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Removal of Some Estrogenic Pollutants from Water by Adsorption

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Abstract: The present research reports the results on removal of some estrogenic compound such as estriol and di-ethyl-phthalate (DEP) from water by using *Saccharomyces cerevisiae* yeast immobilized on silica gel as biosorbent. Biosorption was investigated using batch experiments by considering the influence of initial concentration of estrogenic pollutants from 10 to 100 mg/L. Depending on the initial concentration of the pollutant in aqueous phases the adsorption capacity has varied from 45 to 85 %. The biosorption was mathematically described using Langmuir model and Freundlich equation, and the Langmuir model was found to be in better correlation with the experimental data. The determinate Langmuir parameters were: q_{max} =3.66 (mg/g), b = 0.336 (L/mg) for DEP and q_{max} =15.72 (mg/g), b = 0.0124 (L/mg) for estriol. The Freundlich constants were: k = 1.186 (L/g), n = 2.95 for DEP and k = 3.737 (L/g), n = 1.485 for estriol. The kinetics of biosorption of DEP and estriol by *S. cerevisiae* yeast using first- and pseudo second-order models has shown a better correlation of experimental data with pseudo second-order model.

Keywords: Adsorption, Biosorption, Saccharomyces Cerevisiae, Yeast, Estrogenic Pollutant.

1. Introduction

In the last time, water pollution with natural and synthetic estrogenic compounds has became a concern environmental problem, as they can act as endocrine disrupting compounds (EDCs) and causing adverse health effects on aquatic organisms and humans [1].

The traditional treatment processes applied in water treatment plants are chemical precipitation, membrane separation, ion exchange and adsorption on activated carbon or activated sludge. In the last decade more studies refer to biosorption as a promising alternative or a supplement method for removal of inorganic and organic pollutants.

Biosorption indicates a number of metabolism-independent processes (i.e. physical and chemical adsorption, electrostatic interaction, ion exchange, complexation, chelating and micro-precipitation) taking place in the cell wall rather than oxidation through anaerobic or aerobic metabolism (biodegradation) [2]. Biosorption is characterized by high selectivity and efficiency, cost effectiveness and good removal performance, and can use as raw materials, abundant materials or industrial wastes (fermentation wastes).

The goals of this study work were: to investigate the biosorption on yeast *S. cerevisiae* as an alternatively low-cost method for the removal of estrogenic pollutants, and to apply the adsorption isotherms and the kinetics models to the equilibrium data in order to establish the adsorption mechanism.

2. Experimental

Materials

Estrogenic compounds used in this study, namely estriol (CAS 50-27-1, >98%), a metabolite of 17β-estradiol, and di-ethyl-phthalate (DEP, > 99%), an industrial chemical additive used for impact flexibility of poly-vinyl-chloride (PVC) resins, were supplied from firm Aldrich, respectively Merck Chemicals. For each experiment, working solutions with initial concentration ranging from 10 to 100 mg/L of estrogenic compound were prepared by diluting with appropriate volumes of double distillated water a known volume of stock standard solution (1000 mg/L in ethanol). In the present study a relatively high concentration of compounds in comparison to environmental levels were used to allow for monitoring changes and uptake.

Immobilized *Saccharomyces cerevisiae* from firm Pakmaya on silica gel (70-230 mesh) was used as biosorbent in this study. Immobilization of yeast *S. cerevisiae* was performed according to procedure proposed by Mahan and Holcombe [3], mixing each 1 g powder S. cerevisiae with 3 g of silica gel in wet condition (cca. 10 mL of water. After mixing, the paste was heated in an oven at 105 ^{0}C for 6 h to dry the mixture. The wetting and drying steps were repeated twice to maximize the contact between the yeast and the silica gel. After immobilization the silica gel-yeast was broken and screened to get the original size of silica gel.

Methods

A known weight of biosorbent (0.75 g) was added in each 100 mL of working solution, and batch biosorption experiments were carried out by using a Jar Test apparatus at 100 rpm and at room temperature (20 ± 2 ^{0}C) and pH 5.0. Earlier study has shown no influence of pH values in the range from 2 to 6 [4]. The samples were then filtered or centrifuged, and the absorbance of estrogenic pollutant in the aqueous solution was determined by using UV-VIS Spectrophotometer Jasco V-530. Each determination was repeated three times and the results were given as average values. The standard deviation was less than 10 %.

3. Results and discussion

To determine the biosorption mechanism, and to design the treatment process, equilibrium isotherms and kinetic models were analyzed.

Biosorption isotherms

The experimental results designed to establish the time for reaching equilibrium are shown in Fig. 1 for di-ethyl-phthalate (DEP) and in Fig. 2 for estriol.

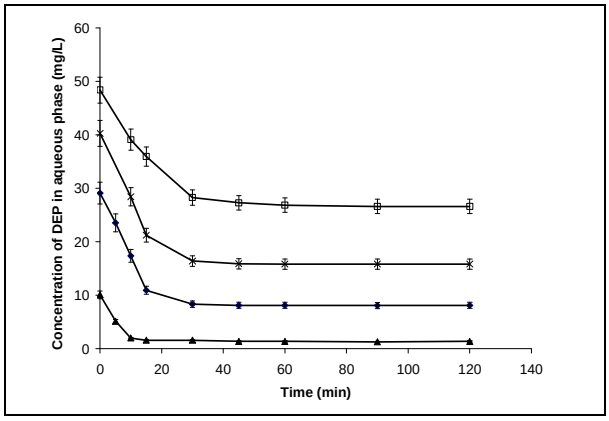

Figure1. Biosorption of DEP for different concentration of solutions.

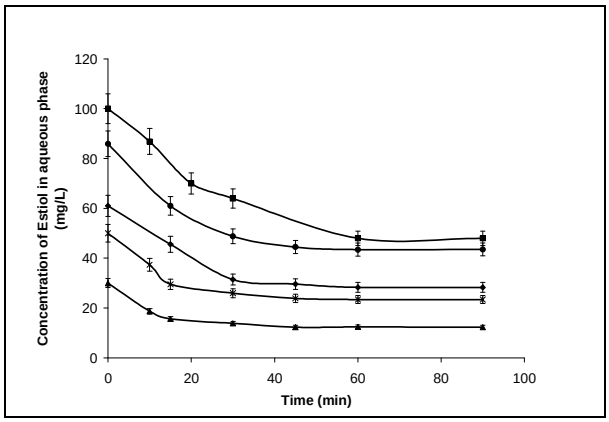

Figure 2. Biosorption of estriol for different concentration of solutions

The biosorption curves plotted in Fig. 1 and Fig. 2 show that the uptake of estrogenic compounds on immobilized yeast follows two stages: an initial rapid stage, which is characteristic to passive uptake such as physical adsorption or ion exchange at the surface of the biosorbent, followed by a slower stage with active uptake.

In the same time, it can be seen, that in the case of DEP, at lower concentration (10 mg/L) equilibrium was reached in about 15 min, but at higher concentration it took between 45 min and 60 min.

In the case of estriol, at lower concentration the equilibrium was reached within 30 min, but at higher concentration it took between 45 and 60 min.

The short time of biosorption experiments until the equilibrium was reached in both cases (DEP and estriol) suggests that the physical adsorption onto the biosorbent surface is the main mechanism of uptake.

The pollutant uptake q (mg/g) was determined considering the volume of solution in contact with the biosorbent, V (L), the amount of added dry biosorbent S (g), the initial concentration of pollutant in working solution C_i (mg/L) and the final equilibrium concentration of pollutant in solution C_{eq} (mg/L):

$$q = V \cdot \left(C_i - C_{eq}\right) / S \qquad (1)$$

The adsorption isotherms are shown in Fig. 3 for DEP and in Fig. 4. for estriol.

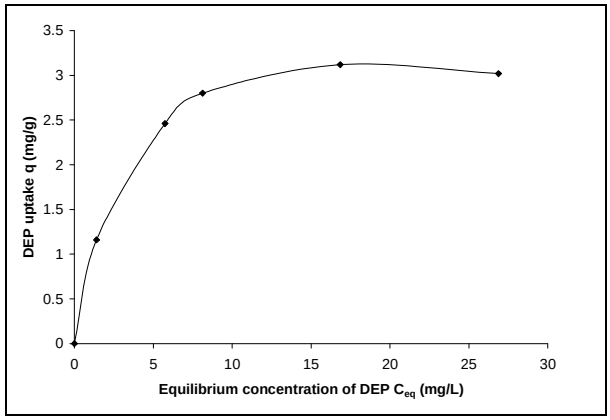

Figure 3. Adsorption isotherm of DEP by *S. cerevisiae* yeast immobilized on silica gel.

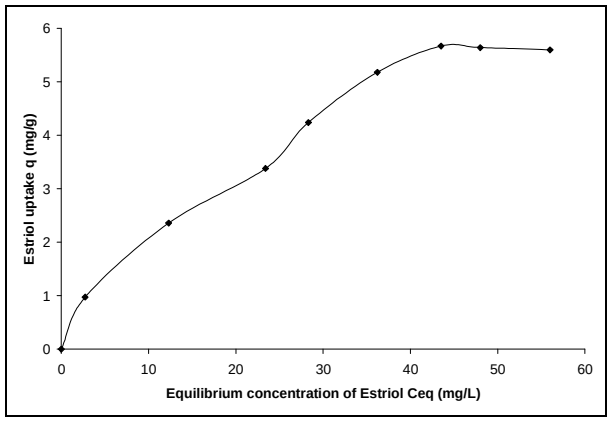

Figure 4. Adsorption isotherm of estriol by *S. cerevisiae* yeast immobilized on silica gel.

Depending on the concentration of estrogenic substances and the binding capacity of the yeast, the adsorption capacity varied from 45 to 85 %.

The adsorption isotherms were mathematically expressed by Langmuir model (2), which is valid for monolayer sorption onto a surface with a finite number of identical sites, and by Freundlich equation (3) which deals with heterogeneous surface:

$$q = \left(q_{\max} \cdot b \cdot C_{eq}\right) \cdot \left(1 + b \cdot C_{eq}\right)^{-1} \quad (2)$$

$$q = k \cdot C_{eq}^{(1/n)} \quad (3)$$

where q_{max} (mg/g) is the maximum adsorption capacity corresponding to complete monolayer coverage (mg/g), interpreted as the total number of binding sites available for biosorption, and b (L/mg) is the Langmuir constant related to the affinity between the sorbent and sorbate, and k and n are Freundlich constants, related to adsorption capacity and adsorption intensity, respectively.

The Langmuir and Freundlich are the most frequently used two - parameters models in the literature describing the non-linear equilibrium between adsorbed pollutant on the adsorbent surface (q_{eq}) and pollutant concentration in solution (C_{eq}) at a constant temperature.

The Langmuir and Freundlich equations were than linearized (4) and (5) and plotted as Fig. 5 to Fig. 8 show:

$$1/q = \left(q_{\max} \cdot b\right)^{-1} \cdot \left(C_{eq}\right)^{-1} + \left(q_{\max}\right)^{-1} \quad (4)$$

$$\log q = \log k + n^{-1} \cdot \log C_{eq} \quad (5)$$

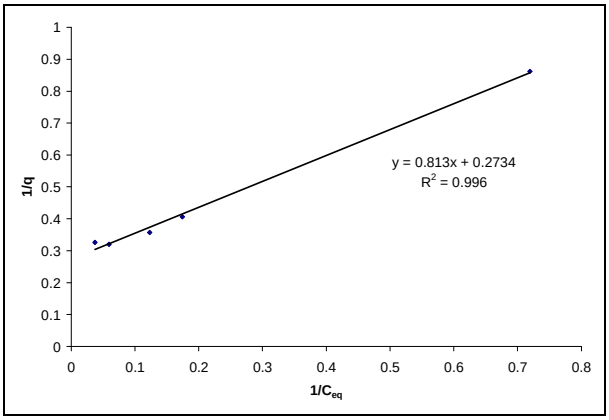

Figure 5. Application of Langmuir model to experimental data for DEP (q_{max}(mg/g) = 3.66, b(L/mg) = 0.336).

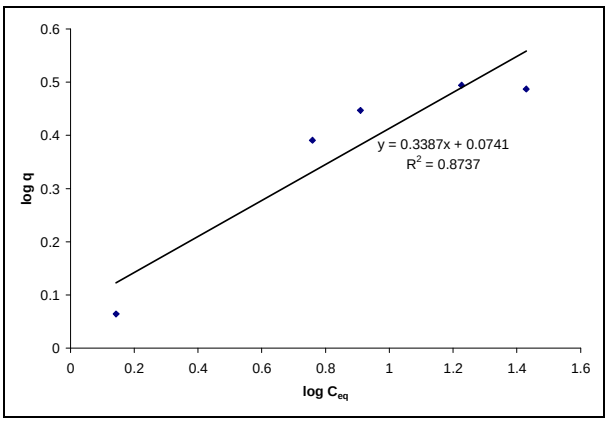

Figure 6. Application of Freundlich model to experimental data for DEP (k (L/g) = 1.186, n = 2.95).

The better correlation of Langmuir model with experimental data comparing the correlation coefficient (R^2) suggests that biosorption of DEP and estriol onto immobilized yeast is a monolayer surface adsorption.

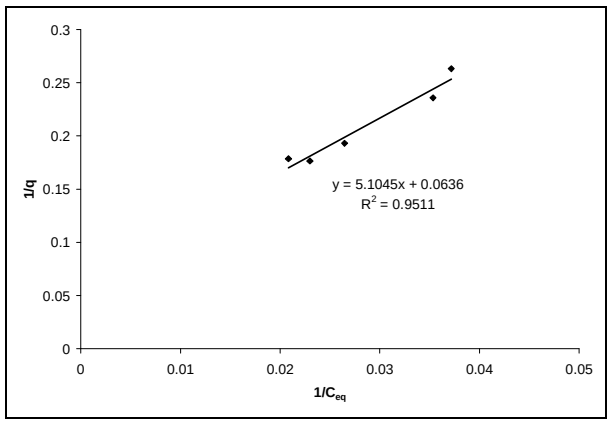

Figure 7. Application of Langmuir model to experimental data for estriol (q_{max} (mg/g) = 15.72, b (L/mg) = 0.0124).

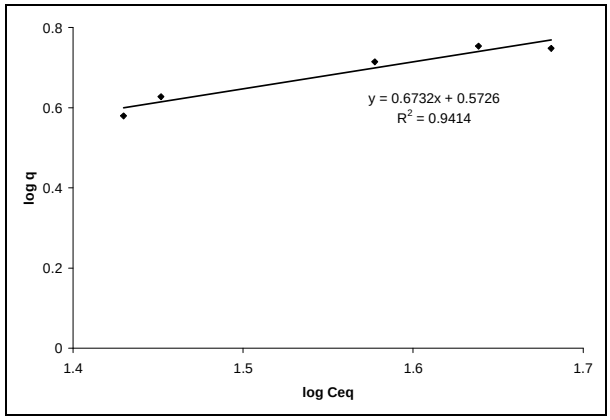

Figure 8. Application of Freundlich model to experimental data for estriol (k (L/g) = 3.737, n = 1.485).

From linear curves, the adsorption parameters were determined: q_{max} = 3.66 (mg/g), b = 0.336 (L/mg), k = 1.186 (L/g) and n = 2.95 in the case of DEP, and q_{max} = 15.72 (mg/g), b= 0.0124 (L/mg), k = 3.737 (L/g) and n = 1.485 in the case of estriol.

The affinity of the biosorbent to the estrogenic compound expressed as the reverse of coefficient b, can be calculated considering the relationship K = 1/b [5]. The resulted values of affinity coefficient are: K = 2.976 (mg/L) for DEP and K = 80.645 (mg/L) for estriol. Analyzing the adsorption parameters, it can be seen, that the *S. cerevisiae* yeast immobilized on silica gel has a higher adsorption capacity and a higher affinity for estriol.

Kinetic modeling

If the movement of pollutant molecules from the bulk liquid to the liquid film surrounding the biosorbent is ignored, the biosorption process follows next steps: transport of solute molecules from boundary film to the external surface of biosorbent (film diffusion), transfer of molecules from the surface to the intra-particular active

sites and than the uptake of molecules by the active sites of biosorbent [2]. In the removal of pollutant from water or wastewater, it is important for design purposes to investigate the mechanisms of adsorption and to control the adsorption rate.

Considering for kinetic study the overall adsorption rate, two models based on the adsorption capacity of adsorbent can are discussed:

- first-Lagergren model [6]

$$\frac{dq}{dt} = k_1(q_{eq} - q) \quad (6)$$

- pseudo second-order model [7]

$$\frac{dq}{dt} = k_2(q_{eq} - q)^2 \quad (7)$$

where q is the amount of adsorbed pollutant on the biosorbent at time t, k_1 is the rate constant of first-order, and k_2 is the rate constant of second-order biosorption.

After integration and applying boundary conditions, (6) and (7) become straight lines, from which k_1 and k_2 can be determined:

$$\log(q_{eq} - q) = \log q_{eq} - \frac{k_1}{2.303} \cdot t \quad (8)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_{eq}} \cdot t \quad (9)$$

The kinetics of biosorption, considering pseudo second-order equation, which gives a better correlation with experimental data are shown in Fig. 9 and Fig. 10.

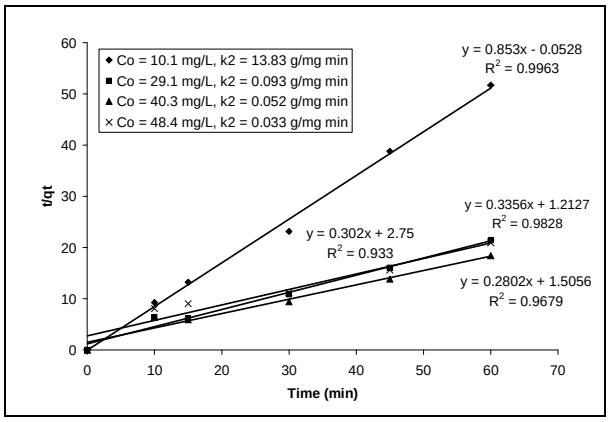

Figure 9. Correlation of experimental data by second-order model for DEP

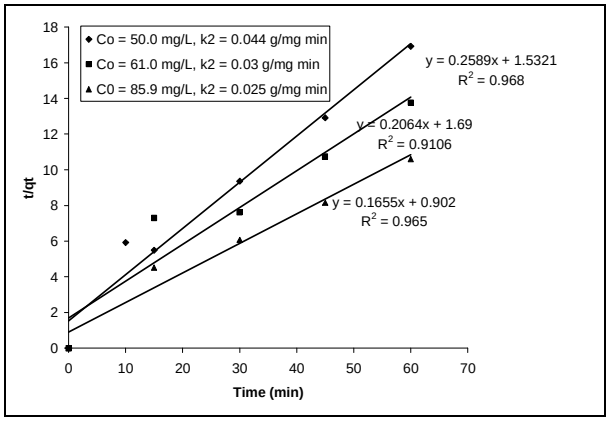

Figure10. Correlation of experimental data by second-order model for estriol

The rate constants of second-order biosorption k_2 found from the fitting of experimental points are shown in the legend of the Fig. 9 and Fig. 10.

4. Conclusions

The results of biosorption of DEP and estriol on *S. cerevisiae* yeast immobilized on silica gel have shown that:

a) The biosorption depends on the initial concentration of estrogenic compounds in tested solution.

b) The better correlation of Langmuir model with experimental data suggests a monolayer surface adsorption of estrogenic pollutant. In the same time, the calculated adsorption parameters suggest a higher adsorption capacity and a higher affinity of biosorbent for estriol.

c) The results have shown that the kinetics of biosorption was adsorbent and compound dependent, and follows a pseudo-second-order kinetics.

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