

# Sorption of Malachite Green by Polymer Composite Sorbents from Aqueous Solution

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**Abstract** In this work, the sorption of malachite green (MG) from aqueous solutions by polymer composite gels (PCG) prepared on the basis of polyacrylic acid and bentonite clay (BG) was studied. It was found that the sorption capacity of PCG containing 50 weight % BG is almost three times greater than that of a gel not containing BG. Moreover, experiments have shown that the sorption capacity of PCG increases with increasing BG content in its composition. Adsorption isotherms were analyzed using the Langmuir and Freundlich models and, by comparing the standard deviations (R<sup>2</sup>), it was concluded that the sorption of MG compositions is better described by the Langmuir model.

**Keywords** Polyacrylic acid, Polymer hydrogel, Bentonite clay, Composite polymer gel, Malachite green, Sorption

## 1. Introduction

As is known, polymer hydrogels (PH), containing charged groups are capable of absorbing and retaining huge amounts of water [1,2]. Such PHs have found application in various fields of science, national economy, medicine, pharmacology, biotechnology, etc. [3-5]. At the same time, research is also being conducted to improve the characteristics of PHs, which will lead to an even wider use of such materials. One of the ways to purposefully improve the physicochemical characteristics of PHs is to obtain polymer composite gels (PCGs) based on them. For this purpose, various components are introduced into the PH composition. Most often, substances such as silicates, carbon-containing particles, metal nanoparticles, etc. are used as components for the production of PCG. [6-9]. This makes it possible to purposefully improve the mechanical and physicochemical properties of PH. Previously, M.Makhkamov and other authors [10,11] obtained PCG based on polyacrylic acid and bentonite clay, and studied the structure, morphology and swelling in aqueous solutions. In this work, the sorption of the organic dye malachite green (MG) by PCG samples obtained on the basis of polyacrylic acid and BG was studied.

## 2. Experimental

### 2.1. Materials

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Acrylic acid (OAO Reaktiv, Russia) was purified by bidistillation. The crosslinking agent N,N'-methylene-bis-acrylamide (BDH Chemical Ltd, England), grade "pure grade" was used. Chemically pure reagents (Sigma-Aldrich; USA) were used to prepare aqueous solutions of MG. Alkaline bentonite clay (BG; Uzbekistan) PVB grade. Purification of BG from impurities was carried out using the water elutriation method proposed by S. Korolkova et al. [12] and Z. Gong et al. [13].

### 2.2. Synthesis of PG and PCG

PG based on polyacrylic acid was synthesized according to the method given in the work of M.Makhkamov et al. [10]. PCG based on polyacrylic acid and BG was prepared according to the method given in the work of U.Mirzakulov et al. [11]. The resulting PH and PCG were purified by washing with distilled water for 20 hours in glass columns, after which they were dried at 318 K to constant weight.

### 2.3. Sorption

The sorption of MG from aqueous solutions by sorbent samples was studied by the spectrophotometric method on a UV 5100 spectrophotometer (Metash, China). To do this, samples of sorbents of the same mass were placed in aqueous solutions of the corresponding salts and at certain intervals the change in the optical density of the solution was measured at a wavelength of 620 nm. The concentration of MG in the solution was determined based on calibration curves depending on the concentration of the MG solution on its optical density. The sorption value ( $q_e$ , mmol/g) was calculated using the formula:

$$q_e = \frac{(C_i - C_e) \cdot V}{m};$$

where:  $C_i$  and  $C_e$  – MG concentrations in solution before and after sorption, mmol/l;  $V$  – volume of solution, l;  $m$  – mass of sorbent, g.

### 3. Results and Discussion

#### 3.1. Structure of PCG

As is known, the mineral montmorillonite, which forms

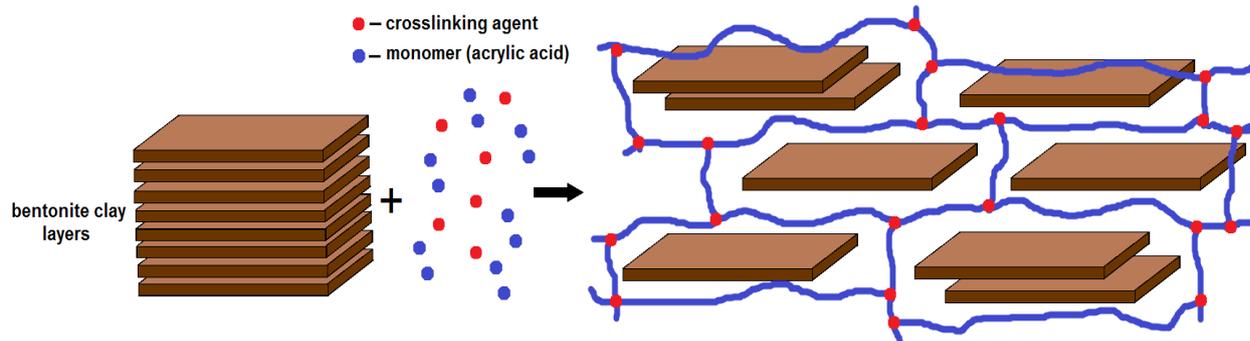


Figure 1. PCG education scheme

In this work, PCGs containing 20 and 50 weight % BG were obtained. The content of the crosslinking agent was 3% by weight of the monomer (acrylic acid).

#### 3.2. Sorption of MG by Sorbents from Solution

Fig.2 shows the absorption spectrum of an aqueous solution of MG in the wavelength range 300-750 nm. As can be seen from the spectrum, the absorption maximum of the aqueous solution of MG is at a wavelength of 620 nm.

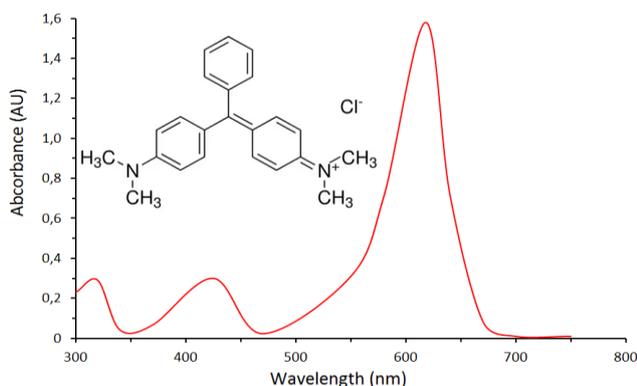


Figure 2. Absorption spectrum of an aqueous solution of MG

Therefore, to determine the change in the concentration of MS in the solution, a calibration graph of the dependence of the optical density of the solution on the concentration of MG at 620 nm was constructed. This dependence had the form of a straight line in the range of concentrations of MG in the solution from 1.0 to  $10.0 \cdot 10^{-5}$  mol/l, on the basis of which the change in the concentration of MG in the solution during the sorption process was determined.

When studying the sorption of MG, we used samples of PCG containing 20 and 50 weight % BG. To compare the

the basis of BG, has a layered structure that swells in polar solvents. Therefore, when preparing PCG, aqueous suspensions of BG were prepared and acrylic acid and a cross-linking agent (N,N-methylene-bis-acrylamide) were added to this suspension. Dissolved monomers also penetrate into the interlayer space of montmorillonite along with water molecules. When an initiator is added, the monomers polymerize to form a spatial network, the cells of which contain layers of montmorillonite (Fig.1).

sorption capacity, samples of BG and PH based on cross-linked polyacrylic acid were also chosen as sorbents. Since they are the main components of the obtained PCGs. Kinetic curves of sorption of MG from aqueous solutions by sorbent samples are shown in Fig.3.

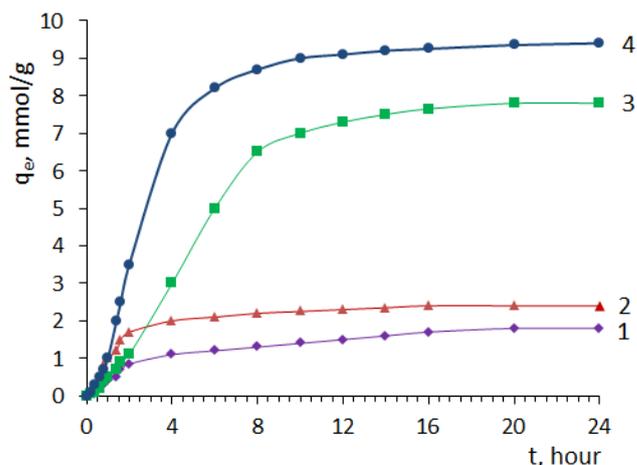
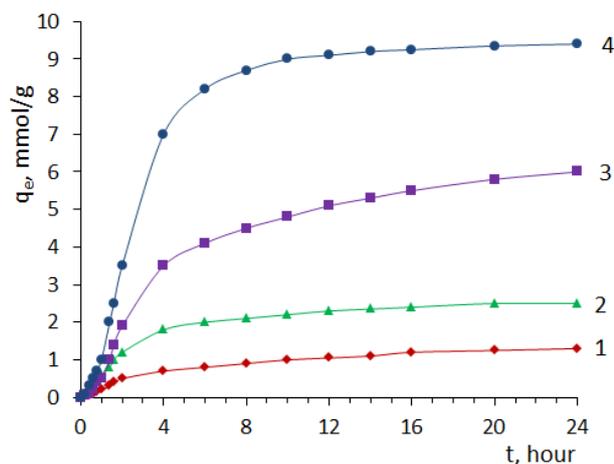


Figure 3. Kinetic curves of sorption of metallic metals from aqueous solutions by sorbents. 1-BG, 2-PG based on polyacrylic acid, 3-PCG containing 20 weight % BG, 4-PCG containing 50 weight % BG. The concentration of the dye in the solution is  $1 \cdot 10^{-4}$  mol/l.  $T=303$  K

As can be seen from Fig.3, the sorption properties of PCG are much higher compared to PH and BG. At the same time, the sorption capacity of PCG containing 50 weight % BG is much higher than the sum of the sorption capacities of PH and BG. It is also clear that the sorption capacity of PCG containing 50 weight % BG is higher compared to PCG containing 20 weight % BG.

The sorption capacity of PCG depends on the concentration of MG in the solution (Fig.4).



**Figure 4.** Kinetic curves of sorption of MG from solution by PCG samples containing 50 weight % BG. 1, 2, 3, 4-concentration of MS in solution is respectively equal to 1.25; 2.50; 5.00; 10.00·10<sup>-5</sup> mol/l. T=293K

As can be seen from Fig.4, the higher the concentration of MG in the solution, the more it is sorbed by PGA. In this case, during the sorption process, noticeable swelling of the PCG samples occurs (Fig.5). As can be seen from Fig. 5, PCG samples extracted from the dye solution after the sorption process have noticeably larger volumes compared to the initial state. This shows that when composites are immersed in a dye solution, both sorption of MG molecules and water occurs simultaneously.

From the isotherm curves of sorption of MG from solution by PCG samples, it follows that adsorption proceeds according to a monomolecular mechanism. Therefore, to describe the distribution of MG molecules between the adsorbent and the liquid, experimental adsorption isotherms were analyzed using the Langmuir [14,17] and Freundlich [15-17] models. As is known, the Langmuir model describes a homogeneous monomolecular adsorption process, i.e. uniform distribution of adsorbed molecules due to the forces of intermolecular interaction on the surface of a solid containing a finite number of active centers with equal

energy. The linear form of the Langmuir isotherm equation is described by the equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_L q_m}$$

where:  $q_e$  – adsorption value, mmol/g;  $q_m$  – maximum adsorption value mmol/g;  $K_L$  – Langmuir constant, l/mmol;  $C_e$  – equilibrium concentration, mmol/l.

Linear correlations of Langmuir isotherms are shown in Fig.6. The main parameters calculated using this model are given in table 1.

As is known, the Freundlich model is used to describe adsorption on a heterogeneous surface. Since adsorption centers according to this model have different energy values, the active sorption centers with maximum energy are filled first. The linear form of the Freundlich equation is:

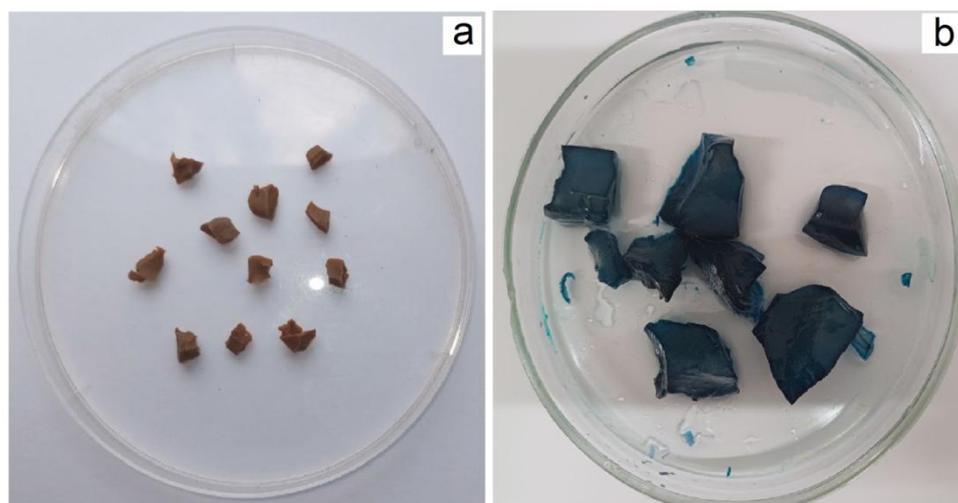
$$\log(q_e) = \log(K_F) + \frac{1}{n} \log(C_e)$$

where:  $K_F$  – the equilibrium constant of the Freundlich equation related to the adsorption capacity;  $1/n$  – a parameter indicating the intensity of the adsorbent-adsorbate interaction.

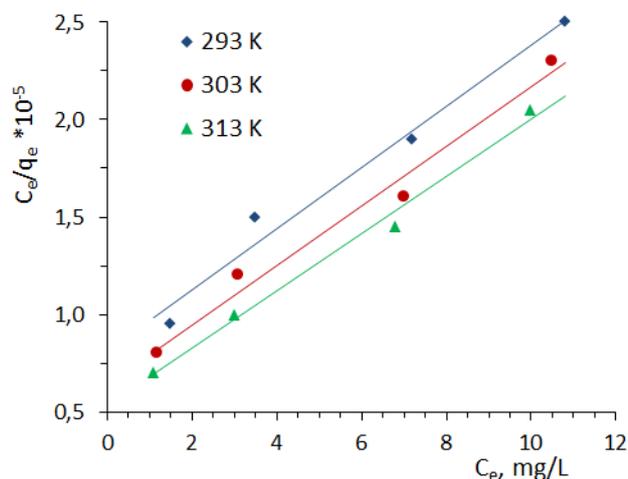
**Table 1.** Parameters of sorption of MG from PCG solution, calculated graphically based on linear Langmuir and Freundlich equations

T, K	Langmuir model			Freundlich model		
	$q_{max}$ , mmol/g	$K_L$	$R^2$	$1/n$	$K_F$	$R^2$
293	9,464	0,2112	0,9773	0,527	2,51	0,8674
303	10,153	0,1989	0,9710	0,516	2,62	0,9519
313	10,507	0,1976	0,9623	0,488	2,62	0,8902

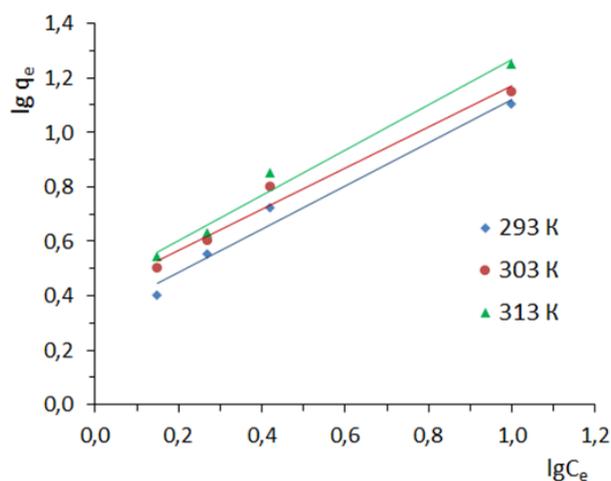
To describe the applicability of the model, the parameter  $1/n$  is used, which is an indicator of the nature of adsorption: at  $1/n=1$ , the distribution of adsorbed particles between two phases does not depend on concentration; at  $1/n=0$  adsorption is irreversible; at  $1/n<1$  adsorption is favorable, and at  $1/n>1$  adsorption is unfavorable. Linear correlations of Freundlich isotherms are shown in Fig.7. The main parameters calculated using this model are given in table 1.



**Figure 5.** Appearance of PCG (a) before and after sorption (b) MG from aqueous solution



**Figure 6.** Adsorption isotherms in coordinates of the linear form of the Langmuir equation. T=303K



**Figure 7.** Adsorption isotherms in coordinates of the linear form of the Freundlich equation. T=303K

From a comparison of the data given in the Table 1, it is clear that the Langmuir model is best suited to describe the sorption of MG by sorbent samples (the highest values of the correlation coefficient- $R^2$ ).

## 4. Conclusions

Thus, the work studied the sorption of MG and its aqueous solutions by various sorbents, for which we used BG, PG based on polyacrylic acid, and PCG obtained by introducing BG into the composition of PH based on polyacrylic acid. Experiments have shown that the sorption capacity of PCG is much higher compared to BG and PH. At the same time, it was also revealed that an increase in the BG content in the PCG composition from 20 to 50 weight % leads to an increase in the sorption of MG from the solution. Sorption isotherms of MG compositions were analyzed using the Langmuir and Freundlich models. It was found that the Langmuir model is more suitable for describing the sorption process.

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