Adsorption of Indigo Carmine onto Chitosan - Cerium Oxide Nanobiosorbent: Adsorption Isotherms, Kinetics, and Thermodynamics

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Abstract. The present work was designed to synthesize a Chitosan (CS) - Cerium oxide (CeO₂) nanobiosorbent and study the adsorption of Indigo Carmine. The adsorption equilibrium data were better fitted in the Freundlich isotherm model, indicating that adsorption is occurring on a heterogeneous surface in the multilayer pattern. Low pH values (3 and 4), low initial Indigo Carmine concentration (50 mg/L), high adsorbent concentration (500 mg/L) and relatively high temperatures (50 °C) exhibited the highest removal efficiency towards the examined dye. The pseudo-second order kinetic model described better the adsorption process; thus, it can be stated that chemisorption between the adsorbent and the adsorbate is occurring. According to the thermodynamic analysis, adsorption process is spontaneous, exothermic and more favorable at high temperatures. FTIR analysis confirmed the adsorption of the dye onto the CS/CeO₂ nanobiosorbent.

1. Introduction

Water contamination is a major concern facing the world nowadays, as numerous pollutants may render water unsafe for humans. Synthetic organic dyes are commonly used in industrial processes, such as food and pharmaceutical, and are among the aforementioned pollutants. They can be found in the aquatic environment due to their incomplete attachment in the desired substrates during production operations [1]. Indigo Carmine (IC) is an organic salt produced by sulfonation of natural indigo and is approved by USA and EU legislation. It is utilized by many industries as colorant, especially by the food industry for products such as chewing gums, sweets, flavored drinks and ice creams [2]. However, studies have linked IC with adverse health effects, including carcinogenesis, neurotoxicity and hypertension. Therefore, its presence in the aquatic environment can pose a serious threat in human health [3].

The most commonly applied method for the purification of IC-contaminated waters is adsorption, because of its high performance, ease of operation, limited operational cost and effectiveness in a wide pH range [4]. In recent years, the interest of the scientific community has been focused on the synthesis of novel adsorbents, which must have increased adsorption
capacities and enhanced mechanical properties. Adsorbents derived from coupling metal oxides, such as cerium oxide, with chitosan present promising results [5].

Cerium oxide (CeO₂) is one of the most abundant rare earth metal oxides, which, due to its exceptional chemical and physical properties, has drawn attention towards its use in the field of water purification. The main advantage of CeO₂ is its low solubility in acidic conditions; when it is utilized as adsorbent, the adsorbate cannot be eluted, thus making it a promising alternative for the adsorption of water contaminants [6]. Chitosan (CS) is a linear, non-toxic, biocompatible, and biodegradable homo-polymer composed of β(1-4)-linked N-acetyl glucosamine; it presents high mechanical strength, which combined with the presence of functional (hydroxyl and amino) groups in its structure make it a prominent adsorbent [7]. Thus, it is expected that the coupling of the aforementioned materials will provide an innovative adsorbent with high adsorption capacity and high mechanical strength, able to purify water by adsorption of pollutants.

The aim of the present study was to synthesize a novel nanobiosorbent (CS/CeO₂) by coupling chitosan with cerium oxide and study the adsorption of Indigo Carmine. The effect of various parameters (pH, initial dye concentration, initial adsorbent concentration and temperature) on the adsorption process of Indigo Carmine was evaluated, along with a detailed assessment of the adsorption isotherms, kinetics and thermodynamics. Finally, FTIR analysis was conducted in order to characterize the adsorbent and verify the adsorption.

2. Materials and Methods

2.1. Materials

Indigo Carmine (molecular weight = 466.4 g/mol, λ_max= 610 nm), was obtained by UNI-CHEM (Beograd, Serbia). High molecular weight Chitosan (deacetylation degree > 75 %) and glacial acetic acid were purchased by Sigma Aldrich Chemical Co. (St Louis, MO). Cerium oxide (> 99 % purity) and glutaraldehyde were purchased by Acros Organics (New Jersey, USA). All other reagents used in experiments were of analytical grade.

2.2. Adsorbent (CS/CeO₂) Synthesis

An amount of 4 g of chitosan was dissolved in 400 mL of an aqueous solution of glacial acetic acid (1% v/v). After the complete dissolution of chitosan, 4 g of cerium oxide were added to the solution and stirred for 2 h to form a homogeneous solution, followed by dropwise addition of a 2 M sodium hydroxide solution resulting in the precipitation of the adsorbent. Subsequently, 40 mL of an aqueous glutaraldehyde solution (2.5% v/v) were added, leading to the crosslinking with the CS/CeO₂ particles. After 24 h of stirring, the obtained CS/CeO₂ was washed with distilled water and freeze-dried.

2.3. FTIR Analysis of CS/CeO₂ Nanobiosorbent

Jasco 4200 (Jasco Inc, Europe) was used for the FTIR analysis of the nanobiosorbent. The analysis was carried out in the range of 400-4000 cm⁻¹ in the form of KBr pellets.

2.4. Experiments of Indigo Carmine (IC) Adsorption

Batch experimental adsorption studies were performed, whereby IC solutions were prepared by dissolving the desired amount of dye in 200 mL of distilled water. We studied the effect of various parameters towards the adsorption of IC, including initial dye concentration, initial adsorbent concentration, pH, and temperature. HCl and NaOH solutions were used for pH adjustment of the dye solution.

2.4.1. Effect of pH. Aqueous IC solutions of initial concentration equal to 100 mg/L and an adsorbent dosage equal to 500 mg/L were placed in a beaker and stirred at 25 °C to study the effect of pH towards the adsorption of IC; the tested pH values were 3, 4, 5 and 6.
2.4.2. Effect of Initial Dye Concentration. Aqueous IC solutions of initial concentration equal to 50, 100, 150 and 200 mg/L (pH = 4) and an adsorbent dosage equal to 500 mg/L were placed in a beaker and stirred at 25 °C to study the effect of dye’s initial concentration.

2.4.3 Effect of Initial Adsorbent Concentration. The effect of the initial adsorbent concentration was studied in aqueous IC solutions of initial concentration equal to 100 mg/L (pH = 4) that were placed in a beaker and stirred at 25 °C. The studied initial adsorbent concentration values were 50, 100, 200, 350 and 500 mg/L.

2.4.4. Effect of Temperature. The effect of temperature towards the IC adsorption was studied in aqueous IC solutions of initial concentration equal to 100 mg/L (pH = 4) and an adsorbent dosage equal to 500 mg/L that were placed in a beaker and stirred. A thermostatic chamber was used in order to achieve the tested temperatures (15, 25, 35 and 50 °C).

At predetermined time intervals, supernatant aliquots from all experiments were collected in order to evaluate the IC concentration. All experiments were duplicated, and the adsorbed amount of IC onto the CS/CeO2 nanobiosorbent was calculated using Equation (1):

\[
q_{e,t} = \frac{(C_0 - C_{e,t})V}{m} \quad (1)
\]

where \(q_{e,t}\) (mgIC/gadsorbent) is the amount of adsorbed IC at equilibrium or at any time interval; \(C_0\) (mg/L) is the initial concentration of IC; \(C_{e,t}\) (mg/L) is the concentration of IC at equilibrium or at any time interval; \(V\) (L) is the volume of the solution and \(m\) (g) is the weight of the adsorbent used.

The removal percentage of the IC dye was calculated using Equation (2):

\[
\% \text{Removal} = \frac{C_{0,IC} - C_{e,IC}}{C_{0,IC}} * 100 \quad (2)
\]

2.5 Determination of IC concentration

Indigo Carmine concentration was determined with a Hitachi U-2900 UV–Vis spectrophotometer (Tokyo, Japan) at 610 nm.

3. Results and Discussion

3.1. Indigo Carmine Adsorption Studies

Table 1 presents the removal percentage of IC and the experimental amount of adsorbed IC at the state of equilibrium by adsorption onto the CS/CeO2 nanobiosorbent for all the studied parameters of experiments.

| Studied parameter | % Removal | qe (mgIC/gadsorbent) |
|------------------|-----------|----------------------|
| pH (V=200 mL, CIC = 100 mg/L, C adsorbent = 500 mg/L and T = 25 °C) | 3 | 99.45 | 198.90 |
|  | 4 | 98.86 | 197.72 |
|  | 5 | 97.61 | 195.22 |
|  | 6 | 96.52 | 193.04 |
| C IC (mg/L) | 50 | 99.68 | 99.68 |
| (pH = 4, V = 200 mL, C adsorbent = 500 mg/L and T = 25 °C) | 100 | 98.86 | 197.72 |
|  | 150 | 97.95 | 293.84 |
|  | 200 | 93.82 | 375.26 |
| C adsorbent (mg/L) | 50 | 26.36 | 527.20 |
| (pH = 4, V = 200 mL, C IC = 100 mg/L) | 100 | 49.18 | 491.80 |
|  | 200 | 88.83 | 355.32 |
and T = 25 °C)  

| T (°C) | 350 | 96.16 | 274.74 |
|--------|-----|-------|--------|
| 500    |     | 98.86 | 197.72 |
| 15     | 98.03 |       | 196.06 |
| 25     | 98.86 |       | 197.72 |
| 35     | 99.21 |       | 198.42 |
| 50     | 99.51 |       | 199.02 |

According to Table 1, higher amount of IC was adsorbed onto CS/CeO₂ nanobiosorbent at low pH values and low initial adsorbent concentration. Furthermore, the adsorbed amount of IC onto the nanobiosorbent was found to be increasing with an increase in the IC initial concentration and in temperature. The % removal of IC was found to be increasing at low pH values, low initial IC concentration and at high initial adsorbent concentration and temperature values. The increase in IC removal efficiency by CS/CeO₂ nanobiosorbent at low pH values can be explained by the attraction between the positively charged IC and the negatively charged CS/CeO₂ nanobiosorbent[8].

3.2. Adsorption Isotherms

Langmuir and Freundlich isotherm models were used to investigate the relation between the quantity of adsorbed IC and the remaining IC concentration in solution at equilibrium. Langmuir model assumes adsorption to occur on a homogeneous surface in the monolayer pattern, and is expressed by Equation (3):

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

where $q_e$ (mg IC/g adsorbent) is the amount of adsorbed IC at equilibrium; $C_e$ (mg/L) is the equilibrium concentration of IC; $q_m$ (mg IC/g adsorbent) is the maximum adsorption and $K_L$ (L/mg IC) is the Langmuir constant representing the affinity within adsorbent and adsorbate.

The dimensionless separation factor ($R_L$) estimates if the adsorption is favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$), or irreversible ($R_L = 0$), and is calculated by Equation (4).

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

On the contrary, Freundlich model assumes that the adsorption is happening on heterogeneous surfaces in the multilayer pattern, and is expressed by Equation (5):

$$q_e = K_F C_e^{1/n} \quad (5)$$

where $q_e$ (mg IC/g adsorbent) is the amount of adsorbed IC at equilibrium; $C_e$ (mg/L) is the equilibrium concentration of IC; $K_F$ ((mg IC/g adsorbent)×(L/mg IC)^{1/n}) is a constant indicating the adsorption capacity of the adsorbent and $n$ is the dimensional Freundlich constant that reflects the intensity of the adsorption.

Figure 1 depicts the graphs of the Langmuir and Freundlich isotherm models for CS/CeO₂ nanobiosorbent, respectively. The calculated constants for both models are presented in Table 2.
Figure 1. (a) Langmuir and (b) Freundlich isotherms for adsorption of IC onto CS/CeO$_2$ nanobiosorbents.

Table 2. Langmuir and Freundlich constants of adsorption of IC onto CS/CeO$_2$ nanobiosorbent.

|                | Langmuir | Freundlich |
|----------------|----------|------------|
| $q_m$ (mg/g)   | K$_L$ (L/mg) | R$_L$ | R$^2$ | K$_F$ | $1/n$ | R$^2$ |
| 454.55         | 0.647    | 0.015      | 0.912 | 0.235 | 196.52| 0.997 |

The correlation coefficients of the Langmuir and the Freundlich isotherm model signify that the isotherm data fit better in the Freundlich model; thus, adsorption of IC onto the CS/CeO$_2$ nanobiosorbent is multilayer and the nanobiosorbent possesses an energetically heterogeneous surface [9]. The calculated constants for both models indicate that the adsorption is favorable and that the synthesized nanobiosorbent presents high IC adsorption capacity.

3.3. Adsorption Kinetics

The experimental data on the adsorption of IC onto the CS/CeO$_2$ nanobiosorbent were fitted on the pseudo-first order (Equation 6), pseudo-second order (Equation 7) and intraparticle diffusion models (Equation 8), with the calculated constants of each model being presented in Table 3.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} * t \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 * q_e} + \frac{t}{q_e} \quad (7)$$

$$q_t = K_{id} * \sqrt{t} + C \quad (8)$$

where $q_e$, (mgIC/gadsorbent) is the amount of adsorbed IC at equilibrium or at any time interval, $k_1$ (min$^{-1}$) is the equilibrium rate constant of the pseudo-first order model, $k_2$ (gadsorbent/mgIC*min$^{-1}$) is the rate constant of the pseudo-second order model, $K_{id}$ ((mgIC/gadsorbent)*min$^{-0.5}$) is the diffusion coefficient and $C$ (mgIC/gadsorbent) is intraparticle diffusion constant of the intraparticle diffusion model.

Table 3. Kinetic parameters for the adsorption of IC onto CS/CeO$_2$ nanobiosorbent (pH = 4, V = 200 mL, C$_{adsorbent}$ = 500 mg/L and T = 25°C).

| $C_{IC}$ (mg/L) | $q_{eq}$ | Pseudo-first order | Pseudo-second order | Intraparticle diffusion |
|-----------------|----------|--------------------|---------------------|-------------------------|
|                 | $q_{cal}$ | $k_1$ | R$^2$ | $q_{cal}$ | $k_2*10^{-3}$ | R$^2$ | K$_{id}$ | C | R$^2$ |
| 50              | 99.68    | 119.73 | 0.082 | 0.991 | 106.38 | 1.345 | 0.997 | 8.99 | 18.24 | 0.836 |
| 100             | 197.72   | 185.87 | 0.078 | 0.999 | 208.33 | 1.102 | 0.999 | 17.29 | 42.88 | 0.732 |
| 150             | 293.84   | 237.30 | 0.051 | 0.989 | 312.50 | 0.999 | 0.999 | 25.84 | 59.73 | 0.815 |
| 200             | 375.26   | 373.51 | 0.037 | 0.972 | 454.55 | 0.997 | 0.997 | 34.88 | 34.88 | 0.953 |

According to Table 3, the pseudo-second order kinetic model provides the best fit for the experimental data. Therefore, IC adsorption onto the CS/CeO$_2$ nanobiosorbent can be
characterized as chemisorption [10]. The decrease in the rate constants for the pseudo-first and pseudo-second order models with an increase in the initial IC concentration is attributed to the limited accessibility to active sites of the CS/CeO$_2$ nanobiosorbent. A rapid transportation of IC to the pores of the nanobiosorbent is responsible for the partially satisfactory values of correlation coefficient for the intraparticle diffusion model.

3.4. Adsorption Thermodynamics

A thermodynamic analysis of the adsorption process was conducted to provide a better insight on the effect of temperature. The thermodynamic parameters of the adsorption, namely the change in the free Gibbs energy ($\Delta G^\circ$), the change in entropy ($\Delta S^\circ$) and the change in enthalpy ($\Delta H^\circ$), were estimated by Equations (9) and (10).

$$\Delta G^\circ = -RT \ln \left( \frac{q_e}{C_e} \right) \quad (9)$$

$$\ln \left( \frac{q_e}{C_e} \right) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R \cdot T} \quad (10)$$

where $q_e$ (mg IC/g adsorbent) is the amount of adsorbed IC at equilibrium; $C_e$ (mg/L) is the equilibrium concentration of IC; $R$ (J/(mol*K)) is the molar gas constant, and $T$ (K) is the absolute temperature.

Table 4 presents the estimated thermodynamic parameters. The feasibility of the adsorption process is expressed by the negative values of $\Delta G^\circ$ at all of the examined temperatures. The adsorption process can be described as exothermic due to the negative value of $\Delta H^\circ$, while the positive value of $\Delta S^\circ$ indicates an increase in the randomness of the system. The aforementioned results specify that the adsorption becomes more favorable at high temperatures.

| $T$ (K)  | $\Delta G^\circ$ (KJ/mol) | $\Delta H^\circ$ (KJ/mol) | $\Delta S^\circ$ (J/(mol*K)) | $R^2$ |
|---------|-----------------|-----------------|-----------------|------|
| 288.15  | -11.02          |                 |                 |      |
| 298.15  | -12.78          |                 |                 |      |
| 308.15  | -14.16          | -30.70          | 145.29          | 0.989|
| 323.15  | -16.14          |                 |                 |      |

3.5 FTIR Analysis

FTIR analysis on the CS/CeO$_2$ nanobiosorbent was conducted before and after the adsorption of IC, with the spectra being presented in Figure 2.

![FTIR spectra of CS/CeO$_2$ before and after the adsorption.](image)

The peak at 2920 and the peaks at 1643 and 3420 cm$^{-1}$ before the adsorption are attributed to C-H stretching bands and the presence of primary amines, respectively. The peak at 1070 cm$^{-1}$ is
the result of the C-N bond stretching, which is present in chitosan, while the presence of cerium oxide in the nanobiosorbent is verified by the peak at 464 cm\(^{-1}\)[11]. Upon the IC adsorption, there is a new peak at 1463 cm\(^{-1}\), which is attributed to the C=C bond present in the indigo carmine. The latter thus proves the adsorption of IC onto the CS/CeO\(_2\) nanobiosorbent[10]. Finally, after the adsorption the bands at 1070, 1643, 2920 and 3420 cm\(^{-1}\) have shifted to 1080, 1653, 2910 and 3425 cm\(^{-1}\).

4. Conclusions

CS/CeO\(_2\) nanobiosorbent was synthesized and its efficiency towards the adsorption of IC was evaluated. Freundlich isotherm model provided a better fit for the equilibrium data of the adsorption than the Langmuir model, thus adsorption is occurring on heterogeneous surface in the multilayer pattern. Highest removal efficiency of IC was observed at low pH values, low initial IC concentration and at high initial adsorbent concentration and temperature values. According to the kinetic and thermodynamic analysis, the adsorption is exothermic, more favorable at high temperatures, and best described by the pseudo-second order model. IC adsorption onto CS/CeO\(_2\) was verified by FTIR analysis. Based on the results of the present study, the CS/CeO\(_2\) synthesized nanobiosorbent presents great potential towards the removal of pollutants from the aquatic environment.

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