



# SORPTION OF DYES BY A POLYMER BASED ON GLYCIDYL ACRYLATE AND CARBOXYMETHYL CELLULOSE

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## Abstract

The sorption capacity of a polymer based on glycidyl acrylate and carboxymethyl cellulose towards dyes such as indigo carmine, Congo red, and pyrazolone yellow was studied. It was shown that the sorption is reliably described by the Freundlich model and has the physical nature. The calculated values of the Gibbs free energy indicate the spontaneous process of sorption of dyes by the resulting polymer.

**Key words:** glycidyl acrylate, carboxymethyl cellulose, dyes, sorption.

## Introduction

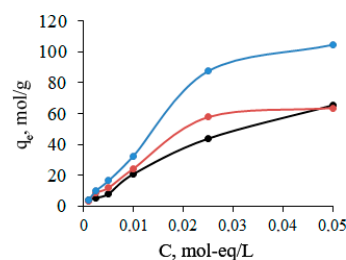
Pollution of surface, ground and waste water from different industrial manufactures and agricultural enterprises with heavy metal ions and organic dyes poses a serious threat to the environment [1, 2].

Various pollutants can be removed from the aquatic environment by a number of methods, including ion exchange [3], coagulation [4], electrokinetics [5], precipitation [6], reverse osmosis [7], sorption/adsorption [8], etc. Due to the low cost, efficiency, selectivity, reusability, and the possibility to remove very low concentrations of pollutants, sorption is currently considered the most promising method. Among sorption materials, the polymers based on glycidyl acrylate (GA) and carboxymethyl cellulose (CMC) are of particular interest owing to the presence of reactive groups capable of forming chemical bonds with molecules and ions of pollutants [9, 10].

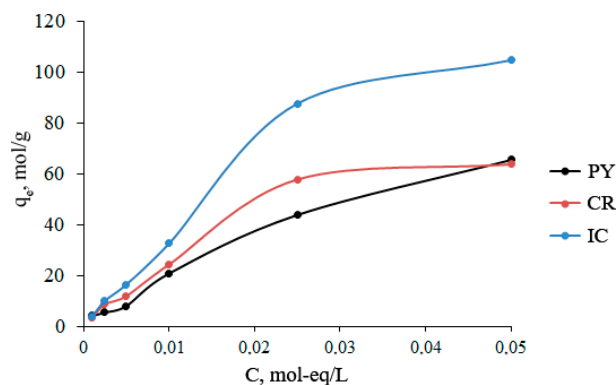
The goal of this work was to study the sorption properties of a polymer based on GA and CMC towards organic dyes of different nature.

## Results and discussion

Glycidyl acrylate was obtained by the reaction of acrylic acid with epichlorohydrin in the presence of tetramethylammonium chloride [11]. The target polymer was synthesized by the addition of GA to CMC in dimethyl sulfoxide in the presence of *N,N*-dimethylaminopyridine under a nitrogen atmosphere at 20–25 °C for 50 h. Upon completion, concentrated hydrochloric acid was added to the reaction mixture and the liquid phase was separated. The residue obtained was washed with water and dried under vacuum. The presence of the corresponding functional groups in the structure of the polymer based on GA and CMC was confirmed by IR and NMR spectroscopy.



Studies on the sorption of indigo carmine (IC), pyrazolone yellow (PY), and Congo red (CR) dyes by the polymer based on glycidyl acrylate and carboxymethyl cellulose were carried out by interacting the polymer ( $0.15 \pm 0.05$  g) with a dye solution (50 mL) in the concentration range of 0.001–0.050 mol/L at 25 °C for 4 h (Fig. 1).



**Figure 1.** Dependence of the sorption capacity on the concentration of the dye solution.

The dye concentration in aqueous solutions was determined using a KFK-3-ZOMZ spectrophotometer. All measurements were performed at a wavelength corresponding to the absorption maxima of the dyes ( $\lambda_{\max}$ ), which were 610, 590 and 350 nm for IC, CR, and PY, respectively.

The sorption of dyes by the resulting polymer was calculated using the following formula

$$q_e = \frac{(C_e - C_0) * V}{m} \quad (1)$$

where  $C_e$  and  $C_0$  are the equilibrium and initial concentrations of the dye in an aqueous solution, respectively, mol/L;  $q_e$  is the equilibrium sorption, mol/g;  $V$  is the solution volume, L; and  $m$  is the mass of the dry polymer sample, g.

The desorption of the dyes by the resulting polymer was carried out in 0.01 N aq. HCl and calculated using formula 2.

$$D = \frac{A_i - A_0}{A_i} * 100\% \quad (2)$$

where  $A_i$  is the absorbance of the solution after desorption,  $A_0$  is the absorbance of a blank sample, and  $D$  is the desorption, %.

The sorption results were processed using the Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich models [12], considering only the sorbate–sorbent interaction, while the competing sorption of water molecules was not taken into account [13, 14]. The calculated sorption parameters are presented in Table 1.

Based on the results of the sorption capacity studies (Fig. 1), it was established that the polymers obtained based on GA and CMC have a higher sorption capacity towards indigo carmine than to the azo dyes (Table 1). This is caused by the low numerical value of the dye molar mass (MM) ( $MM_{IC} = 466$  g/mol,  $MM_{PY} = 534$  g/mol,  $MM_{CR} = 697$  g/mol). The desorption efficiency for IC, PY, and CR was 85.03%, 83.06%, and 88.66% respectively.

Based on the experimental data, it can be concluded that the process of sorption of the dyes by the polymer based on GA and CMC can be reliably described by the Freundlich model, which indicates the presence of a heterogeneous surface that has unequal available adsorption centers with different adsorption energies. According to the Dubinin–Radushkevich model, the numerical values of the apparent sorption energy ( $E$ ) in all cases are  $< 8$  kJ/mol, which indicates the physical nature of sorption. The change in the Gibbs free energy of sorption ( $\Delta G$ ) (Table 2) was determined using equation 3.

$$\Delta G = -RT \ln K_f \quad (3)$$

where  $K_f$  is the Freundlich constant.

**Table 1.** Parameters of the isotherm equations of the dye sorption by the resulting polymer

Dye	Langmuir model			Freundlich model		
	$K_L$ , L/mg	$R_L$	$R^2$	$K_F$ , g/g	$1/n$	$R^2$
IC	1.24	0.44	0.826	0.48	0.90	0.989
PY	1.53	0.18	0.832	0.57	0.89	0.996
CR	1.49	0.25	0.817	0.60	0.88	0.992

Dye	Dubinin–Radushkevich model			Temkin model		
	$K$ , mol <sup>2</sup> /kJ	$E$ , kJ/mol	$R^2$	$B$ , J/mol	$K_T$ , L/g	$R^2$
IC	$4.11 \cdot 10^{-6}$	79.23	0.718	31.50	3.25	0.956
PY	$4.02 \cdot 10^{-6}$	123.55	0.882	55.39	1.41	0.943
CR	$5.10 \cdot 10^{-6}$	107.60	0.891	48.97	2.59	0.899

$R_L$  is the separation coefficient;  $K_L$  is the Langmuir constant, L/mg;  $K_F$  is the Freundlich constant, g/g;  $1/n$  is the adsorption index;  $B$  is the constant that characterizes the adsorption heat, J/mol;  $K_T$  is the constant of sorption equilibrium corresponding to the maximum binding energy, L/g;  $K$  is the constant associated with the energy of adsorption, mol<sup>2</sup>/kJ;  $E$  is the free energy of adsorption, J/mol;  $R^2$  is the approximation coefficient.

**Table 2.** Thermodynamic parameter  $\Delta G$  of sorption by the polymer based on GA and CMC

Adsorbed dyes	$K_f$	$\Delta G$ , J/mol
IC	0.48	–1168.7
PY	0.57	–1387.9
CR	0.60	–1460.9

The negative values of  $\Delta G$  indicate that the dye sorption is spontaneous.

## Conclusions

Hence, it was established that the polymer based on GA and CMC features the sorption capacity towards dyes of different nature. The process of the dye sorption is most reliably described by the Freundlich model.

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