BIOVEGETAL WASTES USED AS BIOSORBENT FOR REMOVAL OF CHEMICAL POLLUTANTS FROM WASTEWATER

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Abstract. *One of the directions of recovery of vegetable waste from various industrial processes is represented by their use as an adsorbent material for the retention of chemical pollutants (organic dyes and metal ions) from wastewater. In this context, we aimed to test the biosorptive potential of some vegetal waste remaining after obtaining vegetal extracts by liquid-solid extraction (using ethanol 96%), from some plants, such as: Primula veris, Achillea millefolium, Origanum vulgare and Artemisia absinthium, extracts used as biopesticides. This type of biosorbent was used for biosorption the reactive Orange 16 dye and Cu (II) ions from aqueous solutions, using a batch system. In order to evaluate the biosorbive potential of this materials, the influence of certain physical parameters such as temperature, pH solution, amount of biosorbent, dye/ metal ion concentration and phases contact time were investigated in case of biosorption process of Orange 16 dye / Cu (II) metal ions.The obtained results confirm that the studied vegetal wastes can be considered as promising biosorbent to retain organic dyes and metal ions from aqueous media. Therefore, the studies will be continued with the modeling of the biosorption equilibrium based on isotherms from the literature, thermodynamic determinations and kinetic studies.*

Keywords*: biosorption, dye retention, metal ions removal, vegetal waste as biosorbent*

INTRODUCTION

Water represents one of the most important environmental component that assures earth life and, at the same time, the quality of human life. Therefore, pollution prevention and development or optimization of techniques, technologies and materials for advanced treatment of wastewaters represents a priority and also a continuous provocation for the specialists in the field of Environmental Sciences [ZAHARIA, 2017a; VAN LOOSDRECHT et al., 2016].

Methods frequently applied in water depollution (precipitation, coagulation – flocculation, oxidation, reduction, ion exchange, membrane filtration, adsorption on charcoal or polymeric materials, electrochemical treatments, inverse osmosis, recuperation by evaporation, solvent extraction, etc.) are not efficient for total elimination of toxic metal ions or organic matter [RASHID et al., 2021; ZAHARIA, 2017b; ZAHARIA et al., 2005]. These methods are characterized by incomplete removal of pollutants, limited tolerance to pH change, moderate or no selectivity for metals, high consumption of reagents, high energy requirements, and production of toxic sludge or other wasted products that also need treatment before disposal.

Taking into consideration the trends of using natural materials for wastewaters cleaning techniques, the specialists' attention has been oriented to developing new techniques of bioremediation, as a part of the environment biotechnologies. These techniques include, among others, the biosorption (adsorption of some polluting chemical species onto natural or biological absorptive materials, namely biosorbents), which remains an open subject for the researchers and specialists in the field [TORRES, 2020; MACHINENI, 2019]

There are a wide variety of natural materials that have been studied and applied as biosorbents for retaining polluted chemical species from aqueous environments, due to their specific characteristics: easiness of procurement, provision of large specific surfaces, high sorption speed, easiness of operation with organic ligands or by physical-chemical methods to increase their sorption capacity, specific and easy subsequent recovery [OJEDOKUN and BELLO, 2016; NASRULLAH et al., 2016; KYZAS et al., 2014; ZAHARIA, 2015; ZAHARIA and SUTEU, 2013].

A type of natural (unconventional) materials used as biosorbent for organic and inorganic species from aqueous medium are the *agricultural* or *agro-industrial solid wastes* consisting mainly from cellulose, hemicelluloses and lignin, structural components that contain a large variety of functional groups (such as carboxyl, hydroxyl and carbonyl) able to bind molecular and/or ionic pollutant species [SUTEU et al., 2011; SUTEU et al., 2016; ISLAMUDDIN et al., 2019] .

In this context, we selected for this study a lignocellulosic material which is represented by the exhausted solid resulting from liquid-solid extraction processes (maceration, Soxhlet extraction, ultrasonic-assisted extraction) practiced on some plants from spontaneous flora, from the region of Moldova (Romania): *Primula veris*, *Origanum vulgare*, *Artemisia absinthium*, *Achillea millefolium*, in order to obtain plant extracts with potential biopesticidal properties [DARABAN et al., 2018a,b; 2020; 2021].

The aim of this paper is to test the biosorbtive potential of this vegetal waste material, in biosorption processes for the retention of reactive dye Orange 16 and Cu (II) ions from aqueous solutions. The influence of some physical parameters (temperature, pH of the solution, amount of biosorbent, initial concentration of chemical species, phases contact time) on the biosorption processes was studied.

MATERIAL AND METHODS

Biosorbent. The material used as biosorbent is represented by a mixture of vegetable waste (*Primula veris*, *Origanum vulgare*, *Artemisia absinthium*, *Achillea millefolium*) resulting from the process of obtaining plant extracts with biopesticidal action, through different liquid-solid extraction variants, where the extractant was 96% ethyl alcohol.

Adsorbate. A reactive dye Orange 16 (O16 - C.I. 18097; MW = 617.54, λ_{max} = 495 nm – Figure 1), was selected as organic chemical pollutant of aqueous system. The stock aqueous solution has 716 mg dye/L concentration, and for the experimental work, solutions were prepared using appropriate dilutions with distilled water.

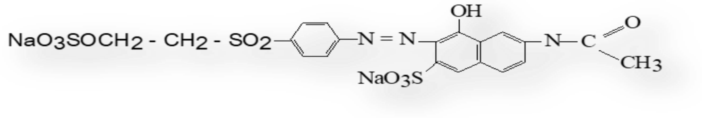


Figure 1. Chemical structure of Orange 16 reactive dye

A stock solution of concentration 635.76 mg of $CuSO_4$ / L was prepared by dissolving $CuSO_4$ x$5H_2O$ in double-distilled water. Working solutions, with concentration of 51.65 mg / L were obtained by dilution from the stock solution.

Biosorption methodology

The biosorption studies were performed in batch system, which involved the introduction of a fixed amount of biosorbent and a 25 mL of dye/metallic ions solution with a concentration of 85.92 mg/L / 51.65 mg/L in 50 mL Erlenmeyer flasks. The solutions pH values were adjusted with 1N HCl or H_2SO_4 and/or 1N NaOH solution. The constant desired temperature was assured by a thermostatic bath. After attainment the equilibrium time, the dye/ metallic ions content in solution was determined spectrophotometrically (using the calibration curve method) by a JK-VS-721N VIS Spectrophotometer at maximum dye wavelength (530 nm) and in case of Cu (II) ions, by determining the aqueous solution absorbance at wavelength λ = 378 nm, after sample treatment with rubeanic acid 0.05% in acetate buffer (pH = 4.6).

The biosorption capacity of the biosorbent (q, mg/g) was calculated with relation (1):

$$q = \frac{C_0 - C}{G} \cdot V \qquad (1)$$

where C_0 and C are the initial and the equilibrium dye/metallic ion concentration in solution (mg/L), G is the amount of biosorbent (g) and V is the volume of dye/metallic ion solution (L).

RESULTS AND DISCUSSIONS

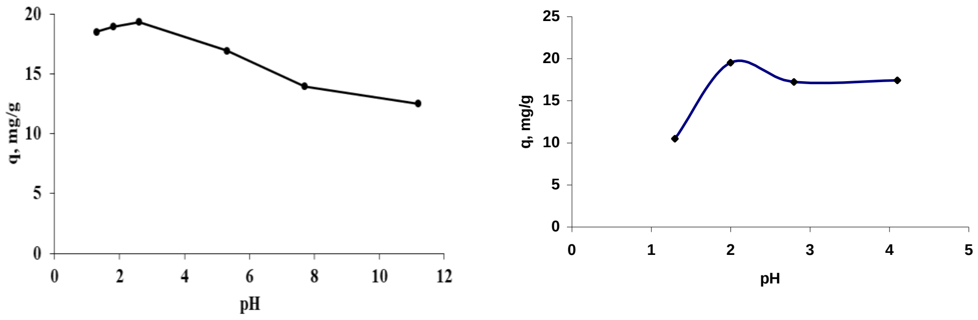
The study aimed to evaluate the biosorption properties of the tested material represented by a mixture of vegetable waste and also to establish the optimal values of some physical parameters (solution pH, temperature, biosorbent doze, initial concentration of chemical species studied, contact time), the variation range being presented Table 1, that influence the development of the biosorption process. The values of these parameters that led to obtaining the highest values for sorption capacity, will be retained and applied in subsequent studies aimed at deepening the biosorption processes analysed now.

Table 1.

Physical parameters that influence the biosorption process of selected chemical pollutants onto biosorbent based on vegetal wastes

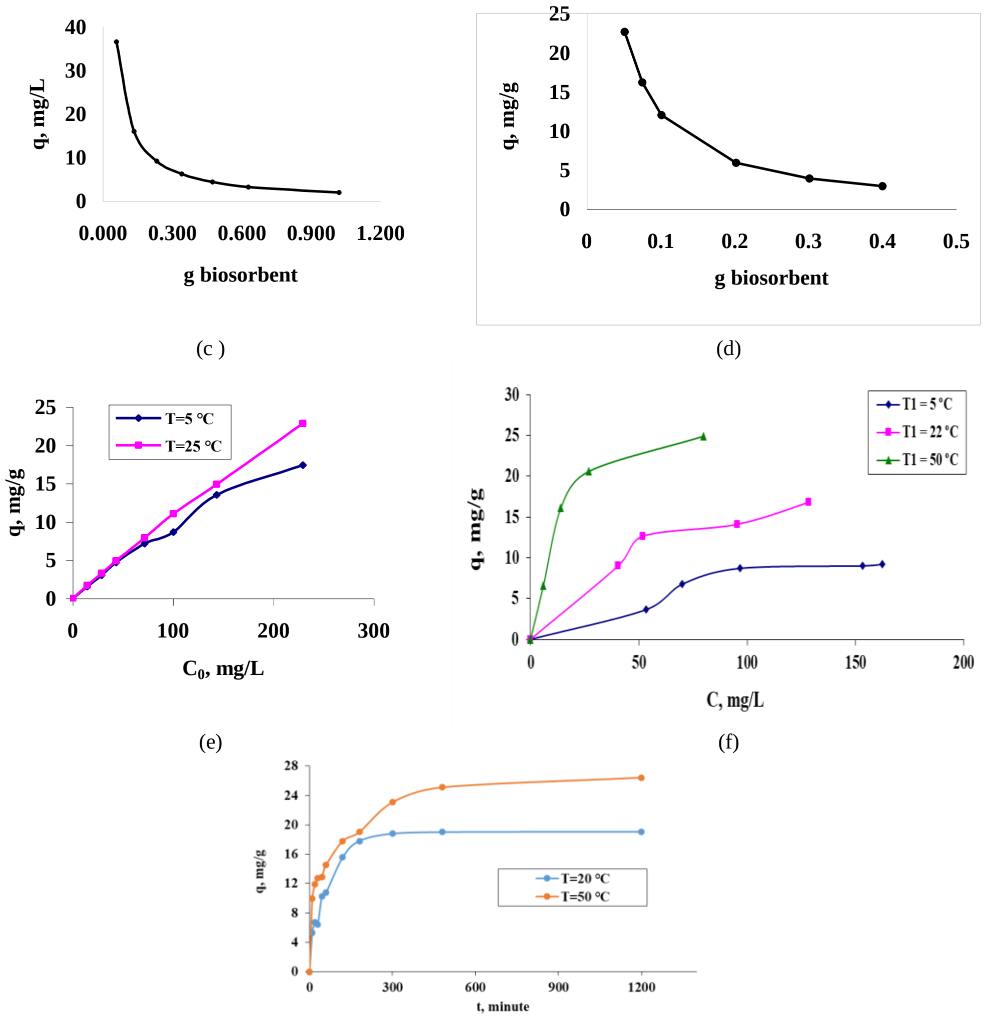
Parameters/ Studied limits of variation	**Type of biomass**	
	Orange 16 dye	*Cu^{2+}*
pH	1-11 (performed with 1N HCl and 1N NaOH solutions)	1-4.5 (performed with 1N H_2SO_4 solution)
T, ^{0} C	5, 20, 50	5, 22, 50
t, min	10 -1200	24
Biosorbent dose, g	2.8	0.051-0.4
Initial pollutant concentration in solution, mg/L	85.92	51.648

The obtained experimental results were presented in Figures 1(a-g).



(a)

(b)



(c)

(d)

(e)

(f)

(g)

Fig. 1. The influence of the operational physical parameters of Orange 16 dye (a, c, e,g) and Cu (II) ions (b, d, f) on biosorption processes onto vegetal wastes (biosorption capacity): (a-b) *solution pH*: Orange 16 dye- C_0 = 85.92mg/L; T=20^{0}C; biosorbent dose = 0.15g; t=24h; Cu (II) - C_0 = 51.648 mg/L; T=20^{0}C; biosorbent dose = 0.05g; t=24h; (c-d) *biosorbent dose*: Orange 16 dye- C_0 = 85.92mg/L; T=20^{0}C; pH=2; t=24h; Cu (II) - C_0 = 51.648 mg/L; T=20^{0}C; pH=3; t=24h; (e, f) *temperature and initial dye concentration*: Orange 16 dye- C_0 = (14.32 -229.12)mg/L; biosorbent dose = 0.2g; pH=2; t=24h; (f); Cu (II) - C_0 = (25.824-206.59) mg/L; biosorbent dose = 0.055g; pH=3; t=24h; (g) *temperature and phases contact time*: Orange 16 dye- C_0 = 85.92 mg/L; biosorbent dose = 0.15 g; pH=2;

The biosorption processes of the studied chemical pollutants, using as biosorbent wastes from extraction processes are dependent on some of physical parameters (Figures 1 (a-g)), as follows:

- An important parameter is the pH of the aqueous solution which is brought into contact with the biosorbent. Its value determines the ionic form of the functional groups of the dye (especially sulfonic groups), the ionic form of the metal species but also the charge of the biosorbent surface, due to the possibilities of dissociation of specific functional groups (for example: -COOH, -OH, -NH_2, - SO_3, -CN etc.). In the dye biosorption, due to its anionic character, the retention is favoured by the acidic environment, the maximum biosorption capacity being registered in a strong acidic environment (pH = 2). In the case of copper ions the retention is maxim at a pH = 2-3 (Figure 1a, b).

- Figure 1c+d shows, in the case of both chemical species studied, a decrease in biosorption capacity with increasing the amount of biosorbent. The highest value of the biosorption capacity for the reactive dye Orange 16 was obtained for 0.15g biosorbent, and in the case of Cu (II) for a quantity of 0.05 g biosorbent. This behaviour is explained by the decrease of the concentration gradient with the increase of the amount of biosorbent.
- The biosorption process is positively influenced by the increase of the temperature as well as of the initial concentration of the studied chemical species (Figure 1e + f). The increase of the adsorption capacity with the increase of the temperature is determined by the intensification of the diffusion processes. The increase of the quantity of adsorbed chemical species with the increase of its initial concentration is achieved up to a certain value, after which a light plateau is reached due the saturation capacity of the biosorbent is reached.
- Figure 1g presents the influence of phase contact time on biosorption process of Orange 16 dye. It is observed that the biosorption capacity increases with the contact time first gradually to a point, in the case of both temperatures, then slower until it reaches a constant value (equilibrium). This is explained by the fact that the active centres are gradually occupied by the dye molecules until they are saturated. The optimal time to reach equilibrium is about 500 minutes. Also, the positive influence of the temperature and the initial concentration of the dye on the biosorption capacity can be observed again.

CONCLUSIONS

The removal study of reactive Orange 16 dye and Cu (II) ions from aqueous solution using as biosorbent vegetal waste from a liquid-solid extraction methods, showed that the tested material has biosorbent properties both against the organic dye Orange 16 and against Cu (II) metal ions. The biosorption of the studied chemical species depends on the pH of the initial solution (the favourable pH value is 2-3), on the dose of biosorbent (in the range 0.15 g for Orange 16 dye and 0.05 g in the case of Cu (II)), the initial concentration of the chemical species, phase contact time and temperature.

From these considerations, it can be concluded that it is of interest to continue the study of biosorption processes of both Orange 16 dye and Cu (II) ions on biosorbent based on vegetal waste, respectively the study of process equilibrium, thermodynamics and process kinetics studies in in order to optimize the biosorption process and also, to extend the application of this biosorbent to the real wastewater treatment systems.

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