

Spent Coffee Grounds as Adsorbents for Pesticide Paraquat Removal from its Aqueous Solutions

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Abstract— Spent coffee grounds were evaluated for adsorption efficiency in the removal of pesticide paraquat from its aqueous solutions. The influence of the adsorbent mass, agitation time, paraquat concentration and pH have been investigated in the batch sorption mode. Adsorption capacity (mg/g) has been found to be 27.87 ± 1.57 mg/g, while the removal efficiency has resulted of 32.25 ± 1.79 %. Adsorption rate was found to be very fast, whereby the time required for equilibrium adsorption occurred within first 20 minutes. The process behavior was predicted using the second-order kinetic model. On the basis of the observed data, further process optimization may be greatly facilitated, thus it is considered that coffee waste may be exploited well for pesticides removal purposes.

Keywords—Adsorption, coffee residues, paraquat, pesticides.

I. INTRODUCTION

THE modern agriculture production depends considerably on the use of pesticides, as protective agents against all sorts of plant diseases [1]. Herbicides represent more than 50% of all pesticides used in most of the major agricultural countries [1], [2]. Paraquat (1,1-dimethyl-4,4-bipyridyl dichloride, Fig. 1) is a very important substance in a group of bipyridylium herbicides, holding the largest share of the global herbicide market [1], [2]. It is quick-acting, unselective

herbicide that leaves no residues because of its rapid, irreversible adsorption to soil [1].

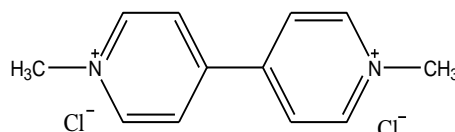


Fig. 1. Chemical structure of paraquat

Increasing the use of paraquat in agriculture and domestic activities is polluting our soil and water resources day by day [3]. There have been many authentic cases of the detection of its residues in water sources [3], [4]. This class of pollutants is of particular importance due to strong toxicity, carcinogenicity and mutagenic effects to humans and animals [2]. Therefore, it is important to prevent the release of these contaminants into the environment [3].

Adsorption is considered to be an attractive method for removing pesticides from dilute solutions [2], [3]. Numerous evidences demonstrated that adsorption is capable of deactivating the equivalent of ample of paraquat applications over a wide range of soils and water solutions [5]. There are many literature surveys about adsorption of paraquat by clays and resins [6]-[13]. Although the adsorption onto commercial activated carbons is popular it is also very expensive, requiring elaborate reactivation and regeneration processes, which subsequently affects the economic viability of the operation. Thus, there is a growing demand to find efficient, low cost and easily available adsorbents, particularly if the adsorbents were recycled waste. This study is, therefore, oriented toward finding of inexpensive plant based waste adsorbent. One such material, under consideration is derived from the coffee waste. Coffee is nowadays one of the most popular commodities consumed all over the world. Consecutively, large quantities of residues occurred in both producing countries as well as consuming countries after beverage preparations. Spent coffee grounds (SCG) are residues with fine particle size, obtained during the treatment of raw coffee powder with hot water or steam for the instant coffee preparation. SCG is generated in extensive amounts, with a worldwide annual generation of 6 million tons, and numerically, about 2 kg of wet SCG is obtained to each 1 kg of soluble coffee produced [14].

Several studies have shown that the activation of coffee waste can result in a product with a comparable surface area to

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commercially available activated carbon, exhibiting promising wastewater remediation performance [2]. Our previous studies revealed excellent crystal violet dye removal capabilities, after the polyphenolic compounds were extracted from the spent coffee residues [15], [16]. As far as is known, no efforts have been made to explore the feasibility of using coffee waste to remove paraquat from aqueous solutions. Therefore, the data obtained at a variety of adsorbent masses, agitation time, paraquat concentration and pH, were interpreted to gain insights into the factors that promote or prevent the adsorption process and the applicability of common kinetic models has been evaluated, as well.

II. MATERIALS AND METHODS

A. Preparation of adsorbent and pesticide stock solution

The espresso coffee was obtained from “Doncafe – Espresso Aromatico – cialde”, Strauss Adriatic d.o.o, Šimanovci, Serbia. The coffee residues after preparation of a beverage were collected, dried and polyphenol compounds were extracted using a microwave oven on the way presented in our previous study [15]. The obtained solid phase was separated and dried in an oven at 105 °C for overnight and employed as adsorbent in the adsorption experiments.

The paraquat pesticide was used as adsorbate in the present study and it was purchased from Sigma-Aldrich. The stock solution of paraquat (1 g/L) in distilled water was diluted for the working pesticide solutions of different concentrations (from 0.2 to 1 g/L) before each adsorption experiment.

B. Batch adsorption experiments

Batch adsorption experiments were performed in 100 mL Erlenmeyer flasks with 50 ml of the pesticide solution and pre-determined adsorbent dose. A whole mixture was placed on a translatory shaker (IKA – KS 4000i control, Staufen, Germany) at room temperature. The experimental parameters: the adsorbent dose, the initial paraquat concentration, the initial pH solution and the rate of stirring were investigated. The effect of the temperature was deliberately excluded from the experiment, keeping in mind the practical application of an embodiment of the process and the remediation of water streams in the environment. Each adsorption experiment was carried out under the conditions where one parameter changed while the other parameters held constant. All of the factor's value ranges were set in an accordance with the preliminary examinations. Each experiment was done in triplicate. After one hour of the process duration, samples were collected and the concentrations of pesticide solutions before and after adsorption were determined using UV/VIS spectrophotometer (Ultrospec 3300 pro, Amersham Biosciences, USA) at 297 nm. The adsorption capacity and the efficiency of paraquat removal were calculated as follows (1) and (2), respectively:

$$\text{Adsorption capacity (mg/g)} q_t = \frac{(C_0 - C_t)}{m} \cdot V \quad (1)$$

$$\text{Removal (\%)} = \frac{(C_0 - C_t)}{C_0} \cdot 100 \quad (2)$$

where C_0 is the initial pesticide concentration (mg/L) and C_t is the residual concentration of the pesticide (mg/L) at different time intervals, V is volume (L) and m is the adsorbent dose (g) [17]-[19].

C. Adsorption kinetic studies

Adsorption kinetic experiments were conducted by 20 g/L of adsorbent mass in different Erlenmeyer flasks containing 250 mL of the pesticide solution of varying the initial paraquat concentrations (0.2, 0.4, 0.6, 0.8, and 1 g/L), placed on a translatory shaker for two hours. The samples were collected at pre-determined time intervals, filtered and analyzed spectrophotometrically for the residual paraquat concentrations.

D. Determination of pH_{pzc}

The point of zero charge (pH_{pzc}), that evaluates the adsorbent surface charge, was determined by adding 50 mL of 0.01 M NaCl into the 100 mL Erlenmeyer flask. pH was adjusted to 2–12 using 0.1 M HCl or 0.1 M NaOH. Thereafter 0.15 g of the adsorbent was added and the resulting pH was measured after 48 h of agitation at room temperature. The point pH_{pzc} is revealed in the place where the pH initial line crossed the pH final curve [20].

III. RESULTS AND DISCUSSION

A. Effect of the adsorbent dose

The effect of the adsorbent dose on the paraquat adsorption was studied in 5, 13 and 20 g/L, whereas other parameters: the initial paraquat concentration (0.2 g/L), the initial pH solution (pH 7) and the rate of stirring (160 rpm) were held constant.

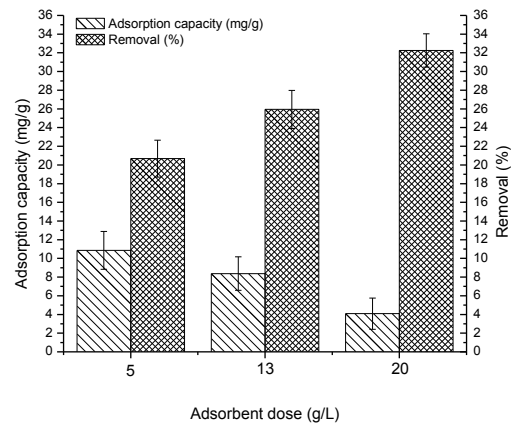


Fig. 2. Effect of the coffee dose on the adsorption process

It is evident from Fig. 2 that the adsorption capacity increased with decreasing the adsorbent dose. This result is in agreement with the report of Tsai, Lai and Hsien (2004) [21] for the adsorption of paraquat onto activated bleaching earth. On the other hand, the removal efficiency increased with increasing the adsorbent dose. The best removal efficiency of paraquat (32.25 ± 1.79 %) in this research was reached in this set of the experimental conditions, with the adsorbent dose of 20 g/L. Leite, dos Reis, Robaina, Pacheco and Cassella (2013) [17] were came to the same inferences about behavior of the removal of paraquat from aqueous medium by Amberlite XAD-2 and XAD-4resins.

B. Effect of the initial paraquat concentration

The effect of the initial paraquat concentration on the paraquat adsorption was studied in 0.2, 0.6 and 1 g/L, whereas other parameters: the adsorbent dosage (5 g/L), the initial pH solution (pH 7) and the rate of stirring (160 rpm) were held constant. This set of the experimental conditions gave the highest adsorption capacity at a concentration of 1 g/L, resulting of 27.87 ± 1.57 mg/g. It was the best reached adsorption capacity in all experiments which were made in this investigation. It was higher almost two times than the maximal adsorption capacity, which was obtained by Tsai, Hsien, Chang and Lo (2005) [22] for adsorption of paraquat onto spent and treated diatomaceous earth. From the Fig. 3. it is clear that the adsorption capacity increased with increasing of initial paraquat concentration, but when it relates to the efficiency of pesticide removal from the solution, the situation was reversed. These results are in a good agreement with the results these were achieved for paraquat adsorption on the other adsorbents [12], [21].

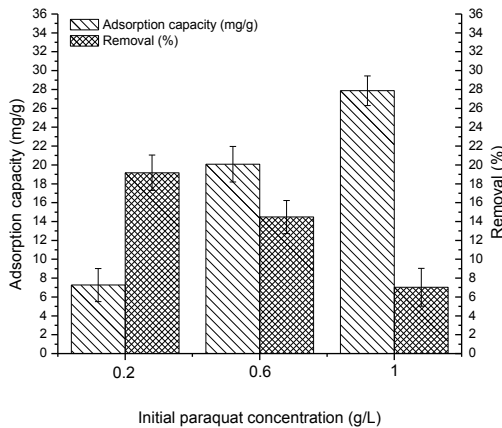


Fig. 3. Effect of the paraquat concentration in the adsorption process

C. Effect of the initial pH solution

The investigation of the effect of the initial pH solution on the paraquat adsorption was studied in a condition of acidity up to neutrality by setting the pH values to 3, 5 and 7, whereas other parameters: the adsorbent dosage (5 g/L), the initial paraquat concentration (0.2 g/L) and the rate of stirring (160 rpm) were held constant. This effect can be explained on the basis of the adsorbent isoelectric point or pH of point of zero charge (pH_{pzc}). The net surface charge of material is equal to zero when the pH value of working solution is the same as the PZC of the material [23], [24], so, under these conditions the adsorbent is neutral and has no charge. Therefore, prior to experiments, zeta potential of spent coffee residues was done. The zero point of charge of the coffee residues–water system was determined to be approximately 5.6. Bearing that in mind, the surface of coffee residues at the experimental conditions of pH less than 5.6 had positive charge, and reverse, the negative charge with the initial pH solution greater than point of pH_{pzc} . The paraquat aqueous solution without adjustment of pH value was equal to 6. Thus, a better adsorption results should be obtained when a solution of pesticide was set to pH 7, which was confirmed by the values obtained in this set of

experiments. Thereby, the easier connection between the cationic paraquat on the negatively charged coffee surface was enabled. The adsorption capacity and removal efficiency were calculated to 17.08 ± 2.91 mg/g and 20.56 ± 0.98 %, respectively (Fig. 4).

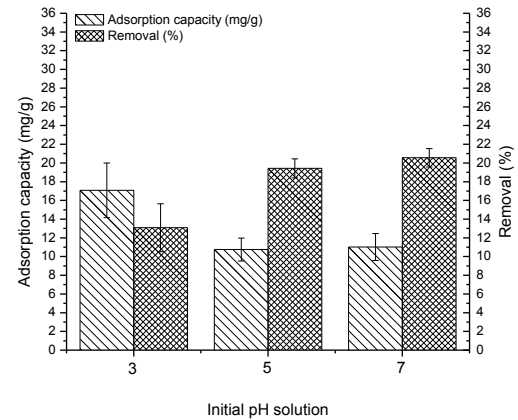


Fig. 4. Effect of the initial pH paraquat solution in the adsorption process

D. Effect of the rate of stirring

The effect of the rate of stirring on the paraquat adsorption was studied in 80, 120 and 160 rpm, whereas other parameters: the adsorbent dosage (5 g/L), the initial paraquat concentration (0.2 g/L) and the initial pH solution (pH 7) were held constant.

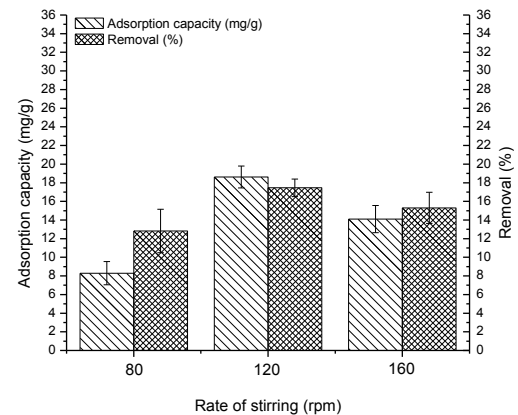


Fig. 5. The effect of the rate of stirring on the adsorption process

The best results of the adsorption capacity and the removal efficiency were obtained with the middle value of the rate of stirring (120 rpm) of 17.46 ± 0.94 % and 18.62 ± 1.18 mg/g, respectively (Fig. 5). It is considered, with the very low rate of stirring, the overall adsorbent dose could not contact the paraquat in the solution because of the turbulence was not sufficiently strong, and the amount of coffee dose of 20 g/L was too much for these mixing conditions [16]. On the contrary, the strong agitation, probably hinders the binding of paraquat particles to coffee surface active sites or affects the desorption of already sorbed pesticides from the adsorbent. The author who studied the effect of stirring rate on paraquat

adsorption onto the bleached earths found that adsorption capacity was increased as the agitation speed increased from 200 to 600 rpm [21], indicating that strong turbulence is required for the decreasing of the boundary layer thickness around the adsorbent particles.

E. Effect of the rate of stirring

The adsorption of paraquat was studied as a function of contact time, ranging between 5 and 120 min, by monitoring the amount of paraquat adsorbed by coffee residues, in order to determine equilibration time for maximum pesticide adsorption. Five different initial paraquat concentrations ranged between 0.2 and 1 mg/mL were evaluated, whereby other parameters were set at the fixed value: adsorbent mass of 20 g/L, agitation speed of 120 rpm and room temperature of 27 °C. In addition, no pH adjustments were involved.

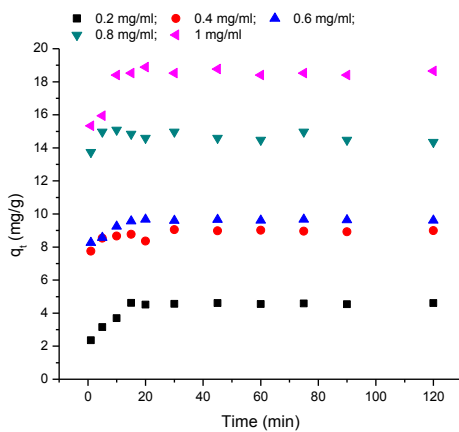


Fig. 6. Effect of contact time for paraquat adsorption onto coffee residues (adsorbent mass 20 g/L, 120 rpm, 27 °C)

It was found that the adsorption rate of paraquat was very rapid. The time required for equilibrium adsorption is 20 minutes, and generally, no change in the adsorbed amount is detected afterward (Fig. 6). The time to reach equilibrium was concentration independent, while the amount of paraquat adsorbed per unit weight of adsorbent, q_e , was highly concentration dependent. When the initial adsorption rapidly occurred, it is considered that the process involves a surface reaction [3]. Then, lesser adsorption would follow, as the available sorption site gradually decreases, or the remaining surface sites were difficult to be occupied [3, 16]. As the initial pesticide concentration increase, the number of molecules competing for the available sites on the surface of activated carbon was high, hence, resulting in higher adsorption capacity [16].

Due to the fast decrease in residual paraquat concentration at a short time scale, a simple kinetic analysis of adsorption, based on pseudo-first and pseudo-second order models, were

employed to fit experimental data. The linearized form of pseudo first-order kinetic model is presented as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \cdot t \quad (3)$$

where q_e and q_t are the amount of paraquat adsorbed on the coffee surface (mg/g) at equilibrium and at time t (h), respectively, and k_1 (1/h) is the rate constant of pseudo-first-order kinetics, and the linearized form of pseudo second-order kinetic model is given as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e} \cdot t \quad (4)$$

where q_e and q_t have the same meaning as mentioned previously and k_2 (g/mg·h) is the rate constant for the pseudo-second-order kinetics [25].

The kinetic parameters determined from the corresponding kinetic order plots are presented in Table 1. High correlation coefficient values, R^2 , suggest that adsorption of paraquat onto coffee residues fitted well pseudo-second-order model (Fig. 7), better than pseudo-first, as regards to all ranges of tested concentrations. In addition, q_e estimated by pseudo-first-order model differs substantially from that measured experimentally, while q_e for the pseudo-second-order model were much more reasonable. According to a principle of pseudo-second order kinetics, the rate limiting step may be chemical sorption through share or exchange of electrons between cationic paraquat and the negatively charged coffee particles surface.

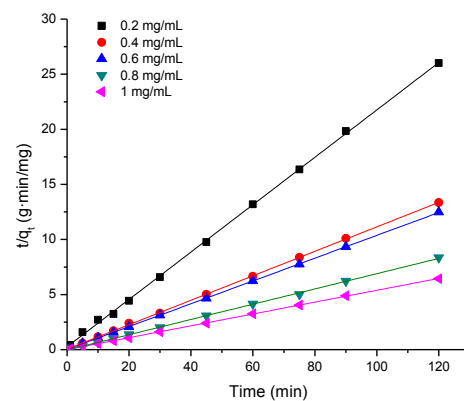


Fig. 7. Pseudo-second-order kinetic plot for the adsorption of paraquat on coffee residues (adsorbent mass 20g/L, 120 rpm, 27 °C)

KINETIC MODEL PARAMETERS FOR PARAQUAT ADSORPTION ON COFFEE RESIDUES AT DIFFERENT INITIAL PARAQUAT CONCENTRATIONS (ADSORBENT MASS 20 G/L, 120 RPM, 27 °C)

Initial concentration mg/mL	$q_{e,exp}$ mg/g	Pseudo-first order kinetic model			Pseudo-second order kinetic model		
		k_1 (1/h)	$q_{e,cal}$ (mg/g)	R^2	k_2 (g/mg·min)	$q_{e,cal}$ (mg/g)	R^2
0.2	4.6125	0.0227	0.1860	0.0216	0.1795	4.6512	0.9995
0.4	8.9796	$5.61 \cdot 10^{-4}$	8.7910	0.4020	0.2894	9.0074	0.9998
0.6	9.6666	0.0271	0.2063	0.1762	0.4295	9.6618	0.9999
0.8	14.475	$1.08 \cdot 10^{-4}$	13.261	0.0873	0.1472	14.434	0.9995
1.0	18.644	$7.16 \cdot 10^{-3}$	0.5076	0.0766	0.2730	18.598	0.9999

The kinetic analysis results are in agreement with previous literature surveys. Paraquat adsorption on different types of adsorbent materials, ranged between well estimated clays and resins up to activated carbons derived from nonspecific materials, also follows a second-order kinetic model [2], [9], [12], [13], [21], [23], [26].

IV. CONCLUSIONS

The present study has demonstrated the ability of inexpensive spent coffee grounds to adsorb and remove the hazardous pesticide paraquat from its aqueous solutions. The results obtained at a variety of adsorbent masses, agitation time, paraquat concentration and pH have provided the screening of the process influential factors. The rate of the adsorption was found to be very fast, and the establishment of a second-order kinetic model has predicted the equilibrium conditions. On the basis of the obtained results, further process optimization for the adsorption improvement could be facilitated. In addition, some economically viable adsorbent modifications may be considered, as well.

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