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Short communication

Adsorptive efficacy analysis of novel carbonaceous sorbent derived from grape industrial processing wastes towards tetracycline in aqueous solution

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ABSTRACT

In present study, a new activated carbon (GPAC) obtained by $ZnCl_2$ activation from grape industrial processing pulps (GP) under optimized conditions, was adopted as an adsorbent to remove tetracycline (TC) from aqueous solution. Batch adsorption experiments tested the effects of adsorbent dose, initial concentration, contact time and temperature on adsorption properties at the natural pH of TC in the aqueous medium. The experiments indicated that the pseudo-second order model was good fit to the kinetic data and the adsorption equilibrium data were better simulated by the Langmuir model. Maximum adsorption capacity was found as 625 mg/g at pH 5.7 and 35 °C. Thermodynamic parameters showed that the process was spontaneous and endothermic.

1. Introduction

Tetracyclines (TCs) are one of the most commonly used antibiotics. They are extensively applied to human and livestock therapy, and are difficult to metabolize. TCs have been used extensively for disease control and in livestock feed for several decades, due to their excellent therapeutic value [1]. TCs in the environment have become a source of growing concern in recent years. With application of livestock wastes to agricultural fields, adsorption to soils affects transport and degradation of TCs in the environment. Therefore, it is urgent to develop efficient and economical technologies to remove TCs. There are many technologies available for TC removal including adsorption, oxidation, and photochemical degradation [2]. Among the available removal methods, adsorption, which is an efficient, economical and simple process, is widely used for low concentrations of antibiotics. Adsorption by porous materials is effective in removing antibiotics from aqueous solution due to the low energy cost, high adsorption capacity, and relatively low environmental impact [3].

Adsorption from pharmaceutical manufacturing wastewater or remediation of the contaminated environment using activated carbon (AC) is more practical, lower in cost, more efficient and a more environment-friendly approach, compared to the previously described methods of TC removal. However, commercially available ACs are very expensive. Therefore, in recent years, various kinds of AC have been prepared from low-cost precursor materials, which are predominantly biomass wastes. To the best of our knowledge, the present study is the first one to study the adsorption of TC by AC prepared grape industrial processing pulps (GP). Grape is used in food and wine production industry. Although Turkey ranks fourth with 4 million tons in the world grape production, and in the wine production (about 20,000 tons) is 38th [4]. According to grape processing industry, weight of fresh grapes arises about 10–20% solid waste.

The main objective of the present work was to investigate the performance of a novel AC (GPAC) under optimum preparation conditions from GP by $ZnCl_2$ activation for the TC remove from aqueous solution.

2. Materials and methods

2.1. Material

GPAC was prepared by $ZnCl_2$ activation using GP as a precursor. Its preparation, effects of preparation parameters, physical and chemical properties was discussed in our previous study [5]. Its physical and chemical properties are given in the Table 1. TC (purity >98.5%, empirical formula $C_{22}H_{24}N_2O_8 \cdot H_2O$, $M_W = 444.43$ g/mol) and other used chemicals were purchased from Sigma -Aldrich Co. (Ankara, Turkey).

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Table 1
Physical and chemical characteristics of GPAC [5].

Ultimate analysis (dry basis, %)		Proximate analysis (dry basis, %)	
Moisture	4.57	Carbon	81.76
Ash	14.23	Hydrogen	2.70
Volatile matter	17.00	Nitrogen	0.99
Fixed carbon	64.20	Sulfur	0.05
Yield	76.55	Oxygen[a]	14.50
Burn off	23.45		
Textural characteristics		Surface chemical characteristics	
S_{BET} (m^2/g)	1455	Carboxylic (meq/g)	0.55
V_{tot} (cm^3/g)	2.32	Phenolic (meq/g)	0.17
V_{mic} (cm^3/g)	0.13	Lactonic (meq/g)	0.52
V_{mes} (cm^3/g)	2.19	Acidity (meq/g)	1.24
V_{mic} (%)	5.39	Basicity (meq/g)	0.88
V_{mes} (%)	94.61	pH_{pzc}	5.86
D_P (nm)	6.80	pH	6.20

S_{BET}: BET surface area; V_{tot}: total pore volume; V_{mic}: micropore volume; V_{mes}: mesopore volume; V_{mic} (%): micropore contribution; V_{mes} (%): mesopore contribution; D_P: average pore diameter; pH_{pzc}: point of surface zero charge.
[a] By difference.

2.2. Batch adsorption studies

Batch adsorption experiments were conducted with the GPAC in a 100 mL Erlenmeyer flask containing 50 mL TC solution in a water bath shaker (Daihan WSB 30) to elucidate the optimum experimental parameters. The effects of various operating parameters on adsorption at a natural pH (5.7) in aqueous solutions of TC were studied by varying the parameters while keeping other parameters constant. These parameters included the dose of GPAC (10–50 mg/50 mL), initial concentration of TC (200–400 mg/L), contact time (5–480 min), ionic strength (0–0.5 mol/L) and temperature (15–35 °C). The residual TC concentrations were analyzed using a UV–vis spectrophotometer (PerkinElmer Lambda 25) at a maximum wavelength of 360 nm.

Kinetic studies investigated the effects of contact time and initial concentrations to estimate kinetic parameters. For this experiment, 10 mg of GPAC was added to 50 mL of TC solutions at different initial concentrations (200–400 mg/L). The mixture was stirred in a water bath at 25 °C and 120 rpm. At predetermined time intervals (5–480 min), 10 mL sample was removed and filtered.

Isotherm studies were conducted by agitating TC solutions of different concentrations (150–500 mg/L) with the optimal dose of GPAC at 15, 25, and 35 °C.

2.3. Reusability studies of GPAC

Adsorption–desorption cycles were studied to test the reusability of GPAC. Recovery of TC from TC-loaded sorbent was performed with NaOH solution. Initially, 10 mg of the sorbent were added to 100 mg/L of TC solution and agitated for 1 h. The adsorbed amount was calculated and the TC-loaded sorbent was washed with distilled water and added to 0.05 M NaOH solution for 1 h. This adsorption–desorption cycle was repeated five times.

3. Results and discussion

3.1. Optimization of TC adsorption conditions

3.1.1. Dose effect

GPAC dose varied from 10 to 50 mg, while initial TC concentration, temperature, pH and contact time were 100 mg/L, 25 °C, 5.7 and 1 h, respectively (figure not shown). The amounts of TC adsorbed onto the GPAC, with increases in the sorbent dose from 10 to 50 mg, decreased from 98.5 mg/g to 53.7 mg/g. These results may be due to a reduction in the total adsorption surface area available to TC, resulting from overlap or aggregation of adsorption sites. Therefore, the optimum dose was selected as 10 mg for use in future experiments.

3.1.2. Effects of contact time and initial concentration

The experiments were conducted at different times and initial TC concentrations, with a 10 mg sorbent dose at 25 °C (figure not shown). TC adsorptions were rapid in the initial stages of contact time and gradually decreased with time until they reached equilibrium. The rapid adsorption was likely due to the abundance of active sites on the sorbent surface during the first 180, 240 and 320 min at initial concentrations of 200, 300 and 400 mg/L. To confirm that contact time was sufficient, additional adsorption experiments were conducted with 24 h contact time. The amounts of TC adsorbed per unit dose of GPAC increased with an increase in initial TC concentration. The mass transfer driving force would become larger, resulting in higher TC adsorption.

3.1.3. Effect of temperature

The effect of adsorption temperature at 15, 25 and 35 °C, while GPAC dose, initial TC concentration and contact time remained constant (figure not shown). The adsorption capacity of TC increased from 417 to 625 mg/g by increasing solution temperature from 15 to 35 °C, indicating that the TC adsorption onto GPAC was endothermic processes. This was likely due to the increase in the rate of molecular diffusion and the decrease in solution viscosity with increasing temperature, facilitating adsorbate molecule diffusion across the external boundary layer into the internal pores of the sorbent [6].

3.2. Kinetic data analysis

To investigate the adsorption mechanism, two conventional kinetic models, namely pseudo-first order [7] and pseudo-second order [8] were used to analyze the kinetic data (Fig. 1). The linearized kinetic equations used are as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

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

where q_t (mg/g) is amount of adsorption at time t (min). C_t (mg/L) is the equilibrium TC concentration at time t. k_1 (1/min) and k_2 (mg/g min) are the rate constants related to the pseudo-first and pseudo-second order kinetic models, respectively.

Applicability of the kinetic models is compared by judging the correlation coefficient, R^2, and normalized standard deviation, Δq (%), and the agreement between calculated q_e ($q_{e,cal}$) and experimental q_e ($q_{e,exp}$) values. The Δq (%) is defined as:

$$\Delta q(\%) = \sqrt{\frac{\sum_{i=1}^{N}\left[(q_{e,exp} - q_{e,cal})^2 / q_{e,exp}\right]}{N-1}} \times 100 \quad (3)$$

where N is the number of data points, and $q_{e,exp}$ and $q_{e,cal}$ (mg/g) are the experimental and calculated adsorption capacities, respectively. The higher the value of R^2 and lower the value of Δq (%), the more accurate is the predictive model.

The kinetic parameters and the R^2 and Δq (%) values of both kinetic models at different initial concentrations, are presented in Table 2. The pseudo-second order kinetic model had the best-fit, according to the high R^2 and low Δq (%) (Fig. 1). The q_e values calculated according to the pseudo-second order were closer to the $q_{e,exp}$ values, when compared with the pseudo-first order. These results indicated that the pseudo-second order kinetic model was suitable for explanation of the TC adsorption processes onto GPAC.