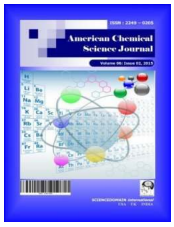

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Equilibrium, Kinetic Studies on the Adsorption of Acid Green 3 (Ag3) Dye Onto *Azolla filiculoides* as Adosorbent

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Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

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ABSTRACT

Batch studies were conducted for Equilibrium, kinetics studies on the biosorption of Acid Green 3 from aqueous solution by *Azolla filiculoides*. The variation of pH, dose of adsorbent, contact time, concentration of Acid Green 3 Dye was investigated. The optimum conditions for the adsorption process was determined as follow: pH= 3, contact time = 90 min, adsorbent dosage=4 g/L and dye concentration=10 mg/L. The most AG3 dye removal efficiency of 99.1% was obtained in optimum conditions. Kinetic analyses were conducted using pseudo-first and second-order models. The regression results showed that the adsorption kinetics was more accurately represented by pseudo-second-order model. The adsorption isotherms are described by means of the Langmuir, Freundlich, Tempkin and Redlich–Peterson isotherms. It was found that the Langmuir equation fit better than the other equation. The study showed that *Azolla filiculoides* could be used as a new and efficient adsorbent material for the removal of dyes from aqueous solution.

Keywords: Adsorption; acid green 3; kinetics; equilibrium; Azolla filicoloides.

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1. INTRODUCTION

The dyes which are extensively used in various industries such as textiles, tanneries, photo printing, paper and etc, is considering as important chemical pollutant due to their harmful and hazardous properties [1,2]. It have been reported that 60% of dyes are used in this textile industry [3,4] The used dyes in this industry are placed in three categories including anionic, cationic and non-ionic [5,6]. The acid dyes are belonging to anionic group which there are acid group (sulphonate, carboxyl) in their molecular structure and they are water soluble dyes [7,8]. The presence of some dyes in water, even in 1 mg/L, can create the unpleasant aesthetic [9,10]. Of other adverse effect of dyes in water body can implied to reduce the light penetration and affecting on photosynthesis [11,12]. Many researches indicated that the dyes can influence the human health by their carcinogenic and mutagenic properties [13,14]. Therefore, the colorful wastewater must be treated to preserve the environment and human health [15]. Some of dyes are difficulty treatable by the conventional method due to their complex molecular structure; therefore, various techniques such as advanced oxidation technology, electrochemical treatment and membrane filtration are examined by researcher but these methods are not economic [16-18]. The adsorption process is known as effective, low-cost and popular method in the removal of pollutants recently [19]. Although commonly used adsorbent for dye removal is the activated carbon [20], however it is proven that it is not economical adsorbent [21]. Therefore, there are significant efforts in the world to discover the inexpensive and high ability adsorbent as proper alternative to activated carbon. Various attempts is performed on dye removal by different material such as red mud, chitosan [22], fly ash [3], rice husk [6], Seed Powder [23], nut shell [24], canola [5], Canola [25], Moringa Peregrina [26], Lemna [27] and etc. They have been demonstrated high ability for dye removal from aqueous solution. Azolla which is one of most available and rapid growth algae in water surface was the subject of present study. This algae can extensively found in north of Iran [28]. Although the Azolla can remove pollutant from environment however the rapid growth of Azolla can create problematic conditions [29,30]. Therefore, the using the Azolla as an adsorbent can be good approach to dissolve the problems [31]. According to above, the aim of this study was to investigate the Acid Green3 (AG3) removal by Azolla from aqueous solution. The effect of important parameters including pH, contact time, adsorbent dose, and dye concentration on AG3 dye removal efficiency was studied. Furthermore, the isotherm and kinetic study was performed.

2. MATERIALS AND METHODS

2.1 Preparation of Adsorbent

Azolla was collected from rice paddy in Sari city; Then It was dried in the sunlight, and was crushed and sieved to particle sizes in the range of 1–2 mm. The biomass was treated with 0.1 M HCl for 5 h and it was washed with distilled water and finally washed biomass was dried at 105º in oven [32]. The resultant biomass was subsequently used in sorption experiments.

2.2 Instruments Used for Characterization

The specific surface area of dried Rice Stem before use was determined by the BET-N2 method using an ASAP 2000 apparatus based nitrogen adsorption–desorption isotherms at 77 K.

The surface images of dried Azolla before and after adsorption process were captured by scanning electron microscopy (SEM). The SEM was performed using a Philips XL30.

2.3 Preparation of Dye Solution

Acid green 3 (AG3) dyes was obtained from Sigma–Aldrich Corporation. The properties and chemical structure of the dye are shown in Table 1 and Fig. 1.

2.4 Batch Adsorption

Various experimental conditions including contact time(10-180 min), initial solution pH(3-11), adsorbent dosage (0.05-0.7 g) and initial concentration of AG3 dye (10-500 mg/L) which may influence the adsorption of AG3 on dried *A. filiculoides* were tested using batch experiments. Initial AG3 dye solutions with different concentrations were prepared by diluting a AG3 dye stock standard solution of 1000 mg/L with distilled water. The solution pH was adjusted using either diluted 0.1 M HCL or 0.1 M NaOH solution. The experiments in batch system were carried out in a 100 ml Erlenmeyer flask. In every experiment, a certain concentration of AG3 and specific dose of

adsorbent spilled into the Flask and completely mixed with shaker at 120 rpm for 180 minutes. Then the sample was centrifuged at 3600 rpm for 10 minutes. The residual concentrations were measured using spectrophotometer (DR2800) in λ_{max} of 636 nm [9]. All batch experiments were carried out in triplicate.

The amount of dye adosorbed was calculated from the difference between the dye quantity added to the biomass and the dye content of the supernatant using the Eq 1: Where q_e is the dye uptake (mg/g), C_0 and Ce the initial and final dye concentrations in the solution (mg/L), respectively, V the solution volume (L), and M is the mass of biosorbent (g) [33].

$$q_e=(C_O-C_e)\ V/m \quad (1)$$

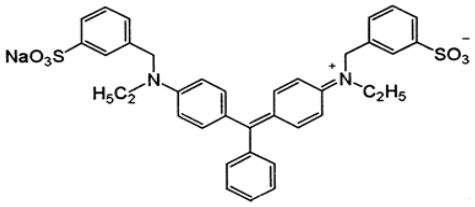

Fig. 1. The chemical structures acid green 3

Table 1. The charactristics of acid geen 3(9)

C.I. name	Molecular weight	λ_{max} (nm)	Molecular formula
Acid Green 3 (AG3)	690.82 g/mol	636	$C_{37}H_{37}N_2O_6S_2Na$

3. RESULTS AND DISCUSSION

The specific surface areas of modified azolla were determined in size of 36 m^2/gr. Scanning electron microscopy (SEM) images were used to analyze the surface structure of azolla (Fig. 2). It was found that the adsorbent has heterogeneous surface structure with deep pores. The specific surface area of adsorbent was one of the most important parameters on adsorption ability. The specific surface area is related to the number of active adsorption sites of dried azolla. The adsorption increased with the specific surface area and pore volume of the sorbent [34]. The surface area of dried Rice Stem was 36 m^2/gr which it indicated that the modified azolla area have relatively good ability to remove the pollutants. The natural azolla has a positive charged surface; this causes a relatively high adsorption capacity for reactive acid dyes with a negative sulfonate group due to reception occurring between the dye and the azolla surface [16].

3.1 Effect of Contact Time and Initial AG3 Concentration

The effects of Contact time on the removal of AG3 dye from aqueous solutions were investigated by using different Contact time in the range of 10-180 min and initial AG3 dye concentration of 10 mg L^{-1} at pH=3 and biomass concentration of 4 g L^{-1} .As shown in Fig. 3, biosorption of AG3 dye on dried azolla increased rapidly within the first 60 min and then was slowed from 60 min to 90 min and finally, it reached to equilibrium after 1.5 h. From this result, it can be said that kinetics of dye removal efficiency is formed in two phases: First, an initial rapid phase where the adsorption of dye molecules was fast and instantaneous, and the second phase was a slow stage in which the contribution to the total reactive dyes removal efficiency was relatively small, and finally the removal of dye reached equilibrium [35,36]. Data on the adsorption kinetics of dyes by various adsorbents have shown different ranges of adsorption rates. For example, the equilibrium times reported for the adsorption of dye were 90 min for the adsorption of dye on Wheat shells and Coffee husks [37,38].

The experimental results of sorption of AG3 dye on *Azolla filiculoides* at various concentrations are shown in Fig. 4. Increase of concentration decreased the dye adsorption percentage. As the AG3 dye concentration was increased from 10 to 500 mg l^{-1}, the equilibrium adsorption capacity (qe), increases from 1.4 to 39.28 mgg^{-1}, whereas the AG3 dye removal efficiency decreased from 98% to 55%. The initial dye concentration provides an important driving force to overcome all mass transfer resistances of the AG3 dye between the aqueous and solid phase. This probably occurs due to this fact that by increasing of the surface charge on the adsorbent, the adsorption sites of top surfaces of adsorbent are saturated and the removal efficiency decreased [39]. Similar results have been reported in literature [6,16].

3.2 Effect of pH and Adsorbent Dosage

In order to evaluate the effect of pH on the adsorption of AG3 dye onto azolla, the adsorption experiments were carried out with initial AG3 dye concentration of 10 mg L^{-1} and biomass concentration of 4 g L^{-1} by varying the

pH of the solutions over a range of 3–11 (Fig. 5). The uptake of AG3 dye by the biomass is almost constant in the pH range of 3–5; however, when the pH value exceeds 5, the adsorption of AG3 decreases abruptly. One of the main variables affecting the adsorption process is pH which not only influencing the surface charge of adsorbent, the degree of ionization of the material present in the solution and the dissociation of functional groups on the active sites of the adsorbent, but also the solution dye chemistry [40]. In fact, pH must control the adsorption of dyes onto suspended particles because both adsorbed molecules and adsorbent particles may have functional groups which are affected by the concentration of H+ ions in the solution and are involved in the molecular adsorption process at the active sites of adsorbent [6]. The biosorption decreased significantly with increasing solution pH from 3 to 11. Several investigations have also shown that the Azolla biomass will have higher adsorption at low pH values [41,42] and similar results are shown using removal dyes on another adsorbent [5,6].

The experimental results of sorption of AG3 on *Azolla filiculoides* at various biomass dose are presented in Fig. 6. As the biomass weight was increased from 0.5 to 7 g l^{-1}, the equilibrium adsorption capacity (q_e), decreased from 37.5 to 6.45 mgg^{-1}, whereas, the AG3 removal efficiency increases from 37.5% to %90.3. The increase in % removal was due to the increase of the available sorption surface and availability of more adsorption sites. A similar behavior was reported for the adsorption of acid orange 7 on dried Rice Stem [6] and Acid Blue 113 on canola biomass [5].

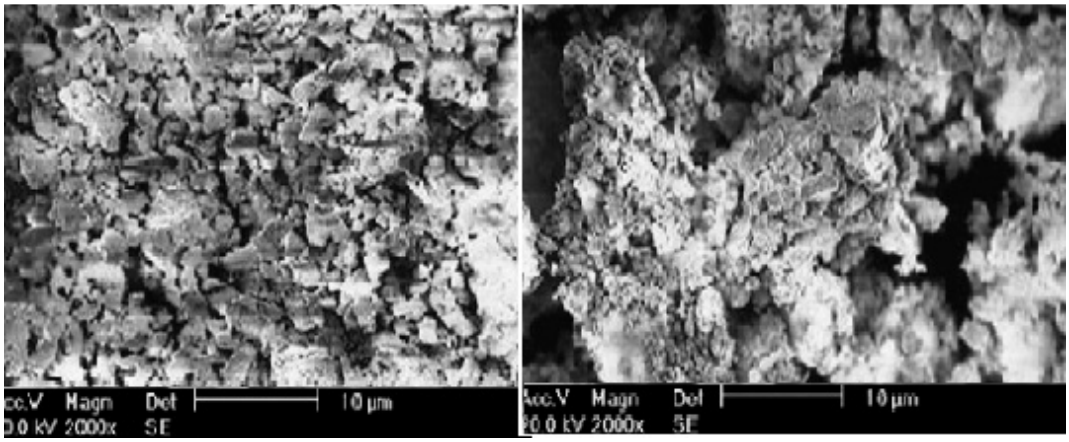

Fig. 2. The SEM image of modified azolla before and after used

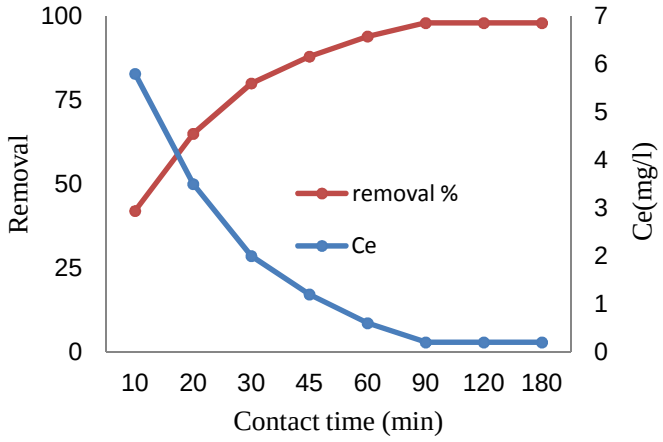

Fig. 3. Effect of contact time (AG3 concentration: 10 mg/L, dosage: 4 g/L, pH = 3)

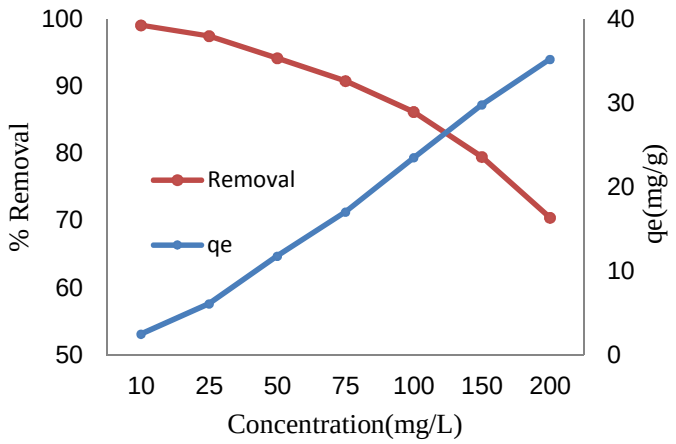

Fig. 4. Effect of AG3 concentration (time = 90 min, dosage: 4g/L, pH = 3)

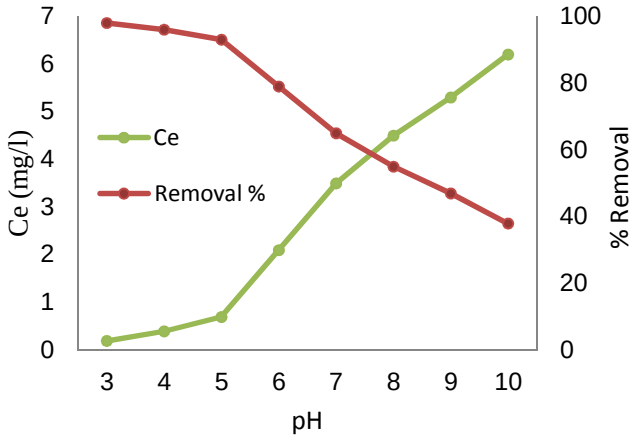

Fig. 5. Effect of pH (Con: 10 mg/L, dosage: 4 g/L, time: 90 min)

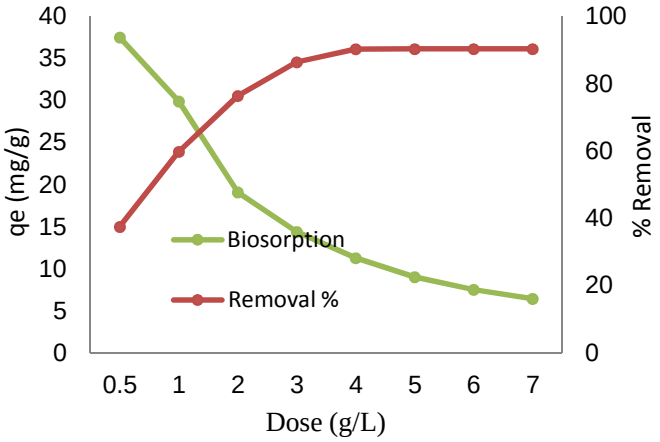

Fig. 6. Effect of adsorbent dose (time = 90 min, PH = 3, Con: 50 mg/L)

3.3 Adsorption Isotherms

Adsorption isotherm experiments were conducted by equilibrating modified azolla in Erlenmeyer flasks containing 100 ml of dye solutions of varying initial dye concentrations (10–500 mg/L). The mixture was stirred magnetically at 120 rpm until reaching equilibrium by varying the temperature range of 30 and 40℃. After equilibrium, samples were centrifuged and analyzed for the residual dye concentrations. The amounts of each dye adsorbed by the modified azolla were calculated using Eq. (1). The equilibrium of adsorption was evaluated by using the following isotherm models.

The Langmuir isotherm is presented the Eq. 2 [43].

$$\frac{Ce}{qe} = \frac{1}{q_m K_L} + \frac{Ce}{q_m} \quad (2)$$

Where qe is the amount of sorbate adsorbed at equilibrium (mg/g); C_e is the equilibrium concentration of the sorbate or the sorbate unadsorbed in the solution (mg/L); q_m (mg/g) is the maximum theoretical biosorption capacity and K_L (L/mg) is a measure of adsorption energy that is indicated on the affinity between biosorbent and sorbate.

The Freundlich equation is given by the following Eq. 3 [44]

$$\text{Log } q_e = \frac{1}{n} \log Ce + \log K_F \quad (3)$$

Where q_e is the sorbate adsorbed at the equilibrium (mg/g); C_e is the equilibrium concentration of the sorbate or the unadsorbed sorbate in the solution (mg/L); K_F is a constant, indicative of biosorption capacity.

The Tempkin isotherm has been used by the following Eq. 4 [45,46]:

$$q_e = B_1 \ln (k_t) + B_1 \ln (C_e) \quad (4)$$

A plot of q_e versus ln Ce enables the determination of the constants A and B. The constant B is related to the heat of adsorption.

The Redlich–Peterson equation is given by the following Eq 5 [47,48]

$$\text{Ln } (K_R C_e / q_e\text{-}1) = \ln a_R + \beta \ln C_e \quad (5)$$

Where K_R (L g^{-1}) and a_R (L mg^{-1}) are the R–P constants: β is the exponent which has a value between 0 and 1 and Ce the equilibrium liquid phase concentration (mg L^{-1}).

3.4 Adsorption Kinetics

Kinetic models are used to examine the rate of the adsorption process and potential rate controlling step. In present work, obtained kinetic data from batch studies have been analyzed by using the pseudo second-order and pseudo First-order model.

The pseudo-first-order rate equation is expressed as Eq. 6 [49,50]:

$$log(q_e - q_t) = log(q_e) - \frac{k_1}{2.303} t \quad (6)$$

Where q_e and q are the amounts of AG3 dye adsorbed (mg/g) at equilibrium and at time t (min), respectively, and k1 is the rate constant of adsorption (min^{-1}). Values of k_1 were calculated from the plots of log (q_e − q) versus (t) for different concentrations.

Also the pseudo-second-order rate equation has been given by equation 7 [42,51]

$$\frac{t}{q_t} = \frac{1}{k_2 . q^2} + \frac{t}{q_e} \quad (7)$$

Where K_2 the second order rate constant (g $mg^{-1}min^{-1}$), q and qe are the amount of the adsorbed on the adsorbent (mg/g) at equilibrium and at time t.

The isotherms and kinetics constants are presented in Tables 2 and 3. It can be concluded that the Langmuir isotherm model was more suitable for the experimental data than other isotherms because of the high value of correlation coefficient (R^2 =0.999 and R^2 =0.998).

The Langmuir equation is applicable to homogeneous sorption, where the sorption of each molecule has equal sorption activation energy. The Freundlich equation agrees well with the Langmuir equation over moderate concentration ranges but, unlike the Langmuir expression, it does not reduce to the linear isotherm (Henry's law) at low surface coverage. Both these theories suffer from the disadvantage that equilibrium data over a wide concentration range cannot be fitted with a single set of constants. Tempkin considered the effects of some indirect adsorbate/adsorbate interactions

Table 2. Isotherm model parameters for the removal of AG3 by modified azolla

Tem	Langmuir			Freundlich				Redlich–Peterson			Tempkin		
	q_m	R_L	R^2	K_L	n	K_F	R^2	K_R	a_R	R^2	B	k_t	R^2
30℃	39.3	0.41	0.999	0.24	1.67	5.72	0.912	0.1	2.17	0.989	4.6	3.21	0.952
40℃	37.5	0.38	0.998	0.45	1.49	6.41	0.928	0.11	1.94	0.992	5.2	2.17	0.941

Table 3. The adsorption kinetic model constants for the removal AG3

	Pseudo second-order model			Pseudo first-order model		
co(mg/l)	k_2(g/mg min)	R^2	q(mg g^{-1})	k_1(1/ min)	R^2	q(mg/g)
50	0.092	0.998	7.1	0.1806	0.882	5.42
100	0.0088	0.998	12.4	0.0396	0.914	9.84
200	0.0053	0.999	19.8	0.0408	0.936	16.1
500	0.0017	0.999	39.3	0.0283	0.949	31.7

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 correlation coefficient (R^2) for Freundlich isotherm was 0.912 and 0.928 in temperature 30 and 40℃, which was slightly lesser than the R^2 value obtained from the Temkin, Langmuir and Redlich–Peterson equations which it indicated that the Langmuir model better fitted the equilibrium obtained in this study. This suggested that the adsorption of AG3 dye onto dried *Azolla filiculoides* may be due to monolayer adsorption to the functional groups as binding sites on the surface of the biomass. In this study the obtained qe value in concentration of 500 mg/L was 39.3 mg/g which this value is greater than obtained qe for Lemna (9.8 mg/g), Canola (17.8 mg/g) and Rice Stem (10.2 mg/g). it probably is due to presence of greater specific surface area in azolla adsorbent [5,6,29]. The R^2 of kinetic models suggested that the pseudo second-order model mechanism is predominant which means the uptake process follows the pseudo-second-order expression with correlation coefficients was always greater of 0.998. The correlation coefficient in pseudo second- order model was better than the first order model correlation coefficients and similar results are shown using removal dyes on another adsorbent [6,52].

4. CONCLUSIONS

The adsorption of AG3 dye from aqueous solution using Azolla filicoloides as low-cost adsorbent was investigated under different experimental conditions in batch process. The Langmuir adsorption isotherm was found to be the applicable model for the experimental data with maximum adsorption capacity of 39.3 mg/g. The adsorption kinetics can be predicted by pseudo-second-order kinetic. The results of the present work indicated that *Azolla filiculoides*, a low-cost adsorbent, could be employed as an alternative to commercial-activated carbon for the removal of dyes from aqueous solutions.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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