrazine is deemed to be poisonous to humans because it causes asthma, eczema, blurred vision, migraines, itching, thyroid cancer, and result in acts as hyperactivity and other behavioral problems [10]. However, the reduction of it may make sulfonated aromatic amines compounds that have low toxicity possibility [11]. To remove this dye and other pollutants, a variety of chemical, physical and biological methods have been developed such as chemical oxidation, coagulation, photodegradation, and anaerobic or aerobic treatment [12–14]. All of these methods have several restrictions and involve complex proceedings that are economically infeasible. Adsorption is one of the most effective methods and has been more repeatedly utilized than other methods for the removal of synthetic dyes from aqueous effluents, because of their simplicity in application, design, and the possibility of adsorbents regeneration, insensitivity to poisonous materials, low cost, treatment efficiency even with dilute solution, and it does not acquire high technical experience [15–19]. Besides, it does not produce sludge, as in coagulation–flocculation methods or chemical precipitation [20]. Activated carbon is widely used as an adsorbent due to its high surface area, porous structure, high adsorption efficiency, and ability to adsorbed many organic compounds. But, it requires high energy costs to produce and issue associated with regeneration [21,22]. In addition to a high relative of its price, which limits its utility. Moreover, there was a focus on using low-cost and environmentally friendly materials for contaminant treatment [23]. Therefore, many researchers have studied biodegradable, low-cost substitutes made from natural resources to treat organic pollutants such as dyes from industrial wastewater [24].

Some studies reported that rice husk and commercial granular activated carbon (GAC) were suitable for dye

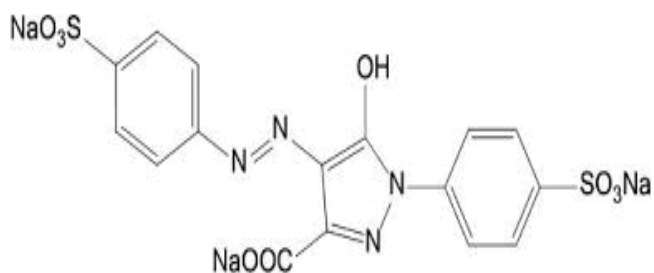


Fig. 1. Chemical structure of tartrazine.

removal from aquatic solutions. Rice husk was efficient in the elimination of Direct Red 23 [25], Methylene blue [26,27], and Metanil yellow dye [28] but it has not been applied for the adsorption of tartrazine yet. On the other hand, the GAC was effective in the removal of direct blue dye 14 [29], Methylene blue [30], and the azo dye [31]. Furthermore, the adsorbents must be sufficient for the removal of several types of dyes.

The present investigation includes the application of commercial GAC adsorbent and rice husk as a low-cost natural adsorbent in order to remove tartrazine dye from an aqueous solution and a comparison between both of them. Different parameters such as: pH, concentrations of dye, contact time, and adsorbent dosage were investigated. Furthermore, isotherm, kinetics, and thermodynamic studies were carried out to evaluate the adsorption capacity of adsorbents and removal efficiency of dye. This investigation is presented an experimental guide for extending the application of natural materials as an efficient adsorbent in tartrazine dye pollution control. It is acquiring special recognition and considers as a promising alternative to conventional water treatment in textile industries.

## 2. Materials and methods

### 2.1. Chemicals

Tartrazine dye has a molecular formula C<sub>16</sub>H<sub>9</sub>N<sub>4</sub>Na<sub>3</sub>O<sub>9</sub>S<sub>2</sub>, a molecular weight 534.4 (Acid Yellow 23, FD&C Yellow 5, E102) and a wavelength of the tartrazine dye is 426 nm was purchased from Sigma-Aldrich Company (German). The amount of dye (0.5 g) was dissolved in distilled water (1 L) to prepare a stock solution of the dye with a concentration of 0.5 g L<sup>-1</sup>. This solution was diluted to obtain the initial concentrations of experimental solutions according to the concentrations of industrial wastewater in the General Company of the Textile Iraqi Industry. Sodium hydroxide (NaOH, purity ≥ 97%) and hydrochloric acid (HCl, purity ≥ 98%) were purchased from Sigma-Aldrich Company (German) and utilized to control the pH values.

### 2.2. Preparation and characteristics of adsorbents

Commercial granular activated carbon was supplied from the Al Doura Refinery, Baghdad, Iraq. The particle size and surface area of GAC were 2 mm and 687.4 cm<sup>2</sup> respectively determined by the Brunauer–Emmett–Teller method (model Q-surf 9600, USA). Rice husk (natural adsorbent) is an undesirable agriculture mass residue was obtained from Najaf, the largest market of agricultural products in Iraq [32,33]. It has been washed with distilled water several times and then filtered to remove the adhering dirt. The cleaned rice husk was oven-dried completely at 65°C for 24 h and then crushed, and sieved to 1.5 mm size. It has a surface area of 342.5 cm<sup>2</sup>. Eggshell and eggplant seed (natural adsorbent) have been collected and washed several times by distilled water and dried for 3–5 d by sunlight. Then, they were crushed to powder, washed with distilled water again five times and dried in an oven up to 120°C for 24 h. Zeolite A and kaolin (commercial adsorbents) used in

the experiments were purchased from Central Drug House (P) Ltd – CDH (India Company) and SCR – Chain Company (India) with a grain fraction of 1 mm.

### 2.3. Batch adsorption experimental set-up

Experiments of batch adsorption in this study were conducted to reach the optimum operating conditions of tartrazine dye removal and were carried out at an ambient temperature of 23°C with different pH 2–12, dye concentration 5–50 mg L<sup>-1</sup> and different amount of adsorbents 0.05–0.2 g of GAC and 0.1–1 g of rice husk, the required values of pH were adjusted by adding either 1 M NaOH or 1 M HCl to the test solution. In 100 mL flasks, a known amount of synthetic or natural adsorbent was added to 50 mL of the test solution at known pH and initial dye concentration. The mixture was shaken using a mechanical shaker (Heidolph Unimax 1010 Model, Germany) at a constant speed 140 rpm. After determining interval time, the samples were withdrawn by using a centrifuge device (model PLC-03, Germany Industrial Corporation) at 2,500 rpm for 10 min to separate the adsorbent from the solution. The spectrophotometric device (Jenway 6850, Germany) with a double beam spectrophotometer was used at 426 nm to evaluate the residual dye concentration in the supernatant.

The percentage of dye removal was determined utilizing the following equation:

$$\% \text{Removal of dye} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

where  $C_0$  and  $C_e$  (mg L<sup>-1</sup>) are the initial and equilibrium concentrations of dye respectively.

### 2.4. Isotherms adsorption

Equilibrium relations between sorbate and adsorbent are determined by isotherms adsorption. The ratio of the adsorbed quantity to that residual in the solution at a constant temperature at equilibrium. To determine the fit model that is utilized in the design process, data of isotherm must accurately proportion with various models of isotherm [34]. Two models of isotherm models Langmuir and Freundlich were examined in this study. The formula of the Langmuir model equation as follows:

$$\frac{C_e}{q_e} = \frac{1}{bq_{\max}} + \frac{C_e}{q_{\max}} \quad (2)$$

where  $q_e$  is the equilibrium capacity of adsorption (mg g<sup>-1</sup>),  $C_e$  is the concentration of tartrazine at equilibrium (mg L<sup>-1</sup>), and  $b$  is the constant of Langmuir (L mg<sup>-1</sup>).  $q_{\max}$  is the maximum capacity of adsorption (mg g<sup>-1</sup>) obtained from the slope and intercept of plot  $C_e/q_e$  against  $C_e$ . This equation was successfully applied to several processes of adsorption [35] and proposes the monolayer covering of the tartrazine dye onto the adsorbent surface of the GAC and rice husk. Also, isotherm data was

studied with the Freundlich isotherm which is based on the heterogeneous surfaces at regular energy and without a restriction for forming the monolayer, which can be expressed by Alkafajy and Albayati [36].

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (3)$$

where  $K_F$  is the adsorption capacity at unit concentration and  $1/n$  is the adsorption intensity.

### 2.5. Kinetics of adsorption

#### 2.5.1. Pseudo-first-order kinetic

The pseudo-first-order equation for calculating the adsorption rate constant is write as follows [37]:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (4)$$

where  $q_e$  and  $q_t$  are the amounts of tartrazine dye adsorbed at equilibrium (mg g<sup>-1</sup>) and at time  $t$  (min) respectively, and  $K_1$  (min) is the adsorption rate constant of pseudo-first-order.

#### 2.5.2. Pseudo-second-order kinetic

Another type that describes the kinetics of the adsorption process is pseudo-second-order kinetics [38]. The equation of this kinetic can be written as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where the equilibrium adsorption capacity ( $q_e$ ) and the second-order constant  $K_2$  (g mg<sup>-1</sup> min<sup>-1</sup>).

### 2.6. Adsorption thermodynamics

Thermodynamic parameters were obtained from the equation of Van't Hoff at 288, 303, and 313 K. The valuation of these parameters was from calculate of Gibbs free energy ( $\Delta G^\circ$ ) utilizing the following equation:

$$\ln K_d = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (6)$$

where  $\Delta H^\circ$  is the change of enthalpy (J mol<sup>-1</sup>),  $\Delta S^\circ$  is the change of entropy (J mol<sup>-1</sup> K<sup>-1</sup>). These parameters have been determined from the intercept and slope of plots  $\ln K_d$  against  $1/T$ . Where  $R$  (8.314 J mol<sup>-1</sup> K<sup>-1</sup>) is the universal gas constant,  $T$  (K) is the temperature and  $K_d$  is the distribution coefficient and determined from the equation below:

$$K_d = \frac{V(C_0 - C_e)}{W \times C_e} \quad (7)$$

where  $V$  is the volume of sample (L) and  $W$  is the amount of adsorbent (g).

The Gibbs free energy is determined from the following equation:

$$\Delta G^\circ = -RT \ln K_d \quad (8)$$

where  $\Delta G^\circ$  is standard free energy change ( $\text{J mol}^{-1}$ ) [39].

### 3. Results and discussions

#### 3.1. Comparison of studied adsorbent types

A comparison study was investigated between the various type of adsorbents natural adsorbent such as eggshell, rice husk, eggplant seed, and commercial adsorbent: zeolite A, kaolin and granular activated carbon to determine the more effective type of natural and commercial adsorbent for treatment of tartrazine in aqueous solution and the results are shown in Fig. 2.

The batch adsorption experiments were carried out by using 0.2 g/50 mL amount dosage of commercial and natural adsorbents at pH = 7, dye concentration  $10 \text{ mg L}^{-1}$ , and at a fixed contact time of 90 min. It was seen that the tartrazine dye removal was minimum when using eggshell (22%) and it was approximately equal (26%) when eggplant, kaolin, and zeolite A were used. Whilst, the removal reached a high by using GAC (100%) as a commercial adsorbent and rice husk (34.8%) as a natural adsorbent. Therefore, these two types were chosen during this study because they are more effective than other adsorbents which were studied in this research.

#### 3.2. Batch adsorption

##### 3.2.1. Effect of pH

The influence of pH on the adsorption of tartrazine dye has been studied. The experiments of the dye tartrazine adsorption process were carried out at a range

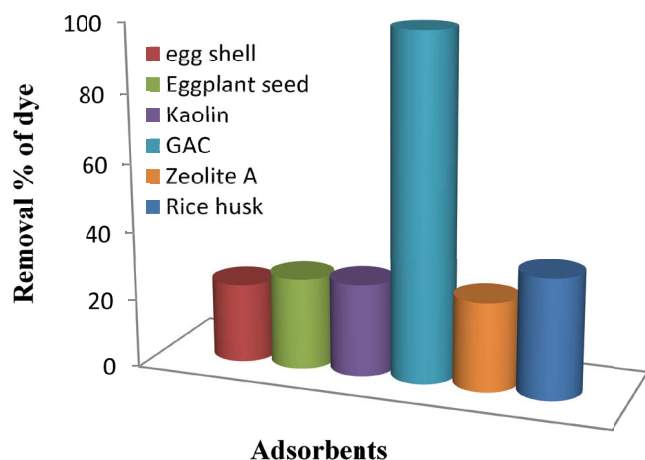


Fig. 2. Effect of different types of adsorbent on adsorption of tartrazine ( $C_0 = 10 \text{ mg L}^{-1}$ ; each type of adsorbent = 0.2 g/50 mL; time = 90 min; pH = 7).

of pH 2–12 and  $23^\circ\text{C}$ . The lowest removal efficiency of dye adsorption by GAC and rice husk was at pH 12 and the highest removal of dye was at pH 2 as demonstrated in Fig. 3. This can be explained because the presence of anionic dye in dissociated form as dye ions in the aquatic solutions:



At pH less than 6, a high attraction electrostatic force significantly presents between the anionic tartrazine dye and the positively charged surface for both GAC and rice husk, therefore the absorption of dye is enhanced. Whereas at a high pH, the positive charge sites for adsorbents will decrease and the surface of there be charged with a negative charge and this case was caused to the repulsion of electrostatic, therefore, lead to low adsorb of anionic dye from the aquatic solution [40,41]. And also with pH increase, the effective compete of  $\text{OH}^-$  ions with ions of dye causing a reduction in adsorption of the dye. Also, the effectiveness of dye adsorption decrease with an increase of pH was observed in research addressing adsorption by utilizing maize silage [42], chitosan materials [43].

In Fig. 3 at the lowest pH, a higher removal of dye was observed 97.83% and 75.83% by GAC and rice husk at 0.1 g/50 mL dye and 90 min respectively.

##### 3.2.2. Effect of initial tartrazine dye concentration and contact time

The effect of tartrazine dye initial concentration  $5\text{--}50 \text{ mg L}^{-1}$  on the removal efficiency using GAC and rice husk 0.1 g/50 mL as adsorbents are illustrated in Fig. 4. The experiments were carried out at pH 2, temperature  $23^\circ\text{C}$ , and different periods of contact time.

It appeared from Fig. 4 that the removal efficiency of tartrazine dye decreased with increasing the tartrazine dye initial concentration, this can be explained due to the saturation of the adsorbent surface in the sites of adsorption, which referred to the probable formation of a monolayer of dye molecules at the interface with the adsorbent [44]. Also, the increase of initial concentration

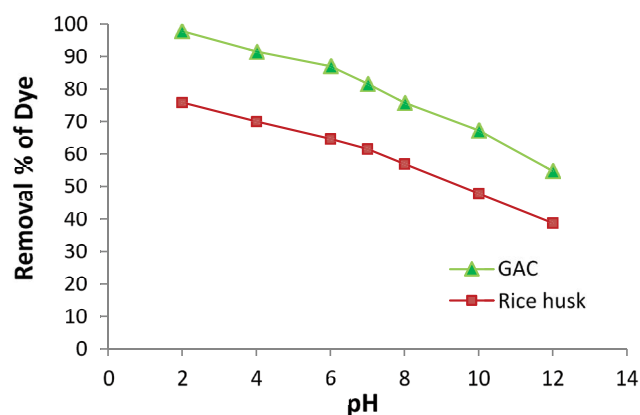


Fig. 3. Effect of pH on adsorption of tartrazine ( $C_0 = 10 \text{ mg L}^{-1}$ ; adsorbent = 0.1 g/50 mL; time = 90 min).

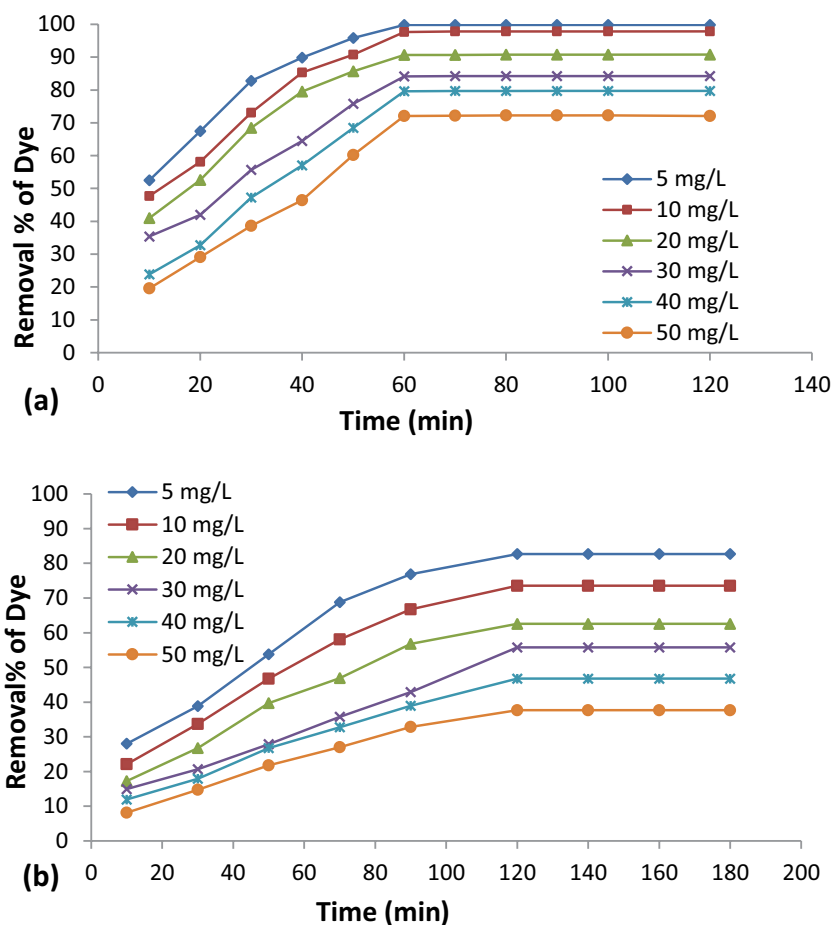


Fig. 4. Effect of time and concentration of dye on adsorption of tartrazine by using (a) GAC and (b) rice husk.

of tartrazine dye promotes the interaction between adsorbents and molecules of tartrazine dye. As a result, the driving force of the concentration gradient increase [45]. The removal efficiency of tartrazine dye reached 99.82% using GAC and 82.67% using rice husk for 5 mg L<sup>-1</sup> of tartrazine dye concentration, while it was 72.04% using GAC and 37.68% using rice husk for 50 mg L<sup>-1</sup>.

Also, it was observed that the tartrazine dye removal was fast in the first stages, and then it reached the equilibrium and was quasi stabilized to the highest value of all dye concentrations studied (Fig. 4). The adsorption was in an equilibrium state between the dye and GAC adsorbent after 60 min and rice husk adsorbent after 120 min of contact time. A cause can be that during a molecules tartrazine dye sorption, at first, the molecules of dye quickly arrived the boundary layer, then they diffuse slowly from the film boundary layer on the adsorbent's surface, because of the occupied many available external sites, and lastly, diffuse in the porous of adsorbents (GAC and rice husk). Similar explanations were suggested by Ahsaine et al. [46].

### 3.2.3. Effect of adsorbent dosage

The effect of adsorbent dosage on the removal of tartrazine dye is illustrated in Fig. 5. It was observed that the

removal of tartrazine increased as the adsorbent dosage increased, the tartrazine removal by GAC (0.05 g) reached 80.88% at 120 min and 5 mg L<sup>-1</sup> tartrazine concentration, while the removal was 90.34% by GAC (0.075 g) at 100 min and 5 mg L<sup>-1</sup> tartrazine concentration. But when the tartrazine concentration 50 mg L<sup>-1</sup> the removal of dye reached 86.56% at 80 min using 0.175 g of GAC, and the removal was 94.56% utilized 0.2 g of GAC at 80 min for 50 mg L<sup>-1</sup> concentration of dye. The tartrazine removal reached 76.95% at 120 min, 5 mg L<sup>-1</sup> tartrazine concentration by using 0.15 g of rice husk, and the removal was 90.45% using 0.2 g of rice husk at 120 min, 5 mg L<sup>-1</sup> tartrazine concentration, but by using 1 g of rice husk the removal of dye reached to 90.87% at 120 min, 50 mg L<sup>-1</sup> tartrazine concentration, while the removal was 70.65% using 0.8 g of rice husk at 120 min, 50 mg L<sup>-1</sup> tartrazine concentration. This can be explained because of the increase of adsorbents dosage that results in the increase of the surface area and therefore an available more sites of adsorption [47]. Similar observations were reported elsewhere [48].

### 3.2.4. Adsorption isotherms

Fig. 6 shows the adsorption isotherms of tartrazine onto adsorbents (GAC and rice husk). The samples of

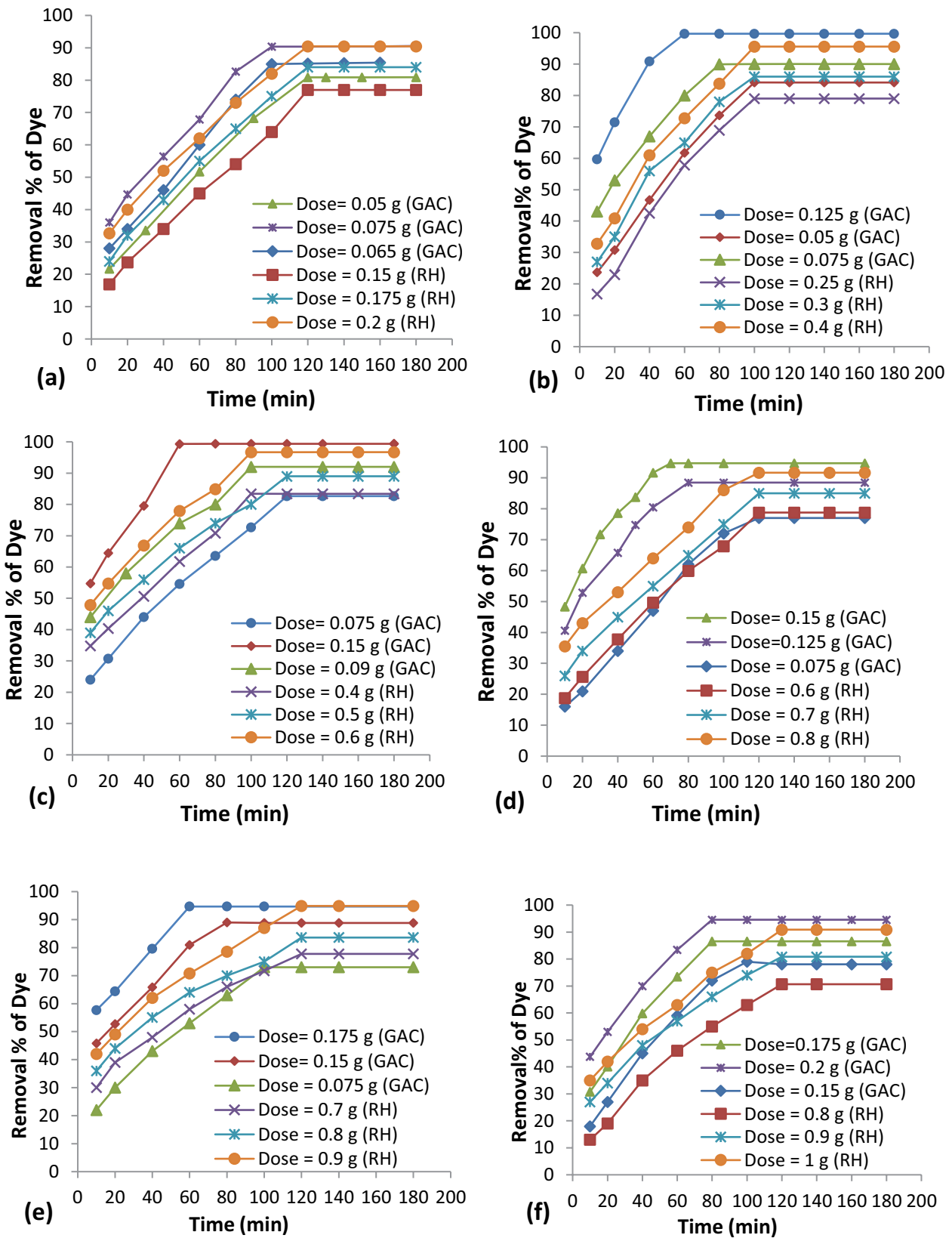


Fig. 5. Effect of adsorbents (GAC and RH) dose adsorbent on the various concentrations of tartrazine dye (a) 5, (b) 10, (c) 20, (d) 30, (e) 40, and (f) 50 mg L<sup>-1</sup>.

aqueous solution were agitated for 60 min (140 rpm) at a constant temperature of 23°C at pH 2, and optimum dose adsorbents dose (0.1 g for GAC and 0.2 g for rice husk). Table 1 presents the correlation coefficient values for both Langmuir ( $q_e$ ,  $b$ ,  $R^2$ ) and Freundlich ( $K_f$ ,  $n$ ,  $R^2$ ) isotherms. It has been found the Langmuir isotherm model is the best fit for the adsorption of dyes on the GAC and rice husk and has a high  $R^2$  value. Similar observations were reported by Józwiak et al. [49] and Ouassif et al. [50].

### 3.2.5. Adsorption kinetics

The experiments of adsorption were performed to analyze the kinetics of adsorption at optimum adsorbents dose of the different dye concentrations at pH 2, the temperature of 298 K, and agitated at 140 rpm and at interval periods time 10–200 min. The values of the rate constant,  $K_1$  of pseudo-first-order, were determined from the linear plots of  $\ln(q_e - q_t)$  vs.  $t$  (Fig. S1), and their values are given in Table 2. The model of pseudo-first-order was observed

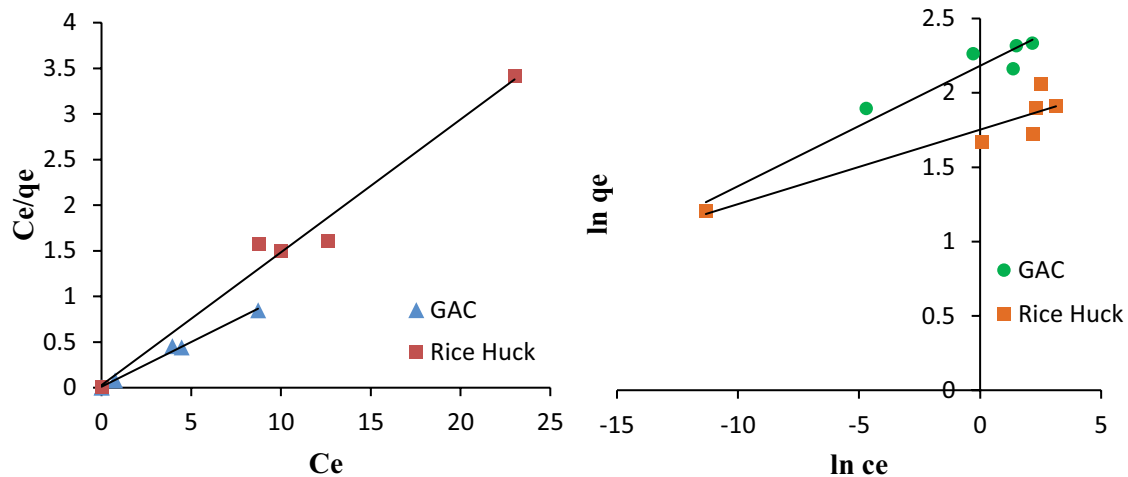


Fig. 6. Adsorption isotherms models of dye by GAC and rice husk (a) Langmuir isotherm model and (b) Freundlich isotherm model.

Table 1

Isotherm parameters for tartrazine adsorbed onto GAC and rice husk with the correlation coefficient

Adsorbents	Langmuir isotherms			Freundlich isotherms		
	$q_{\max}$ ( $\text{mg g}^{-1}$ )	$b$ ( $\text{L mg}^{-1}$ )	$R^2$	$K_f$ ( $\text{mg}^{1-n} \text{g}^{-1}/\text{L}^n$ )	$1/n$	$R^2$
GAC	10.204	0.001049	0.9930	0.458295	0.0810	0.9557
Rice husk	6.868	0.004062	0.9831	0.570613	0.0501	0.8652

Table 2

Kinetic adsorption parameters obtained using pseudo-first-order and pseudo-second-order models

Dye concentration	Adsorbents	Pseudo-first-order			Pseudo-second-order		
		$q_e$ ( $\text{mg g}^{-1}$ )	$K_1$ ( $\text{min}^{-1}$ )	$R^2$	$q_e$ ( $\text{mg g}^{-1}$ )	$K_2$ ( $\text{g min}^{-1} \text{mg}^{-1}$ )	$R^2$
5 $\text{mg L}^{-1}$	GAC	1.5669	0.0256	0.9715	4.4444	0.014139	0.9798
	Rice husk	1.4904	0.0389	0.9689	2.3266	0.030669	0.9733
10 $\text{mg L}^{-1}$	GAC	3.5338	0.0403	0.8609	9.1407	0.004571	0.9858
	Rice husk	1.0459	0.0512	0.8730	1.0520	0.096383	0.9734
20 $\text{mg L}^{-1}$	GAC	3.3038	0.02800	0.8879	15.2905	0.005602	0.9981
	Rice husk	1.4306	0.0198	0.8332	1.7488	0.016754	0.9292
30 $\text{mg L}^{-1}$	GAC	2.3268	0.0121	0.8478	11.6686	0.004544	0.9589
	Rice husk	1.2757	0.0101	0.9055	2.2148	0.032482	0.9596
40 $\text{mg L}^{-1}$	GAC	2.5515	0.0131	0.9101	15.2207	0.004272	0.9812
	Rice husk	1.2789	0.0085	0.9595	2.2899	0.031813	0.9978
50 $\text{mg L}^{-1}$	GAC	3.1963	0.0143	0.9567	19.1938	0.001071	0.9574
	Rice husk	1.3855	0.0051	0.9000	2.8943	0.019246	0.9077

as unsuitable to describe the adsorption kinetics of dye by utilizing adsorbents. The same results have been found for some previous studies by Jóźwiak et al. [49], Ouassif et al. [50], and Ansari et al. [51].

The parameters of pseudo-second-order ( $K_2$  and  $q_e$ ) were obtained by the slope and intercept from the plot  $t/q_t$  against  $t$  (Fig. S2) and in Table 2 had been presented with correlation coefficients. The values of  $R^2$  were high and the plots approved its excellent linearity of the pseudo-second-order model. Furthermore, the pseudo-second-order model was suitable to describe the tartrazine dye adsorption kinetic by

GAC and rice husk and the tartrazine dye adsorption was a multistep process that includes the adsorption onto the external surface and diffusion into the interior of adsorbents. Similar results have been observed for done study by Gautam et al. [52] and Brice et al. [48].

### 3.2.6. Adsorption thermodynamics

The values of the thermodynamic parameters are present in Table 3, by plotting the linear formula of Van't Hoff ( $\ln K_c$  via.  $1/T$ ) as seen in Fig. S3. The  $\Delta G^\circ$  value was negative

Table 3  
Thermodynamic variables for the sorption tartrazine dye on GAC and rice husk at different temperatures

T (K)	GAC			Rice husk		
	$\Delta G^\circ$ (kJ mol <sup>-1</sup> )	$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S^\circ$ (kJ mol <sup>-1</sup> )	$\Delta G^\circ$ (kJ mol <sup>-1</sup> )	$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S^\circ$ (kJ mol <sup>-1</sup> )
288	-0.83327			-3.2385		
296	-1.43522			-5.4557		
303	-2.35771	65.9882	0.2395	-8.80801	23.0630	0.075972
313	-3.30939			-10.7655		

Table 4  
Comparison between this study and other studies

No.	Adsorbent	Removal	Adsorption capacity (mg g <sup>-1</sup> )	Sorption conditions	References
1	Activated carbon biosorbents from <i>Lantana camara</i>	92.8%	90.90	Adsorbent dose = 0.2 g; pH = 2.0; time = 30 min; temperature = 50°C	[52]
2	Polyaniline nanolayer composite	98.0%	2.47	Adsorbent dose = 0.5 g; pH 2.0; temperature = 25°C; time = 60 min	[51]
3	Saw dust	97.0%	4.71	Adsorbent dose = 5 g; pH 3.0; temperature = 45°C; time = 70 min	[43]
4	Chitin		30	Adsorbent dose = 250 mg; pH 3.0; time = 30 min; temperature = 25°C	[53]
5	HDTMA-Br-Modified Colombian Bentonite	98.0%	40.79	Adsorbent dose = 38.04 mg; pH 6.0; time = 60 min; temperature = 20°C	[54]
6	Aminated sunflower seed hulls (SSH-AM)	71%	44.8	Adsorbent dose = 5 g; pH 3.0; time = 240 min; temperature = 20°C	[49]
7	Chitin	55%	24.2	Adsorbent dose = 1 g; pH 1–3; time = 120 min; room temperature	[55]
8	<i>Cucurbita moschata</i> leaves (NPsFeOA)	92%	59.79	Adsorbent dose = 0.5 g; pH 7.0; time = 180 min; temperature = 25°C	[56]
	<i>Beta vulgaris</i> stalks (NPs-FeOB)	95.8%	59.78	Adsorbent dose = 0.5 g; pH 7.0; time = 1,200 min; temperature = 25°C	
9	Zinc-Aluminum layered double hydroxide	97%	282.48	Adsorbent dose = 0.4 g; pH 5.8; time = 60 min; temperature = 25°C	[50]
10	Biosolids-based activated carbon	97.40%	9.87	Adsorbent dose = 1.07 g; pH 2.13; time = 116.95 min; room temperature	[57]
11	Commercial activated carbon	75%	4.48	Adsorbent dose = 12 g; pH 1.68; time = 60 min; temperature = 26°C	[58]
12	Commercial activated carbon	99.81%	3.32	Adsorbent dose = 0.1 g; pH 2.0; time = 60 min; temperature = 23°C; 5 mg L <sup>-1</sup> dye	This study
13	Rice husk	90.45%	1.24	Adsorbent dose = 0.2 g; pH 2.0; time = 120 min; temperature = 23°C; 5 mg L <sup>-1</sup> dye	This study



and refers to the feasibility and spontaneous of the adsorption process at the temperatures applied. The observed decrease in the value of  $\Delta G^\circ$  with an increase in temperature suggested that higher temperatures would ease the tartrazine dye adsorption onto adsorbents (rice husk and activated carbon). The  $\Delta H^\circ$  value was positive and indicates the adsorption of dye on the surface of the adsorbent is endothermic. However, the positive values of  $\Delta S^\circ$  indicate increasing the randomness degree at the interface solid/solution taken place in the inner structure in the tartrazine dye adsorption onto the adsorbents (activated carbon and rice husk) [53]. Similar results were obtained by Gautam et al. [52].

### 3.3. Comparative study

This study was deal with the removal of tartrazine dye utilizing GAC and rice husk in a batch adsorption process due to a high surface area of GAC and a low cost of rice husk compared with the other types of adsorbents. Furthermore, in the actual industrial wastewater treatment, the adsorption process can be applied to obtain the higher removal efficiency of tartrazine dye because of its ability to adapt to many-sided processes, which can reduce the costs of operating and processing. Table 4 shows the comparison between this study and others, for the removal of tartrazine dye and presents that rice husk was a promising adsorbent to remove the tartrazine dye for the first time in the batch adsorption.

## 4. Conclusions

The present study revealed that rice husk is a promising adsorbent for tartrazine dye removal from aqueous solution but its efficiency was less than that of the commercial GAC. The removal of tartrazine increased with increasing both adsorbent dosage and contact time and decreased with initial tartrazine concentrations and pH. The maximum adsorption of dye occurred at pH 2 and 5 mg L<sup>-1</sup> tartrazine concentration which was equivalent of removal efficiency up 99.81% of GAC 0.1 g/50 mL and 90.45% of rice husk at using 0.2 g/50 mL of adsorbents dose. The optimum contact time was observed after 60 min of GAC and 120 min of rice husk. The adsorption data were suited well with the Langmuir model because the correlation coefficient was higher than that of the Freundlich one. This shows that tartrazine is covered on the surface of adsorbent in a monolayer form with homogeneous sites and was observed that the dye removal by using GAC seems to be better than rice husk. The adsorption experiments have appeared that the pseudo-second-order kinetic model were suited well. The thermodynamic studies demonstrated that the values of  $\Delta H^\circ$  and  $\Delta G^\circ$  were positive and negative respectively which indicated the tartrazine dye adsorption on the adsorbents was endothermic and spontaneous in nature. Therefore, the higher removal of tartrazine dye can be reached at the higher temperatures.

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Supplementary Infotmation

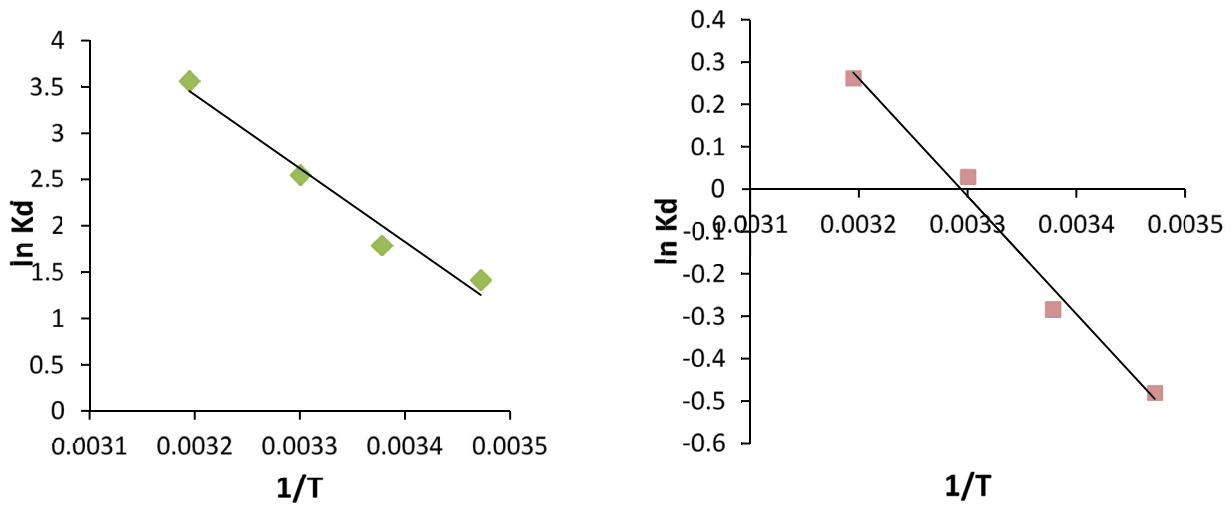


Fig. S3.  $\ln K_d$  vs.  $1/T$  for the adsorption of tartrazine dye by (a) GAC ( $C_0 = 10 \text{ mg L}^{-1}$ ; pH = 2; dose = 0.075 g; time = 100 min) and (b) rice husk ( $C_0 = 10 \text{ mg L}^{-1}$ ; pH = 2; dose = 0.25 g; time = 100 min).

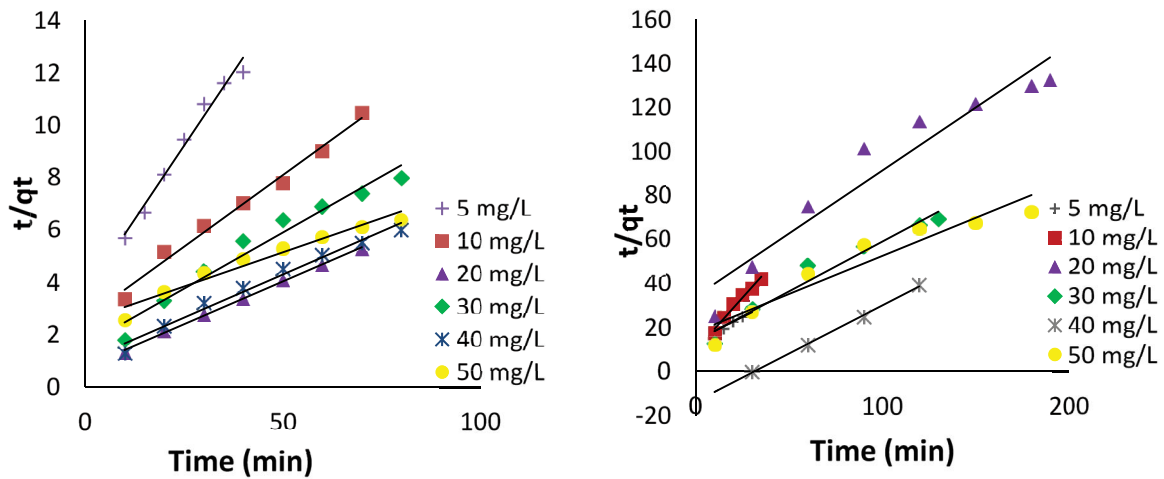


Fig. S2. Pseudo-second-order kinetic plot for adsorption of tartrazine over (a) GAC and (b) rice husk.

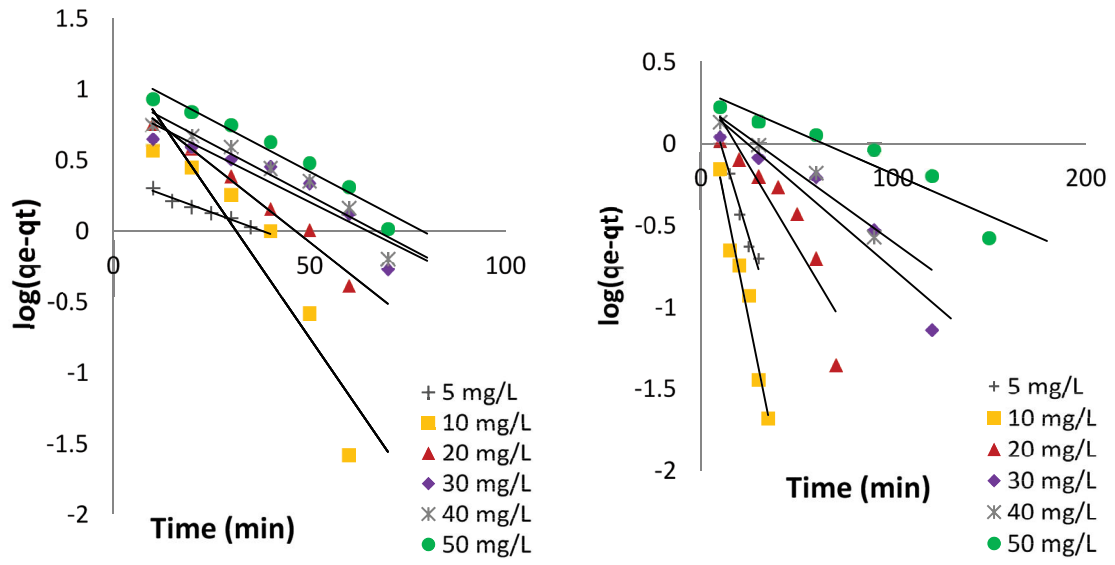


Fig. S1. Pseudo-first-order kinetic plot for adsorption of tartrazine over (a) GAC and (b) rice husk.