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Flower wastes as a low-cost adsorbent for the removal of acid blue 9
Residuos de flores como adsorbentes de bajo costo para la remoción de azul ácido 9

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Abstract

This paper describes the use of flower wastes (carnation, rose and daisy) as a potential, alternative and low-cost adsorbent for the removal of Acid Blue 9 (AB9). The best conditions to achieve an efficient adsorption were evaluated in a batch process. With an acidic pH of 2.0, a removal exceeding 90% was obtained using concentrations of AB9 of 15.0 mgL-1 and a dosage of adsorbent of 4.0 gL-1. The equilibrium of the process was modeled using the Langmuir and Freundlich isotherms, obtaining a better fit with the latter one. Kinetic studies indicated a better fit of the process to a pseudo-second order model and negligible effect of temperature. In addition, the bromatological characterization of the adsorbent is shown.

Keywords: adsorption; isotherms; kinetics, acid blue 9; flower wastes.

Resumen

El presente artículo describe el uso de residuos de flores (claveles, rosas y margaritas) como un adsorbente potencial, alternativo y de bajo costo para la remoción del colorante azul ácido 9 (AB9). Las mejores condiciones para lograr una adsorción eficiente fueron evaluadas en un proceso discontinuo. Un pH ácido de 2.0 permitió obtener una remoción superior al 90%, usando concentraciones de AB9 de 15.0 mgL-1 y una dosificación de adsorbente de 4.0 gL-1. El equilibrio del proceso fue modelado usando las isotermas de Langmuir y Freundlich, obteniendo un mejor ajuste con la última. Estudios cinéticos señalaron un proceso de pseudo-segundo orden y un efecto de la temperatura poco significativo. Adicionalmente, se presenta la caracterización bromatológica del adsorbente.

Palabras clave: adsorción; isotermas; cinética; azul ácido 9; residuos de flores.

1. Introduction

Dyes are widely used in textiles, paper, plastics, rubber, leather, cosmetic, pharmaceutical and food industries. The presence of these dyes in water, even at very low concentrations is highly visible and undesirable [1]. Water pollution due to discharge of colored wastewater negatively affects aquatic life and consequently, the overall ecosystem. Dyes reduce the light penetration required for the photosynthetic activity and therefore, the water self-purification process is reduced. More than 700.000 tonnes and around 1.000 different dyes and pigments are manufactured annually worldwide, 10% of them are discharged in wastewater [2,3].

Carcinogenic agents as benzydine and other aromatic amines compounds that can be transformed in more toxic derivatives as a result of microbial activity, are also used in dye manufacture [4,5].

Brilliant blue (acid blue 9) is a synthetic acid dye, with anionic nature belonging to triphenylmethanes, commonly used for flower dyeing, textile and in food industries. It is a highly stable compound and thus causes the color of effluents for extended periods of time. For the treatment of colored effluents, chemical, physical and biological conventional technologies have been tested; however, the physicochemical ones are often expensive and generate toxic sludge. Likewise, on a large scale it becomes a difficult issue in biological treatments [2].

The adsorption process has been proven to be one of the best water treatment technologies around the world and activated carbon is undoubtedly considered as universal adsorbent for the removal of diverse types of pollutants from water[6]. To diversify the abundantly available agricultural waste, it has been proposed to convert it into activated carbons [7,8]. Nevertheless it has considerable production costs [2]. Therefore, it is necessary to find alternative, efficient and inexpensive methods for the treatment of colored wastewater. Biosorption has several advantages among the methods analyzed for the removal of dyes in solution, and a large number of low-cost adsorbents derived from agricultural, poultry waste and even ashes have been successfully tested [9–20]. Structurally

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agricultural materials consist of lignin, cellulose, hemicellulose and some proteins, which make them effective biosorbents [21].

In this study, the use of three locally available, renewable and previously untested adsorbents, carnation, rose and daisy stalks for the removal of acid blue 9 were evaluated. The aim of this investigation was to use low-cost adsorbents to develop a low-priced dye-removal technology. The effect of various parameters on the process such as pH, adsorbent dosage and initial concentration of dye were analyzed. Also, in order to find information on the physicochemical characteristics of the adsorption, the equilibrium of the process is modeled using the Freundlich and Langmuir isotherms and the kinetics through the equations of the first and second order.

2. Materials and Methods

2.1. Collection and preparation of the flower wastes

The stems of flowers (carnation, rose and daisy) were obtained from a local market. They were washed and dried at 80 °C for 48 hours. Subsequently, they were milled to produce particles of the desired mesh size (500-700 µm) (Physis).

2.2. Flowers waste characterization

2.2.1. Bromatological analysis

Determination of the main components of the studied adsorbent was carried out according to the Van Soest method [22] including the evaluation of acid detergent fiber (ADF), neutral detergent fiber (NDF) and lignin. With this data the content of cellulose and hemicellulose was estimated. Starch content, ash and nitrogen were determined by using the same method. The tests were conducted at the Laboratory of Chemical and Bromatological Analysis of the Universidad Nacional de Colombia - Sede Medellín.

2.3. Chemicals

The textile dye Acid Blue 9 (AB9, CI 42090; industrial grade; molecular weight 792.84, molecular formula $C_{37}H_{34}N_2OS_3Na_2$) was obtained from Merck, Colombia and used without further purification, its chemical structure is shown in Fig. 1.

2.4. Stock solution

A stock solution (500 mgL^{-1}) was prepared by dissolving a determined amount of AB9 in distilled water. This solution was diluted to obtain the desired concentrations.

2.5. Dye concentration analysis

Dye Concentration was determined spectrophotometrically using UV-Vis spectrophotometer (Perkin-Elmer, Lambda 35). The absorbance was recorded at a wavelength of (λ = 629 nm), which correspond to the maximum adsorption peek of AB9 and the concentration was determined in the calibration curve.

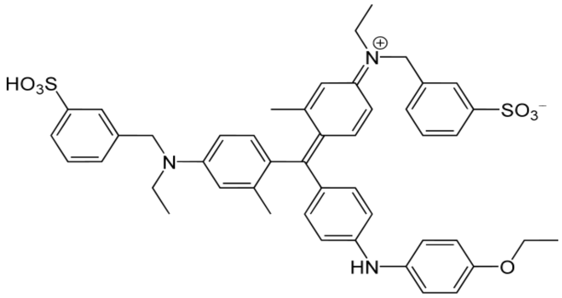

Figure 1. Chemical structure of AB9. Source:Merck

2.6. Biosorption studies

In order to determine the best conditions for dye removal, adsorption tests were carried out in batch and kept in a shaker Heidolp Unimax 2010 at 25±2 °C and 120 rpm. After stirring, samples were centrifuged in a Fisher Scientific and the supernatant was measured for the determination of remnant dye concentration.

2.6.1. Effect of pH on dye adsorption

The pH of the dye solution was adjusted to a range of 2.0-10.0. This modification was carried out using 1.0 M HCl / NaOH (Merck). Each of the adsorbents (carnation, rose and daisy) was added in 30 mg to 10 mL solution containing 15 mg of dye / L.

2.6.1. Effect of flower waste dose on removal efficiency

Adsorbent dosage was varied in the range of 30-800 mg sorbent / mg of dye. A 10 mL solution with 15 mg of dye / L at pH 2.0 was used. The adsorbent used in this experiment and in the following was an equimolar mixture (carnation, rose and daisy) to get results that could be extrapolated to real situations.

2.6.2. Effect of initial dye concentration on dye sorption

The effect of initial dye concentration was analyzed in a range of 0-15 mg / L. The adsorbent dose (40 mg) was added to 10 mL of solution with variable concentration of dye at pH 2.0.

2.6. Equilibrium studies

The obtained data from equilibrium tests were analyzed using the Langmuir and Freundlich isotherms, in order to obtain information on the surface of the adsorbent. There are several theoretical models; however, the Langmuir and Freundlich isotherms are the most common. Quantification of the amount of dye attached to the biomass was performed using the eq. (1):

$$q_{eq} = (C_0 - C_{eq})V/W \tag{1}$$

Where:

q_{eq}: Amount of adhered dye to biomass [mg/g]
C_0, C_{eq}: Initial and equilibrium concentration of the contaminant [mgL^{-1}]
V: Volume of dye solution used [L]
W: Mass of added sorbent [g]

2.7.1. Langmuir isotherm

The empirical model of Langmuir sets up the existence of a uniform layer in which there is a finite number of equivalent active sites distributed homogeneously. This model states through eq. (2) that:

$$q_{eq} = q_{max*b*C_{eq}}/(1 + b * C_{eq}) \tag{2}$$

With:

q_{max}: Langmuir constant denoting the maximum adsorption capacity of biomass [mg/g]
b: Langmuir constant that indicates the affinity for the active sites

Specific constants can be obtained from the intercept and slope of linearized eq.(2):

$$\frac{1}{q_e} = \left(\frac{1}{Q_{max}}\right) + \left(\frac{1}{b * Q_{max}}\right)\left(\frac{1}{C_{eq}}\right) \tag{3}$$

2.7.2. Freundlich isoterm

In this model a mixed monolayer is considered in which the active sites are not independent or equivalent. The specific adsorption capacity is given by eq. (4):

$$q_{eq} = K_f C_{eq}^{1/n} \tag{4}$$

With:

K_f: Freundlich constant related to biomass adsorption capacity
n: Freundlich constant that indicates the intensity of adsorption

From the slope and intercept of the linearized equation, the value of the constants can be determined through eq. (5):

$$\ln q_{eq} = \ln K_f + (1/n)\ln C_{eq} \tag{5}$$

2.7. *Kinetic studies*

Kinetic studies were performed in order to determine whether the controlling steps are mass transfer or chemical reaction processes. Pseudo - first order and pseudo - second order equations were used, ignoring the movement of the dye ion from the liquid bulk to the liquid film or boundary layer surrounding the adsorbent.

The first order kinetic is based on the adsorbent capacity and is generally expressed by eq. (6).

$$dq/dt = k_1(q_{eq} - q) \tag{6}$$

Where q_{eq} and q are the amounts of adsorbed dye on the biosorbent at equilibrium and at time t, respectively (mg/g) and k_1 is the rate constant of first-order biosorption (1/min). After integration and applying boundary conditions, t = 0 to t = t and q = 0 to q = q; the integrated form of eq. (6) becomes:

$$\log(q_{eq} - q) = log(q_{eq}) - k_1 t\,/2.303 \tag{7}$$

A fit of the experimental data through the straight line of log (q_{eq} – q) vs. *t* would imply the applicability of this kinetic model. In this case, the parameter q_{eq} must be known. It might happen that q_{eq} is unknown and the adsorption process becomes extremely slow, the amount adsorbed being significantly smaller than the equilibrium amount. For this reason, it is necessary to extrapolate the experimental data to t = ∞ or use trial and error. Moreover, the pseudo - first order model usually fit just over the first period of sorption (20 - 30 min) and does not describe the entire process well [23].

On the other hand, the pseudo - second order kinetic describes all stages of adsorption: external film diffusion, adsorption and internal particle diffusion. The model is based on the adsorbent capacity and assumes the adsorption processes involves chemisorption mechanism. Furthermore, it considers adsorption to be the rate controlling step and is expressed as follows:

$$dq/dt = k_2(q_{eq} - q)^2 \tag{8}$$

Where k_2 is the rate constant of second-order biosorption (g/mg/min). For the boundary conditions t = 0 to t = t and q = 0 to q = q; the integrated form of eq. (8) becomes:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_{eq}}t \tag{9}$$

If the second order kinetic is applicable, the plot of t/q against t should give a linear relationship. There is no need of knowing any parameter beforehand. The rate constant is also expressed as a function of temperature by the following Arrhenius type relation:

$$k_2 = A_0 \exp(-E_A/RT) \tag{10}$$

Where A_0 is the frequency factor of sorption and E_A is the activation energy of sorption. The magnitude of activation energy may give an idea about the type of sorption.

3. Results and Discussion

3.1. *Bromatological analysis*

It is important to highlight the lack of reports about bromatological composition of these three types of flowers and their mixture. This fact reflects the flower stalks have been little explored as adsorbent material. Table 1 shows the chemical analysis for its major components. The percentages of cellulose, hemicellulose and lignin polymers for the foliage mixture satisfy the required conditions of a potential adsorbent, as has been reported for other agricultural residues with considerable adsorption capacity [24,25]. The ash content is lower when compared to the average value reported for other adsorbents [24–26].

3.2. *Effect of pH value on the adsorption process*

Experimental results show that the adsorption of AB9 is a process highly dependent on the pH. Maximum removal was observed at pH 2.0 with the three kinds of adsorbents (carnation, rose and daisy). By contrast, the adsorption is minimal at higher pH values (3.0-10.0), (Fig.2).

The pH range used did not include extreme values due to degradation of the dye at these points. The dye adsorption capacity at pH 2.0 was 2.08, 3.04 and 3.09 mg/g sorbent, for rose, carnation and daisy, respectively. Similar phenomenon was reported with anionic dyes, with a maximum adsorption at pH 2.0 [15], [23]. This result could be explained by electrostatic interactions between active sites and dissolved molecules. At low pH values, active sites on the surface of the adsorbent are protonated and then positively charged, which enhances electrostatic forces of attraction with anionic molecules, such as AB9. When the pH is increased, the adsorbent is negatively charged and therefore raises repulsion with the dye molecule.

Table 1. Chemical analysis for the flower stalks composition.

Composition	Percentage
FDA	67.80
FDN	77.90
Lignin	17.60
Starch	2.20
Ashes	1.54
Nitrogen	0.90
*Hemicellulose	10.1
*Cellulose	50.2

*calculated. Source: Authors

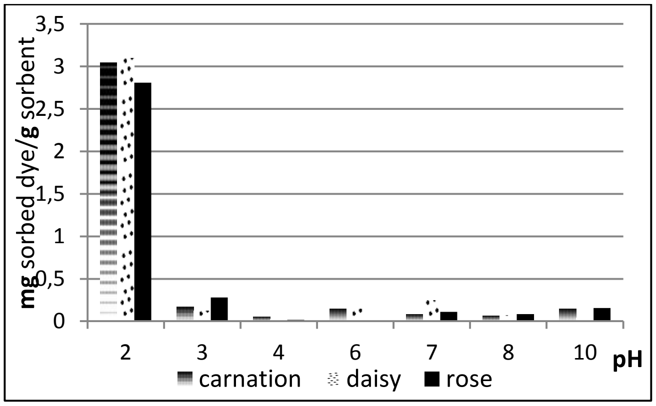

Figure 2. Effect of pH on the adsorption of AB9 by three flower wastes; adsorbent dosage: 30 mg; initial dye concentration: 15 mgL^{-1}; volume: 10 mL; contact time: 24 h; stirring speed: 120 rpm. Source: Authors

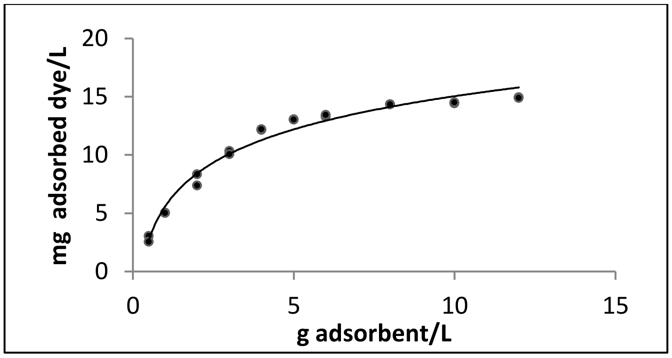

Figure 3. Effect of adsorbent dosage on the adsorption of AB9. Initial dye concentration: 15 mgL^{-1}; volume: 10 mL; pH= 2.0; contact time: 24 h; stirring speed: 120 rpm. Source: Authors

3.3. *Effect of sorbent dose on adsorption process*

The experiments showed as expected that the adsorption of AB9 increased when a greater amount of adsorbent is used (Fig. 3). At low doses of adsorbent (1.0 gL^{-1}) the quantity of dye removed was 5.04 mgL^{-1}. Nevertheless, when using doses of adsorbent higher than 5.0 gL^{-1}, the amount of removed dye increased to 14 mgL^{-1} approximately. Akar and coworkers [28], also found similar results for removal of acid blue 40 on *Thuja orientalis* biomass. Is clear that with higher doses of adsorbent for a determined dye concentration, the available sites over the surface increase, and hence, more dye molecules are retained by the sorbent. In Fig. 3 the influence of the sorbent mixture dosage on dye removal is plotted.

Preliminary studies were performed at different contact times (Table 2). Satisfactory removal of the dye at 24 hours was achieved suggesting this interval as adequate to perform further studies.

3.4. *Effect of initial dye concentration*

It was determined that initial dye concentration is highly influential on the removal percentage. As the initial concentration of AB9 increases, more molecules are adsorbed per unit mass of adsorbent until a constant value, later all active sorption sites are saturated, and then any transfer from the liquid phase is not possible. The increase

Table 2. Removal percentages at different contact times.

Time (h)	Temperature (% removal)		
	25 °C	42 °C	54 °C
2	73.9	80.6	88.1
8	81.1	87.7	94.9
12	84.0	94.0	95.2
24	96.7	95.5	96.0

pH = 2.0, adsorbent dosage 7.0 gL^{-1}, stirring speed 120 rpm. Source:Authors of the initial dye concentration from 1.0-18.0 mgL-1, improved the uptake capacity from 0.1-3.0 mg of dye adsorbed / g adsorbent in the three assessed temperatures 25, 42 and 54 °C, (Fig. 4).

The temperatures were selected in order to be consistent with a process in which there is a minimal energy demand. It is important to remark that we seek to design an economical and efficient process for its possible scaling. As can be observed, temperature had a minimal effect on removal effiency. Aksu and Dönmez [23] also found similar trends for the adsorption of acid blue 161 by Trametes versicolor and remazol reactive blue for various types of yeast, respectively.

This initial increase in adsorption process with dye concentration is due to the more availability of dye molecules in solution to be adsorbed. The major quantity of dye influences the increase in driving force and decreases the resistance to mass transfer from the liquid phase to solid phase. Higher dye concentrations were not used in order to avoid exceeding the limit for the absorbance measurements.

3.5. *Equilibrium studies*

The obtained data from the equilibrium study of adsorption process of AB9 were modeled according to Langmuir and Freundlich isotherms at different temperatures (25, 42 and 54 °C). Taking into account the correlation coefficient, the Freundlich isotherm showed a better fit with an average $R^2 = 0.992$ in the range of concentrations and temperatures evaluated, even though both models fitted very well (Table 3).

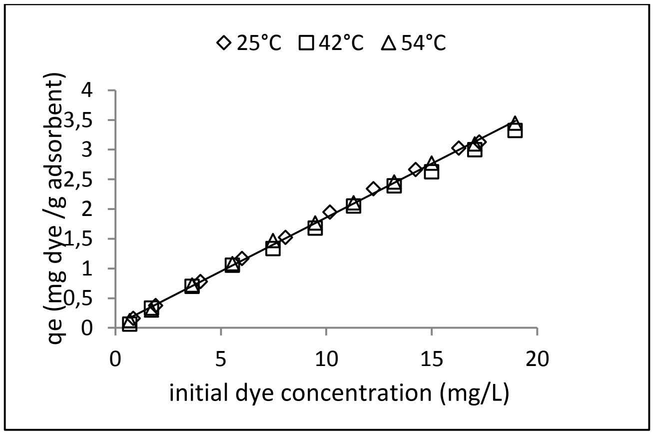

Figure 4. Effect of initial AB9 concentration on its adsorption. Adsorbent dosage: 4.0 gL^{-1}; pH = 2.0; volume: 10 mL; contact time: 24 h; stirring speed: 120 rpm. Source: Authors

Table 3. Equilibrium parameters for the adsorption of AB9 on flower stalks.

Temperature	Freundlich			Langmuir		
	K_f	n	R^2	Qmax	b	R^2
25 °C	1.223	1.056	0.992	18.55	0.042	0.989
25 °C	1.274	1.204	0.995	6.24	0.153	0.997
25 °C	1.298	1.034	0.980	40.16	0.018	0.988

pH = 2.0, adsorbent dose 4.0 gL^{-1}, contact time 24 h, stirring speed 120 rpm. Source: Authors

The linearized plots of Freundlich isotherms at different temperatures are presented in Fig. 5

The Freundlich constant K_f increased from 1.22-1.29 with a rise in temperature of 25-54 °C, indicating its slight influence on the process. The higher the temperature, the better the uptake capacity. This might be due to a rise in interactions and collisions frequency among active surface and dye molecules. The value of *n*, however, shows an irregular pattern, reaching its highest value at 42 °C (n = 1.204). The intensity of biosorption seems to increase until 42 °C and then registers a lower value at 54 °C (n = 1.034).

This behavior could be explained by repulsive interactions at the surface, which reduce binding force between sorbent and solute. This result suggest, first that the increasing temperature has a negligible effect on the performance of the process and secondly, the surface of the adsorbent presents heterogeneous nature with different binding sites and nonequivalent adsorptive energies including electric interferences rather than a homogenous and equivalent monolayer. Osma and coworkers [15] reported a similar adjustment for the adsorption of reactive black 5 on sunflower waste.

According to the Langmuir model, it was not possible to determine a clear relation between temperature and adsorption affinity, nor with adsorption capacity.

3.6. *Kinetic studies*

The adsorption process showed a better fit for the pseudo - second order model kinetics, Table 4 and Fig. 6. Therefore, the reaction takes place in heterogeneous conditions because it depends on the amount of solute adsorbed in a time t and on the equilibrium. It indicates that the rate limiting step might be chemical biosorption involving the exchange of electrons between the dye ions and the adsorbent. Results show a negligible effect on temperature. Similar results were obtained for the adsorption of remazol reactive dye and yeasts and AB40 by cone biomass of *T.orientalis* [23], [28].

In physical adsorption the energy requirements are usually low (no more than 4.2 $kJmol^{-1}$) since the forces

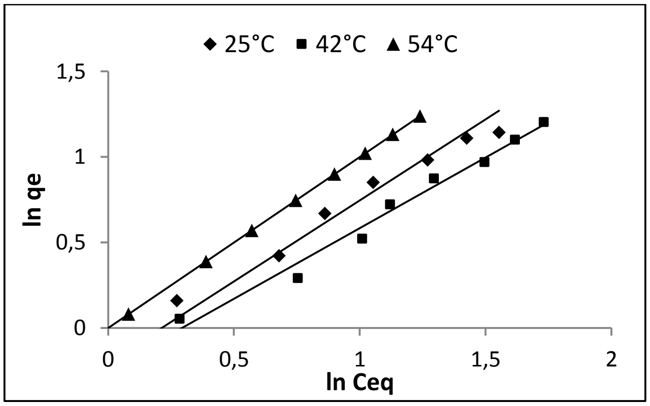

Figure 5. Linearized Freundlich isotherm at different temperatures. Source: Authors

involved are weak. Chemical adsorption is specific and involves forces much stronger than in physical adsorption [27]. Therefore, the kinetic parameters found such as activation energy (E_A = 8838.8 Jmol^{-1}) and Arrhenius constant (Ao = 0.003) indicate a chemical nature for the adsorption process of AB9 by flower stems (Table 4).

4. Conclusions

The adsorption experiments demonstrated the great potential of flower stalks as a low-cost and easily available adsorbent for the removal of AB9. It was observed that the extent of adsorption increased by lowering of initial pH up to 2.0, the uptake capacity being a maximum at this value. It was also noted that the specific adsorption capacity decreases with increasing the ratio of adsorbent-dye. The process followed Freundlich isotherm model, showing a slight increase in the uptake capacity with temperature. The adsorption process was better described by pseudo-second order kinetics.

Although the potential of flower wastes as adsorbent for the removal of synthetic dyes was proved, further research is required in order to improve its adsorptive capacity, for example, through chemical modification of the surface of this material. We also suggest the evaluation of isotherms different to Freundlich and Langmuir in order to support the observations of this study. The structural characterization of the material through SEM and IR analysis is being developed in order to get a deeper understanding of the process.

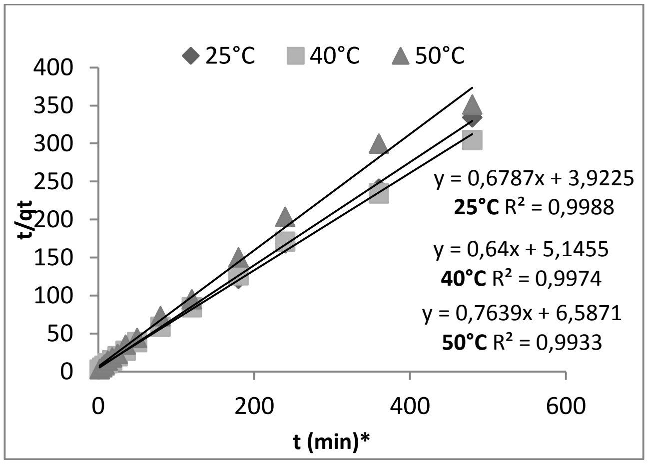

Figure 6. *Pseudo*-second order kinetics, t/qt vs. t (min). Source: Authors

Table 4. Kinetic parameters for the AB9 adsorption by flower wastes.

Temperature	Pseudo-first order			Pseudo-second order		
	r2	k1	qe	r2	k2	qe
20 °C	0.631	0.004	0.582	0.999	0.117	1.473
42 °C	0.676	0.003	0.700	0.997	0.080	1.563
50 °C	0.730	0.006	0.546	0.993	0.089	1.309

Source: Authors

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