

## THE ADSORPTION OF TARTRAZINE, CONGO RED AND METHYL ORANGE ON CHITOSAN BEADS

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Low molecular weight chitosan, prepared as chitosan beads was used for the adoption of Tartrazine (TAR), Congo Red (CR) and Methyl Orange (MO). The efficiency of dyes removal from aqueous solution was investigated, therefore samples containing various concentrations of TAR, CR, and MO were mixed with chitosan beads and the adsorption was estimated using a validated chromatographic method. The results provided by the UPLC method were fitted to Freundlich, Temkin and Dubinin-Radushkevich adsorption models.

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### 1. Introduction

Around 50% of all dye diversity is represented by azo dyes and due to their extensive applications and persistence they pose a clear environmental hazard [1]. Tartrazine (TAR), Congo Red (CR), and Methyl Orange (MO) (Figure 1) are azo colorings used commercially in paper, foods, textiles, drugs and other products. These colorants cause adverse effects on human health if their concentrations exceed the limits set by existing laws and regulations [2].

Because of the high stability of these dyes, conventional physico-chemical and biological removal methods may not be completely effective for their elimination [3]. Adsorption is a popular technique because of its simplicity and high efficiency, as well as the availability of a wide range of adsorbents. It has proven itself an effective method for removal of various dyes from wastewaters [4-8]. The adsorption process has an edge over the other treatment methods due to its sludge free operation, and thorough removal of dyes even from dilute solutions [3].

There is a growing interest in finding low cost, locally available and effective materials for the removal of dyes. Several non-conventional, low price adsorbents such as bentonite [9], leaf [10], fly ash [11], activated red mud [12], rice husk [13], and fungi [14] have been used for the removal of azo dyes from aqueous solutions. Unfortunately, not all of these adsorbents are effective against anionic dyes due to their hydrophobic or anionic surfaces. Therefore, more efficient adsorbents are needed [15].

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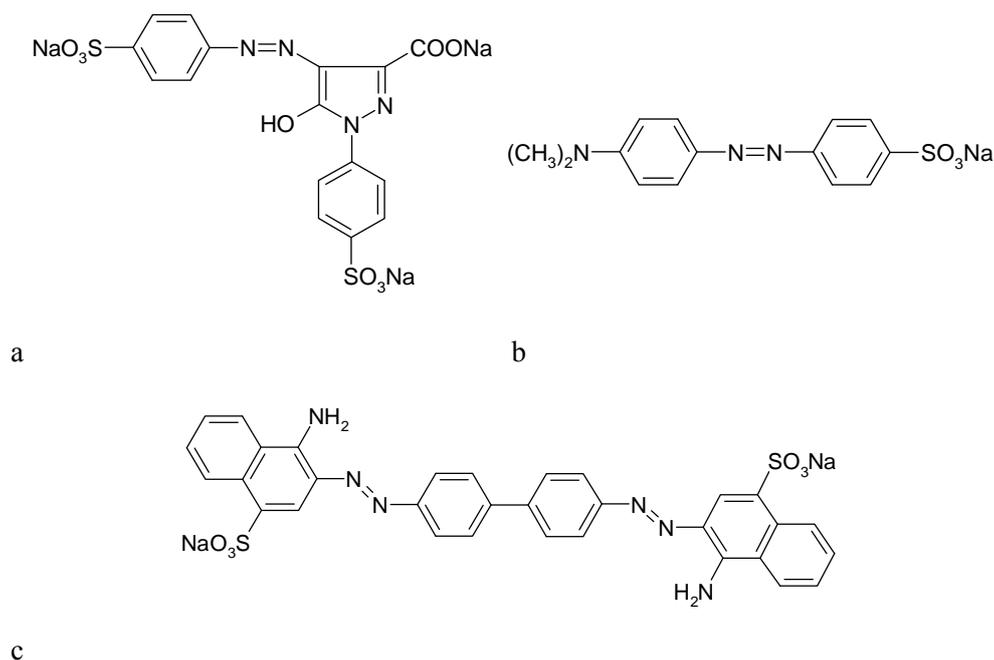


Fig. 1 The chemical structures of industrial dyes: (a) tartrazine; (b) methyl orange; (c) congo red

Biopolymers are promising biosorbents for the treatment of wastewater against dye pollution. Among biopolymers, chitosan, a chitin derivative, should be highlighted [16]. Chitosan, the deacetylated form of chitin, is a polymer composed of glucosamine residues linked by  $\beta$ -(1,4) glycosidic bonds. Chitin is itself a waste product of the seafood processing industry, extracted mainly from crab, shrimp, prawn, and krill shells [17]. Chitosan can be readily obtained from the alkali treatment of chitin and has many applications in various industries, such as agriculture, biomedicine, environment, cosmetics and food [18]. Recently, several studies brought attention to the high potential of chitosan for the adsorption of dyes [19], metal ions [20-22] and proteins [23] from aquatic environments. The extensive use of chitosan as a dye adsorbent is due to its high hydrophilicity, presence of a large number of hydroxyl and amino groups with high activity as adsorption sites, non-toxicity, abundance in nature, biocompatibility, biodegradability, bioadhesivity, film-forming ability and most of all, because of its exceptional chelating behavior [24].

Many techniques have been employed for the assessment of azo dyes, such as UV-Vis spectroscopy [25], UV-Vis spectroscopy coupled with a calibration method [26], ELISA [27] potentiometry [28], HPLC [25, 29], HPLC-MS [30, 31], UPLC [32]. In the present study, the analysis technique used for the determination of azo dyes was based on a previously developed and validated UPLC method, giving special consideration to the discrimination between the three dyes in mixtures [33].

Due to the fact that there were signaled some examples of small fur and textile plants that have dumped wastewater containing CR, MO and TAR into rivers, the objective of this work was to develop a simple, accurate, sensitive, economical, reproducible, and rapid method for the adsorption of mixtures of the three dyes onto chitosan beads, as a means of their removal from wastewaters.

## 2. Experimental

### 2.1. Reagents and Chemicals

Chitosan with low molecular weight (LMW), with 75-85% degree of deacetylation, TAR, CR, MO, sodium chloride, acetic acid and sodium hydroxide were purchased from Sigma Aldrich Chemie GmbH (Germany). All other chemical were analytical-reagent grade.

Standard stock solutions of TAR, CR, and MO were prepared in 0.1 M sodium chloride solution (TAR 1.0048 mg mL<sup>-1</sup>, CR 1.008 mg mL<sup>-1</sup>, and respectively MO 1.001 mg mL<sup>-1</sup>). Diluted standard solutions were obtained in and the adsorption experiments were carried out in acetate buffer (pH 5.6; 0.1 M). A thermostated shaker (Vibramax 100 Heidolph), with a constant speed of 300 rpm at 25±1°C, was used for the adsorption process.

## 2.2. Preparation of Chitosan Beads

The chitosan solution was prepared by dissolving approximately 1.00 g chitosan powder into 30 mL of 2% acetic acid solution. The viscous solution was left overnight before adding drop wise into a precipitation bath containing 500 mL of 0.5 M NaOH, which neutralized the acetic acid within the chitosan solution and, thus, the chitosan gel was turned into spherical homogeneous chitosan gel beads. The aqueous NaOH solution was kept under a mild, continuous stirring. The wet chitosan gel beads were extensively rinsed with distilled water to remove any NaOH and sieved on 1 mm mesh. Prior to the measurements the chitosan beads were kept at 4°C, after adding a few drops of chloroform in order to avoid bacterial degradation.

## 2.3. Adsorption Experiments

For adsorption isotherm studies, various dye concentrations were tested. Solutions of dyes with concentrations between 0.75 µg L<sup>-1</sup> and 30 µg L<sup>-1</sup> were obtained by diluting with ultrapure water the appropriate volume of TAR, CR, and MO stock solutions. The adsorption of a mixture of these dyes was carried out in a batch process at room temperature (25±1°C). The batch adsorption experiments were conducted in 50 mL Erlenmeyer glass flasks, by placing approx. 0.4 g of chitosan beads in 20 mL of dye solutions and were stirred at 300 rpm for 2 hours. Samples from the adsorption experiments mixtures were taken at zero and 2 hours time and injected in the chromatographic system. For these analyses it was used an UPLC system (Milford, USA; via Hemtek, Belgrad, Serbia and Chromaktiv, Bucharest, Romania) consisted in Acquity Binary Solvent Manager, Acquity Sample Manager and Acquity PDA Detector (set to collect data between 210 and 500 nm) and an Acquity UPLC BEH C<sub>18</sub> 2.1 mm x 50 mm column (1.7 µm particle diameter). The elution was performed at 0.3 mL min<sup>-1</sup>, using the following gradient elution program made with 100% MeOH as mobile phase A and 0.1 M acetate buffer in 10% MeOH as mobile phase B: equilibration with 50% mobile phase A, hold the equilibration conditions 0.3 min, linear increase till 1.5 min to 70% mobile phase A, then increase to 100% mobile phase A in 0.5 min, hold this condition for 0.5 min, and re-equilibration [33].

The adsorption capacity of adsorbent material,  $q_e$  (mg g<sup>-1</sup>), was determined with the relation:

$$q_e = \frac{(A_0 - A_e)V}{W} \quad (1)$$

where  $A_0$  is the initial area of the peak representing a dye (µV s) at the beginning of the adsorptions experiment,  $A_e$  is the final (equilibrium, at 2 hours in our case) area of the peak representing the same dye (mg L<sup>-1</sup>),  $V$  is the volume of dye solution (20 mL) and  $W$  is the weight of chitosan beads (0.4 g) employed. For the sake of simplicity and for time-efficiency, areas of the peaks were used in all equations, instead of concentrations.

The UPLC method was tested for applicability in determining the concentration of TAR, MO, and CR from aqueous solutions that were submitted beforehand to adsorption onto chitosan beads. In order to describe the removal mechanism of TAR, MO, and CR from water phase onto chitosan beads, three widely used isotherm models (Freundlich, Temkin and Dubinin-Radushkevich isotherm models) were applied.

The Freundlich isotherm [34] is an empirical equation that comprises the heterogeneity of sites and the presence of multilayer of adsorption sites with growing energies Equation 2.

$$q_e = K_f A_e^{1/n} \quad (2)$$

where  $q_e$  is the amount of dye adsorbed at equilibrium per mass of chitosan ( $\text{mg g}^{-1}$ );  $A_e$  is the area of the peak describing a dye in aqueous phase at equilibrium; the Freundlich coefficients  $n$  and  $K_F$  are obtained from plotting  $\ln q_e$  as a function of  $\ln A_e$ , as can be observed from the linear form of Freundlich equation (Equation 3):

$$\ln q_e = \ln K_F + \frac{1}{n} \ln A_e \quad (3)$$

Furthermore, from the linear form of Freundlich equation the factor  $b_F$  can be determined. Its value can be calculated as  $1/n$ , which represents the slope of the straight line obtained from the previously mentioned plot. The value of  $b_F$  describes the adsorption intensity or the surface heterogeneity. If the adsorption process is described by chemisorptions, the value of the  $b_F$  factor should be between 0 and 1. The closer the value of  $b_F$  is to 0, the more heterogeneous the solid phase surface is [35].

The Temkin isotherm equation predicts that the heat of adsorption of all the molecules in the layer reduces linearly with the filling of empty adsorption sites, as a consequence of interactions between an adsorbent and the adsorbate [36]. The Temkin isotherm, in its non-linear Equation 4 and linear Equation 5 forms, respectively, is given below:

$$q_e = B \ln K_0 A_e \quad (4)$$

$$q_e = B \ln K_0 + B \ln A_e \quad (5)$$

where  $K_0$  ( $\text{L g}^{-1}$ ) is the equilibrium binding constant, representing the maximum binding energy, and constant  $B$  is related to the heat of adsorption and its value is  $\frac{RT}{\Delta Q}$ . From the value of  $B$ , conclusions can be drawn regarding whether the adsorption process is an exothermic or endothermic reaction. A plot of  $q_e$  versus  $\ln A_e$  facilitates the determination of the isotherm constants  $B$  and  $K_0$  from the slope and intercept of the straight line plot [37].

The Dubinin–Radushkevich isotherm model [38] is a temperature-dependent two-parameter isotherm that describes the porous structure of the sorbent. The Dubinin-Radushkevich mechanism of adsorption is defined by a Gaussian energy distribution onto the heterogeneous surface of the sorbent [39]. The linear Dubinin-Radushkevich equation is given below, as Equation 6:

$$q_e = q_{DR} \exp(-k_{DR} \varepsilon^2) \quad (6)$$

where  $q_e$  is the adsorption capacity ( $\text{mg g}^{-1}$ ),  $q_{DR}$  ( $\text{mg g}^{-1}$ ),  $k_{DR}$  ( $\text{mol}^2 \text{K J}^{-2}$ ) are Dubinin-Radushkevich isotherm constants and  $\varepsilon$  is given by the relation:

$$\varepsilon = RT \left(1 + \frac{1}{A_e}\right) \quad (7)$$

where  $A_e$  is the area of the peak describing a dye in aqueous phase at equilibrium,  $R$  is the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and  $T$  is the temperature ( $^{\circ}\text{K}$ ) at which the adsorption process took place.

In order to obtain the values of the isotherm constants, a plot was done of  $\ln q_e$  as function of  $\varepsilon^2$ , based on the linear form of the Dubinin-Radushkevich equation (Equation 8).

$$\ln q_e = \ln q_{DR} - k_{DR} \varepsilon^2 \quad (8)$$

### 3. Results and Discussion

#### 3.1. Adsorption experiments

Following the adsorption of dyes onto chitosan beads, the resulting peak area values were used to determine the value of the adsorption capacity, and afterwards, both the peak areas and

adsorption capacity values were fitted to three theoretical isotherm models, i.e. Freundlich, Temkin and Dubinin-Radushkevich. Figures 2, 3 and 4 present, for all three dyes, the linear representation of the Temkin, Freundlich and Dubinin-Radushkevich isotherms.

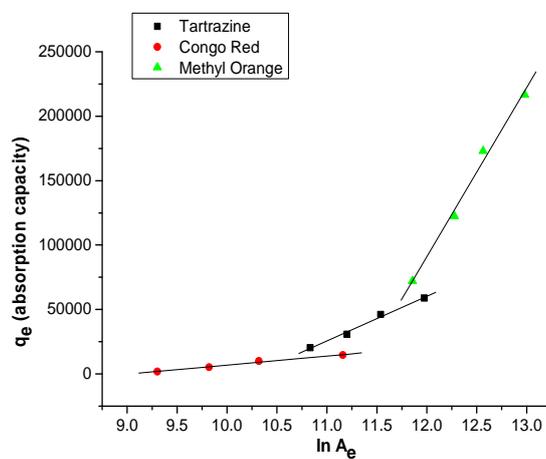


Fig. 2 Adsorption isotherms of TAR, CR and MO on the chitosan beads, linearized according to Temkin equation.

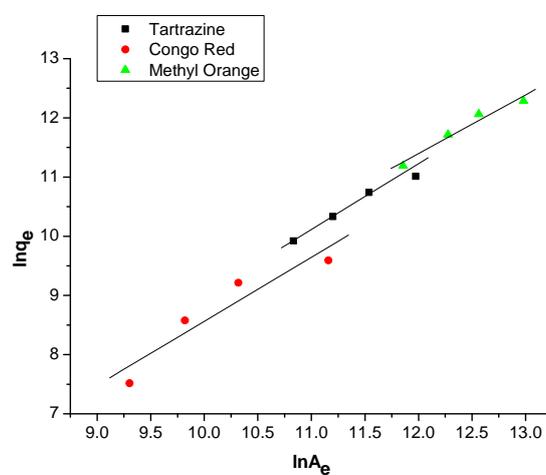


Fig. 3. Adsorption isotherms of TAR, CR and MO on the chitosan beads, linearized according to Freundlich equation.

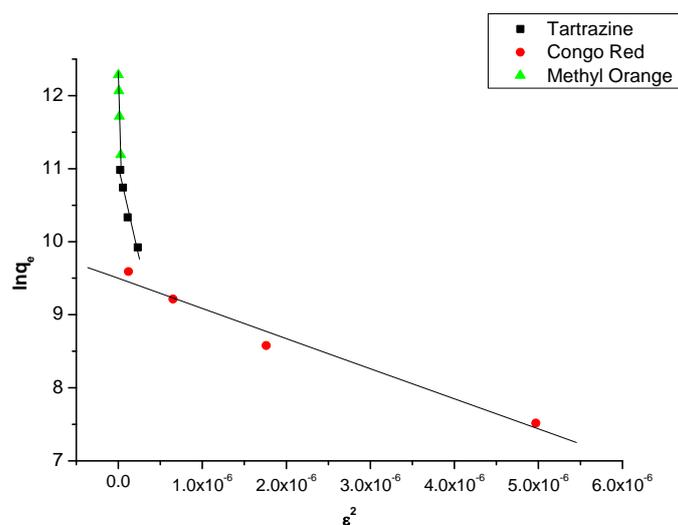


Fig. 4. Adsorption isotherms of TAR, CR and MO on the chitosan beads, linearized according to Dubinin-Radushkevich equation.

Table 1. Experimental isotherm constants and correlation coefficients for the adsorption of TAR, CR, and MO onto chitosan beads using experimental data

	Constant	TAR	CR	MO
Freundlich model				
	n	1.0566	0.9244	1.0089
	$K_F ((\text{mg g}^{-1})(\text{mL mg}^{-1}))$	0.7535	0.1047	0.6081
	$b_F$	0.9464	1.0818	0.9912
	$R^2$	0.9722	0.8891	0.9638
Temkin model				
	$K_0 (\text{L mg}^{-1})$	$3.49594 \times 10^{-5}$	0.000121	$1.2298 \times 10^{-5}$
	$R^2$	0.9908	0.988	0.9916
Dubinin-Radushkevich model				
	$k_{DR} (\text{mol}^2 \text{K J}^{-2})$	484.5041	40.0999	$3.8774 \times 10^3$
	$q_{DR} (\text{mg g}^{-1})$	$6.1258 \times 10^4$	$1.3333 \times 10^4$	$2.2997 \times 10^5$
	$R^2$	0.9582	0.9745	0.9729

Table 1 lists the calculated results (adsorption constants and correlation coefficients) for the adsorption processes. The primary observation is that the Temkin equation is the best model to describe dyes adsorption on the chitosan beads under the concentration range studied (correlation coefficient,  $R^2 > 0.988$ ). Also from the linear Temkin equation,  $\Delta Q$  was calculated and for all three dyes its value was higher than 0, proving that the adsorption of dyes onto chitosan beads is an exothermic reaction, corresponding to data regarding azo dyes from literature [40]. Freundlich isotherm model also provides some hints regarding aspects of the mechanism of adsorption. Due to the fact that the  $b_F$  constant has values lower than 1 for TAR and MO, it can be suggested that the adsorption of the two dyes onto chitosan beads is described by chemisorptions, consequent with data from literature [41].

#### 4. Conclusions

The adsorption studies indicate that TAR, CR, and MO can be efficiently adsorbed onto chitosan beads. For low concentrations of dyes, our data is well correlated with the data presented in the literature, proving that chitosan beads have high adsorption capacity. The mechanism of adsorption is best described by the Temkin isotherm model, meaning that the adsorption of dyes onto chitosan beads is explained by a homogenous distribution of binding energies which is reduced linearly with the increase of interactions between the sorbent and sorbate. Data obtained from the Freundlich model isotherm, also indicates that the surface of the sorbent is homogenous and that for TAR and MO the mechanism of adsorption is described by chemisorptions. From the values of  $\Delta Q$ , it can be concluded that the adsorption process of the three azo dyes onto chitosan beads is an exothermic reaction.

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