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Rapid cationic dye adsorption on polyphenol-extracted coffee grounds—A response surface methodology approach

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ABSTRACT

The Box–Behnken design under the response surface methodology (RSM) with five interacting parameters (adsorbent dose, initial dye concentration, time of agitation, initial solution pH and time of the adsorbent microwave activation) was employed to interpret the adsorption characteristics of cationic dye onto polyphenol-extracted coffee grounds in water solutions.

Experimental results indicated that coffee ground is excellent low-cost biosorbent with dye removal ability more than 95% for a very short time (under conditions of 250 mg/L initial dye concentration and 15 g/L of adsorbent dose). The maximum adsorption capacity was 36.82 mg/g, whereby the adsorption rate was very fast (around 15 min). Batch mode experiments and kinetic regression results showed that the adsorption process was more accurately represented by a pseudo second-order model. *Freundlich* isotherm model was superior to the *Langmuir* isotherm model. FT-IR studies revealed that adsorption process was due to adsorption mediated by different functional groups present on the coffee surface.

1. Introduction

Quite often large amounts of coloured waste water are generated in industries which use dyes to impart a desired colour to their products (food, paper, rubber, textile, plastics). Aside from unpleasant aesthetic aspects, the presence of dyes in natural streams can cause serious harm to the aquatic life by disturbing the food chain organisms and leading to ecological disbalance. Further, it can cause injuries to humans and animals [1], by direct contact (eye burns), inhalation (rapid or difficult breathing) or ingestion (nausea, vomiting, mental confusion and others) [2]. Adequate treatments need to be employed for removal of dyes prior to discharge into receiving water streams. Adsorption has proven to be an effective method for waste water decolorization. Numerous adsorbents were investigated for dye removal from water solution even in a real system such as wastewater from the textile industry [2]. The agro-industrial waste materials are of special interest because of their numerous advantages: availability, technical feasibility, engineering usable, cost effective [3]. Moreover, after adsorption, such materials can be biologically treated (through *e.g.* solid-state fermentation or composting) for further bio-transformation or remediation of adsorbed dye [4]. Various coffee residues demonstrate adsorption ability for different pollutant removals [1,5–8]. Recently, the coffee grounds have been used for adsorption studies either as chemically modified (*e.g.* as activated carbon) [9,10] or non-modified material [11]. According to work of Kyzas [11], the non-modified coffee grounds can be efficient biosorbent for real textile industry waste water as well as for mixed dye model solution with high concentration (700 mg/L).

Our previous studies showed that the espresso coffee ground is a good source of polyphenolic compounds with high antioxidant effects [12,13]. After extraction of polyphenols coffee ground may still have practical value as biosorbent. In order to investigate the factors that influence the efficiency as well as capacity of such biosorbent in the dynamic model system, the response surface methodology was employed as well as adsorption isotherms and kinetic studies. The response surface methodology (RSM) is well known statistics-based procedure that represents an assemblage of experimental design and multiple regression-based methods and can be successfully applied where several factors might influence a process. Considering that adsorption presents complex and multi influential system, there was a considerable need for applying RSM technique. More detailed explanation of RSM can be found in Mona et al. [14]. The Crystal Violet dye (CV) was used for model solution. The effects of five parameters: adsorbent dose, initial CV concentration, time of agitation, initial solution pH and time of the adsorbent microwave activation were investigated by applying Box–Behnken design under response surface methodology (RSM) (Design Expert software, Version 8.0.7.1, Stat-Ease, Inc., Minneapolis, USA).

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2. Materials and methods

2.1. Preparation of adsorbent

The espresso coffee was obtained from "Doncafe – Espresso Aromatico – cialde", Strauss Adriatic d.o.o, Šimanovci, Serbia. After preparation of a beverage (using Didiesse FROG espresso machine, during 25 s), spent coffee was collected, dried and polyphenol compounds were extracted using a microwave oven (400 W), for 2 min in a solution of ethanol (1:6, w/v) [13]. The obtained solid phase was separated using a vacuum pump and was dried in an oven at 105 °C for overnight. Further preparation of spent coffee was carried out by physical activation conducted in the air by a microwave oven at 400 W (household microwave oven, LG MC7849HS), while activation time was varied and it was used as a processing parameter.

2.2. Preparation of dye stock solution

Crystal Violet (CV) dye (Acros Organics, NJ, USA) was used in our experiment. The working concentrations of the dye in aqueous solutions were varied from 50 to 250 mg/L by diluting the CV stock solution (500 mg/L) with distilled water. The initial solution pH was adjusted to 3–9 using 0.1 M HCl or 0.1 M NaOH. Fresh dilutions of desired dye concentrations were prepared at the beginning of each experiment.

2.3. Experimental design

Box–Behnken design, which is well suited for fitting a quadratic surface and usually works well for the process optimization, was used for the experimental design [14]. In order to evaluate the influence of operating parameters on the CV removal efficiency (response Y_1) and adsorption capacity (response Y_2), five independent variables were chosen: adsorbent dose (A), initial CV concentration (B), time of agitation (C), initial solution pH (D) and time of microwave activation (E). The theoretical consideration and model equations are described in the works of other researcher [14–17].

2.4. Batch experiments

Sorption studies were conducted by varying the process parameters formed by Box–Behnken design. The range and level of variables that were used in this experimental design were decided on the basis of prior examinations. Table 1 shows the highest and lowest limits of the independent variables.

100 mL of the dye solution with appropriate concentration and initial pH was taken into 250 mL Erlenmeyer flask. The adequately weighted adsorbent was added and the flasks were placed on a translatory shaker (IKA – KS 4000i control, Staufen, Germany) with 200 rpm agitation speed at room temperature (RT = 27 °C). After a certain time, samples were collected, vacuum filtered and analyzed by UV/vis spectrophotometer (Ultrospec 3300 pro, Amersham Biosciences, USA) at 540 nm (the maximum absorption wavelength for CV) for residual dye concentration in the aqueous solutions. The CV removal in the aqueous solution by coffee residues was computed by following equation:

$$\text{CV removal}\,(\%) = \left(\frac{C_i - C_f}{C_i}\right) \times 100 \quad (1)$$

where C_i and C_f are the initial and final CV concentrations (mg/L), respectively [15].

Adsorption capacity q_t (mg/g) was computed by following equation:

$$q_t = \frac{(C_i - C_e)V}{m_{ads}} \quad (2)$$

where m_{ads} is adsorbent dose (g), V is volume of solution (L), C_i is initial dye concentration (mg/L) and C_e is the residual concentration of the dye (mg/L) at different time intervals [15].

All the experimental sequences received by the Design Expert software were performed in triplicate and their mean values are reported here.

Table 1
Experimental ranges and levels of the independent variables in the experimental design.

Factors	Range and level		
	−1	0	+1
A: adsorbent dose (g 100/mL)	0.5	1.5	2.5
B: initial CV concentration (mg/L)	50	150	250
C: time of agitation (s)	30	315	600
D: initial solution pH	3	6	9
E: time of activation (s)	30	60	90

2.5. Adsorption isotherms and kinetic studies

Langmuir and *Freundlich* models were employed for adsorption isotherm modelling of the experimental data. Linear regression is commonly used to determine the best-fitting isotherm and the applicability of isotherm equations is compared by judging the correlation coefficients, R^2 [6].

Langmuir isotherm is based on two assumptions that the forces of interaction between adsorbed molecules are negligible and once a molecule occupies a site no further sorption takes place. The *Langmuir* isotherm can be linearized as four different types where simple linear regression will result in different parameter estimates [18]. In our work we confirmed the model given by the linear form of *Langmuir*-1 equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (3)$$

where q_e (mg/g) is the amount of dye adsorbed per unit weight of adsorbent, C_e (mg/L) is equilibrium concentration of solute, q_m (mg/g) indicates the monolayer sorption capacity of adsorbent and the *Langmuir* constant K_L (L/mg) is a direct measure of the intensity of adsorption and can be calculated from the plot C_e/q_e versus C_e [19,20].

The feasibility of adsorption in a given concentration range over adsorbent, was also evaluated from the relation:

$$R_L = \frac{1}{(1 + K_L C_0)} \quad (4)$$

where R_L is the dimensionless factor called separation factor or equilibrium parameter, C_0 (mg/L) is the initial concentration of dye and K_L (L/mg) is previously mentioned the *Langmuir* isotherm constant. Adsorption is considered favourable when $0 < R_L < 1$ [6].

Freundlich isotherm is an empirical equation based on sorption on a heterogeneous surface or surface supporting sites of varied affinities [6].

The linear form of *Freundlich* is given by the following equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

where K_F (mg/g) and $1/n$ (L/g) are *Freundlich* constants, related to adsorption capacity and adsorption intensity, respectively [6,19]. K_F and $1/n$ can be calculated from the plot of $\log q_e$ versus $\log C_e$.

Adsorption kinetics involves searching for a model that best represents the experimental data as a function of operational