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Rhodamine B Hazardous Dye Removal via Adsorption Using Hg(II) Coordination Polymer

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Abstract

Herein, we have reported the Hg(II) coordination polymer ,(**Hg-CP**), formulated $\{[Hg(L)](Cl_2)](CH_3CN)_2\}_n$, behaved as adsorbent against Rhodamine B dye stuff. UV-Vis absorption spectroscopy was used to conduct dye adsorption investigations on coordination polymers. Adsorption experiments were carried out in acidic (pH=3) and neutral (pH=6) media and the results showed that the compound removed the cationic Rhodamine B from water. In acidic media, the adsorption capacity of the **Hg-CP** was more than neutral media. Also, **Hg-CP** could selectively adsorb Rhodamine B dye from the Rhodamine B/Methyl orange dye mixture. The colour of the **Hg-CP** was white before adsorption, whereas it changed after adsorption as Rhodamine B adhered to the surface of **Hg-CP**.

Keywords: Coordination polymers, cyclotriphosphazene, benzimidazole, dye adsorption, Rhodamine B.

1. Introduction

In recent years, studies on coordination polymers have been very popular because they can be synthesized with metal salts in a short time. At the same time, the fact that coordination polymers have many application areas such as gas storage, magnetism, sensing, luminescence, catalysis, and dye adsorption increases their importance [1-6]. Especially studies on dye adsorption using coordination polymers have attracted attention day by day because organic dyestuffs cause considerable impurities when involved in water resources [7,8]. Rhodamine B (RhB) dye is one of the synthetic aromatic dyes, and it is extensively utilised as a colouring agent in the production of food and textile products (Figure 1). RhB poses hazardous environmental and health risks. It has been proven that if a source of water is contaminated with even small amounts of RhB, it can cause subcutaneous tissue-derived sarcomas, which are highly carcinogenic [9]. Therefore, it is very important to remove RhB from the wastewater.

Cyclotriphosphazenes are important inorganic heterocyclic compounds that are composed of phosphorus and nitrogen atoms. They easily undergo nucleophilic substitution reactions because they contain an active six P-Cl bond.

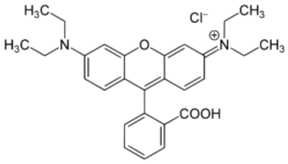
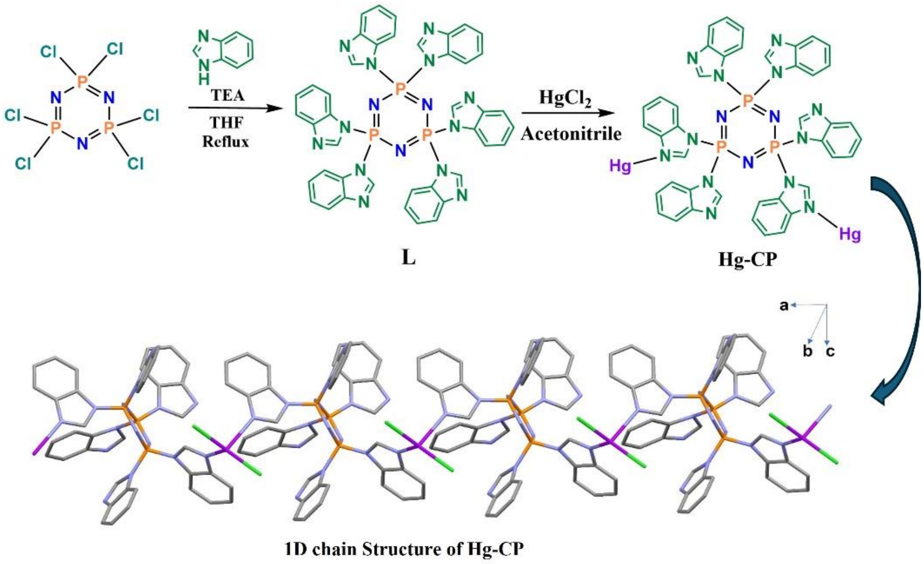


Figure. 1. Structure of RhB dye.

There has been a discernible surge in research on coordination polymers based on cyclotriphosphazene in the last several years. The cyclotriphosphazene derivatives, which have six arms bearing donor N atoms, act as multidentate ligands, which allow the formation of 2- and 3-dimensional coordination polymers [10,11-16]. Owing to the d10 configuration of the group 12 metal, which provides flexible coordination geometries, coordination polymer studies with these metals have attracted important attention [17]. The formation of Hg(II) complexes is rare compared to other group 12 metal complexes. Dye adsorption studies with cyclophosphazene polymers and composites are available in the literature [14.15,18-22]. However, when the literature is examined, the number of studies on the dye adsorption of cyclotriphosphazene-based coordination polymers is quite limited [14,15]. A study was conducted wherein a completely 2-methylimidazole-substituted cyclotriphosphazene ligand was used to create 2D and 3D Ag (I) coordination polymers.

Adsorption experiments showed that $\{[Ag_3(MeIm\text{-}Cp)_2](NO_3)_3\}_n$, which is a 3D coordination polymer, removed the anionic methyl orange (MO) and tartrazine (E102) from water but showed no adsorption behaviour against the cationic methylene blue (MB) [14]. In our previous study, cyclotriphosphazene ligand that was fully substituted with benzimidazole (**L**) was synthesised as a starting material and prepared into two coordination polymer, namely $\{[Ag(L)](CH_3PhSO_3)](CH_3CN)_4\}_n$ and $\{[Hg(L)](Cl_2)](CH_3CN)_2\}_n$. While both coordination polymers did not show adsorption against anionic MO and E102, they showed adsorption against cationic MB dye [15]. Some adsorption experiment results from the literature are given in part of results and discussion.

In this work, we synthesised **Hg-CP**, $\{[Hg(L)](Cl_2)](CH_3CN)_2\}_n$, according to literature [15] (Scheme 1) and investigated the adsorption ability against cationic RhB dye. Furthermore, we examined whether the compound selectively adsorbs RhB from the RhB/MO (cationic/anionic dye mixture). The results clearly demonstrated that **Hg-CP** easily adsorbed RhB from the aqueous solution and dye mixture, especially in acidic media.



Scheme 1. Synthetic pathways and structure of Hg-CP.

2. Materials and Methods

Hexachlorocyclotriphosphazene and benzimidazole (99%) was obtained from Aldrich. $HgCl_2$ was purchased from Merck. Acetonitrile (≥99.0%) was bought from Merck. Adsorption studies were performed by Shimadzu 1900i UV-Vis. spectrometer. Zeta potential analyser (Malvern-Zetasizer nano ZS) was used to analyse the surface charges of samples. PXRD analyses were performed at room temperature up to resolution of $2\theta = 2.0\text{–}50°$ on a Rigaku X–ray diffractometer D-Max Rint 2200 Series instrument using Cu K_α radiation at 40 kV and 40mA.

2.1. Dye adsorption studies

Synthetic dye manufacturing is rising steadily alongside the everyday increase in its application in industry. An enormous ecological risk arises when wastewater and these dangerous pigments are mixed. For this reason, there is an increasing amount of research focused on the removal of dyes from wastewater through the adsorption method.

The adsorption behaviour of **Hg-CP** against RhB was investigated in batch experiments. First, the UV absorbency of the standard RhB and MO solutions at various known concentrations was tested to create a working curve, and then calibration graphics were achieved with a correlation coefficient (R) higher than 0.999. RhB solutions at a concentration 10 mg/L in distilled water were prepared as a standard stock solution. 10 mg of the **Hg-CP** were immersed in a 25 mL aqueous dye solution. For acidic conditions, a 0.6 M HCl solution was added to aqueous dye solutions until the pH value was 3.

Afterwards, to prepare the RhB+MO dye mixture, 25 ml of RhB dye solution, and 25 ml of MO dye solution were taken from stock solutions and mixed together. Subsequently, 20 mg of coordination polymer was added to this mixture. For pH 3 media, a 0.6 M HCl solution was added to the dye mixture. Dye solutions containing **Hg-CP** were monitored at different time intervals using UV-visible spectroscopy and measured in the 300-800 nm wavelength range.

The adsorption capacity (q_e) and the percentage of removal efficiency (R%) of **Hg-CP** were calculated using the following equations:

$$q_e = \left(\frac{C_0 - Ce}{m}\right) \times V \qquad (1)$$

$$R\% = \left(\frac{C_0 - Ce}{C_0}\right) \times 100 \qquad (2)$$

C_0 is the first concentration of dye (mg/L) and C_e is the amount of dye still present in the solution following adsorption (mg/L). V is the volume of solution (L), m is the mass of adsorbent used (g).

3. Results and Discussion

The acquired spectra from UV-visible spectroscopy were compared to the absorption bands of the pure dye solutions at 464 nm (MO) and 554 nm (RhB) wavelengths [23]. The natural pH of RhB aqua solution containing **Hg-CP** is 6. The UV graphic obtained from the adsorption study performed on this media can be seen in Figure 2a. **Hg-CP** exhibited dye removal behaviour towards RhB from water in neutral media (pH=6). In the adsorption study, after adjusting the pH to 3, it was observed that the colour of the dye solution became entirely clear, indicating an increased amount of RhB adsorbed (Figure 2b). The measurements clearly indicate that **Hg-CP** adsorbed the RhB from water with saturated adsorption amounts of 4.89 mg/g (pH 6) and 18.14 mg/g (pH 3) through complicated adsorption processes (Figures 2c and 2d).

We studied the kinetics of RhB adsorption of **Hg-CP**. Due to showing good linearity and a coefficient R^2 value closer to 1, the pseudo second order and pseudo- first-order kinetics model is more suitable for pH 6 and pH 3 media, respectively (Table1). This result revealed that chemical interactions were slightly more dominant in the pH=6 medium, but when pH was lowered to 3, physical interactions became more dominant because of the significant change in surface charges.

The pseudo-first order rate equation:

$$\mathrm{loq}(q_e - q_t) = \mathrm{loq}(q_e) - \frac{k_1}{2{,}303}t \qquad (3)$$

The pseudo-second order rate equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (4)$$

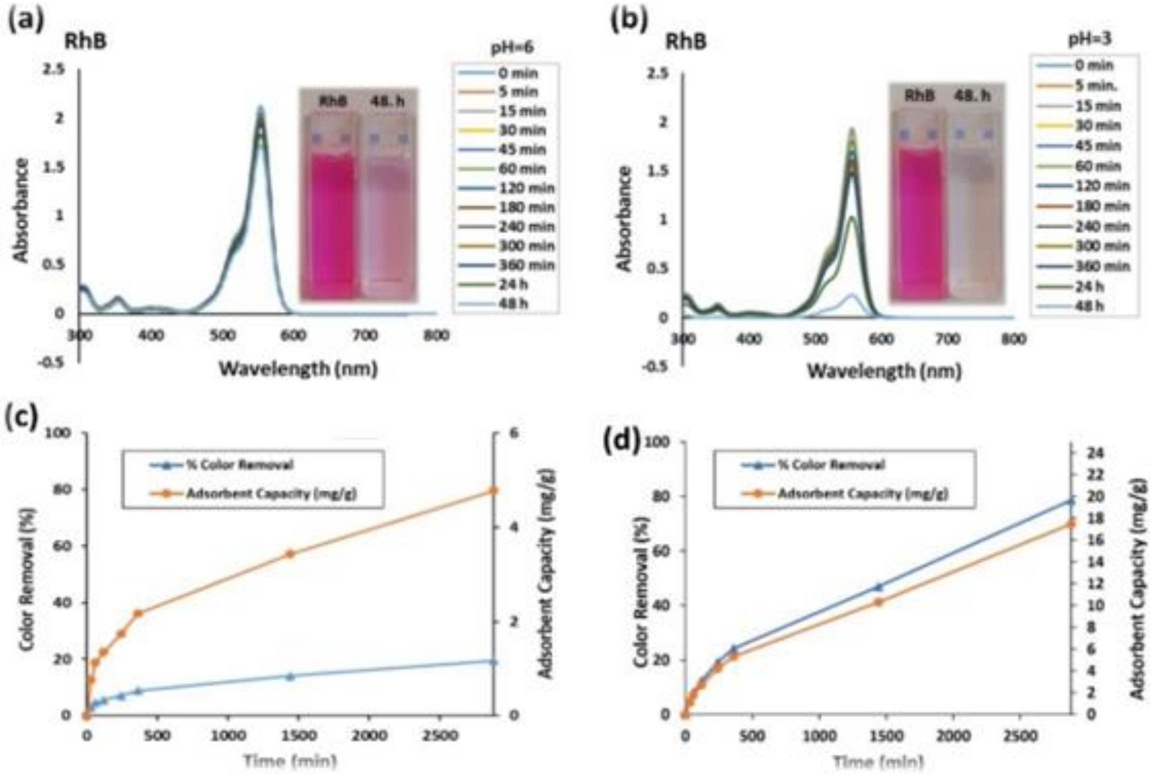


Figure 2. Time-dependent UV-Vis spectra of the aqueous solution of RhB treated by at pH=6 (a), pH=3 (b) and time-dependence of adsorption profiles of RhB over at pH 6 (c) and pH=3 (d).

Table 1. Kinetic parameters of RhB adsorption of **Hg-CP** at pH 6 and pH 3.

	Pseudo-first order model			**Pseudo-second order model**		
pH	k_1	q_e	R^2	k_2	q_e	R^2
6	0.0006909000	3.937313537	0.93	0.00072465	4.894762604	0.956
3	0.0004606000	18.14261982	0.94	0.000061871	21.36752137	0.841

Here, q_e is the quantity of material adsorbed per unit of adsorbent at equilibrium (mg/g), qt is the amount of substance adsorbed per unit adsorbent at any given moment (mg/g), t is the adsorption time (min), k_1 is the rate constant of the pseudo first order model (min^{-1}), k_2 is the rate constant of the pseudo second order model (g mg^{-1} min^{-1}).The surface charge measurement for **Hg-CP** was carried out in deionized water, and the surface charge was found to be negative (approximately -9.25 mV) at pH=6 (Figure 3a). Because of the negative surface charge's tendency to reject anionic dyes and adsorb cationic dyes through electrostatic interaction, the surface charge was crucial for adsorption and separation processes.

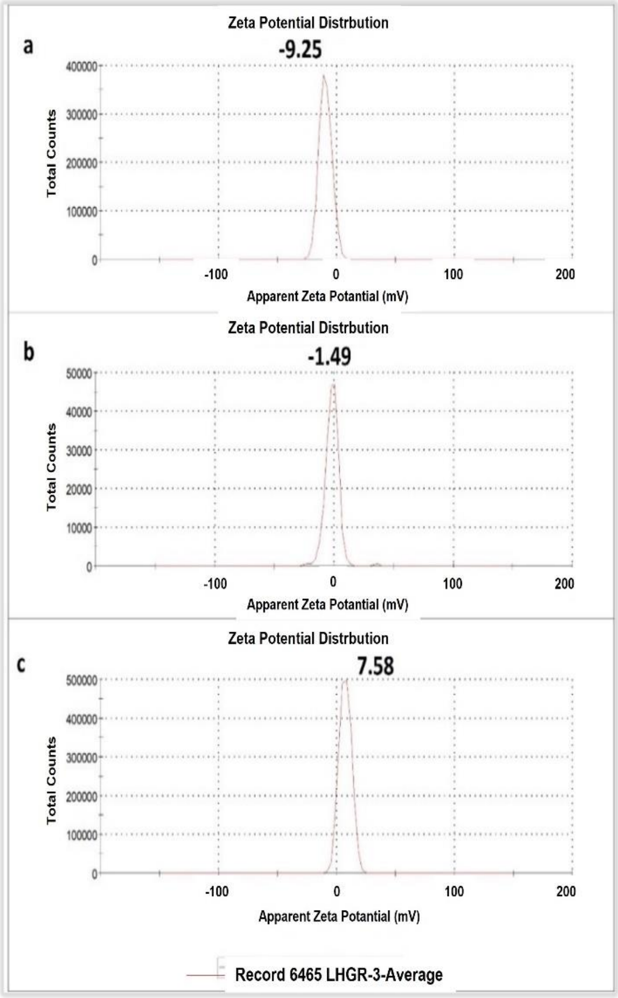


Figure 3. Zeta potential analysis of a) **Hg-CP** in aqua b) **Hg-CP** after adsorption at pH=6 and c) **Hg-CP** after adsorption at pH=3.

The surface value of **Hg-CP** after RhB adsorption in pH = 6 media is -1.49 mV (Figure 3b). As RhB, a cationic dye, was adsorbed on the surface, the surface charge was affected positively. In the adsorption experiment conducted in a medium with pH = 3, the surface charge was observed to shift to a positive value (7.58 mV) (Figure 3c) which indicates that the amount of cationic RhB adsorbed on the surface increases. This can be seen from the UV graphics in Figure 2b and the color change in the bathtub pictures.

In the study, it was also investigated whether **Hg-CP** selectively adsorbs RhB dye from the RhB/MO (1:1) mixture or not. For this purpose, firstly, the adsorption of the compound against MO dyestuff was examined. We have shown in our previous study that this compound does not adsorb MO dye in a neutral environment. Therefore, we only examined the situation in an acidic environment and checked its adsorption in pH 3 media. It can be seen that **Hg-CP** did not exhibit any adsorption behaviour against MO in acidic media (Figure 4). Namely, in the adsorption experiment for MO, it was determined that **Hg-CP** did not adsorb the dye in either pH = 6 or pH = 3 media.

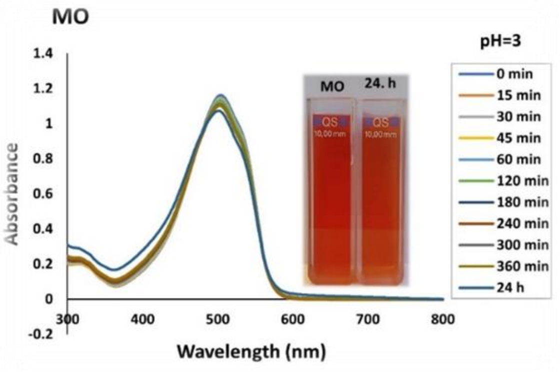


Figure 4. UV-Vis absorption spectra of the aqueous solution of MO treated by Hg-CP with time dependence at pH=3.

When the UV-Vis graph in Figure 5a is examined, it is seen that **Hg-CP** selectively adsorbs RhB from the RhB/MO mixture. **Hg-CP** adsorbed the RhB from water with a saturated adsorption amount of 15.45 mg/g at pH 3 (Figure 5b).

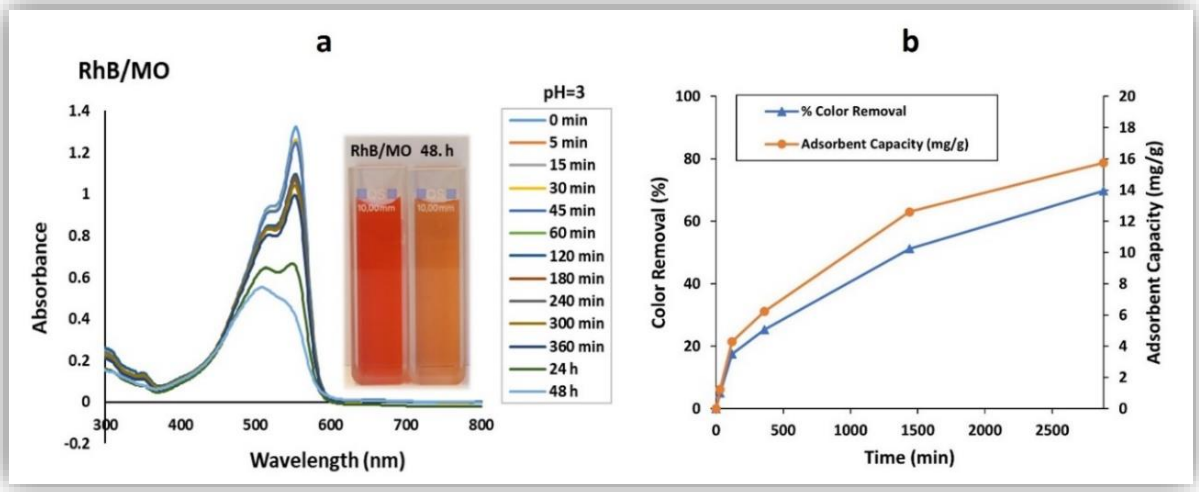


Figure 5. a) Time-dependent UV-Vis absorption spectra of the aqueous solution of RhB/MO treated by **Hg-CP** at pH=3. b) Time-dependence of adsorption profiles of RhB/MO over **Hg-CP** at pH 3.

Table 2. Kinetic parameters of RhB/MO adsorption of **Hg-CP** at pH 3.

Pseudo-first order model			Pseudo-second order model		
k_1	q_e	R^2	k_2	q_e	R^2
0.0009212000	15.4525444	0.9643	0.000115705	18.72659176	0.9312

According to kinetic studies on the adsorption of dye mixtures, the adsorption model is compatible with the pseudo-first-order model (Table 2).

The images of the before and after adsorption are given in Figure 6. As an indicator of adsorption, **Hg-CP** that was white before the adsorption process turned the colour of RhB after adsorption. When examined carefully, it can be seen with the naked eye that, after adsorption, the colour appearing at pH = 3 is darker than pH = 6.

The stability of the adsorbent is important for adsorption studies. The diffractogram of **Hg-CP** gained by the PXRD technique before dye adsorption studies was compared with the diffractograms obtained after RhB adsorption in pH 3 media. It is seen that the peaks are largely matched, and it was observed that the structure of **Hg-CP** remained intact after adsorption in an acidic environment. Likewise, there was also no change in the PXRD pattern after the adsorption of RhB dye from the RhB/MO mixture. As a result, the coordination polymer maintained its first structure before adsorption, and its structure did not change (Figure 7).

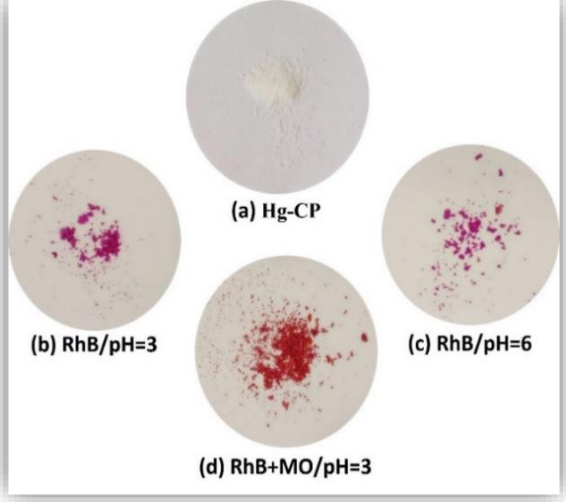


Figure 6. For **Hg-CP** (a) before adsorption,(b) after RhB adsorption at pH=3, (c) after RhB adsorption at pH=6, (d) after RhB+MO adsorption at pH=6.

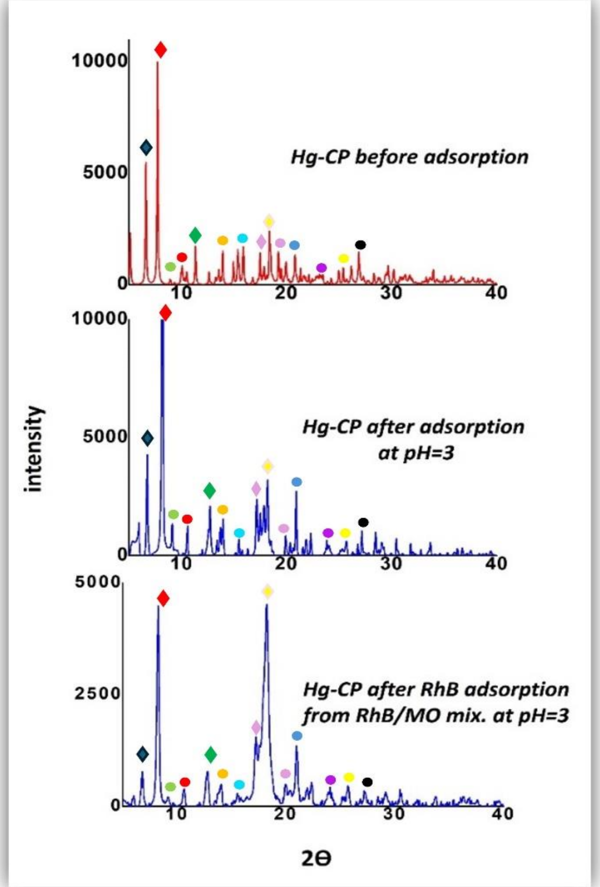


Figure 7. Matched-PXRD diffractogram of **Hg-CP** before and after adsorption.

The surface morphologies of the adsorbent before and after adsorption were also investigated and shown in Fig. 8. When comparing the SEM images of **Hg-CP** before and after adsorption (Figs. 8a and 8b), it is seen that the morphology of the surface of the complexes changed. The analyses support dye stuff adsorbed on the surfaces of the **Hg-CP**.

When the literature is reviewed, studies on dye adsorption are generally carried out with cyclotriphosphazenes or polyphosphazene composites. Most of these studies are about MB dye adsorption. There are a few studies on cyclophosphazene-based coordination polymers. A comparison of the MB dye adsorption capacities of some cyclophosphazen derivatives in the literature is given in Table 3. Considering the results of the studies, it can be seen that the dye adsorption capacities of the materials prepared as composites are better. In addition, the dye adsorption capacities of the coordination polymers synthesised by our group, which are lined 5th and 6th in table 3, are also promising.

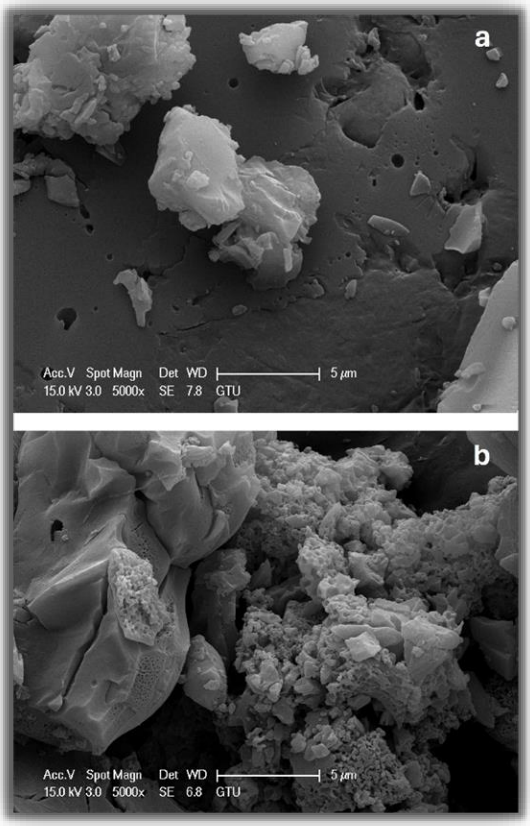
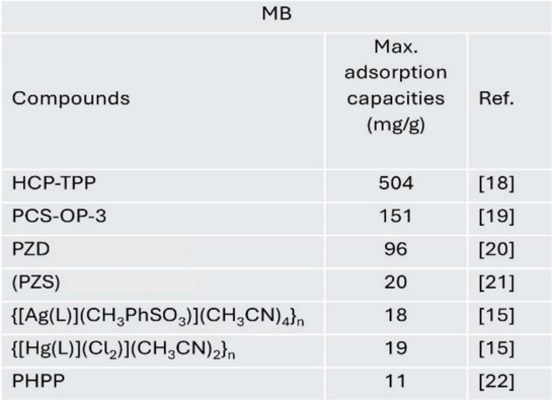


Figure 8. SEM image of Hg-CP before (a) and after (b) adsorption.

Table 3. MB dye adsorption capacities of some cyclophosphazen derivatives.



MB		
Compounds	Max. adsorption capacities (mg/g)	Ref.
HCP-TPP	504	[18]
PCS-OP-3	151	[19]
PZD	96	[20]
(PZS)	20	[21]
$\{[Ag(L)](CH_3PhSO_3)](CH_3CN)_4\}_n$	18	[15]
$\{[Hg(L)](Cl_2)](CH_3CN)_2\}_n$	19	[15]
PHPP	11	[22]

Among these compounds, the adsorption capacity of the $\{[Hg(L)](Cl_2)](CH_3CN)_2\}_n$ (**Hg-CP**) against cationic RhB dye was found to be 18.14 mg/g in pH 3 media and 4.89 mg/g in pH 6 media in this study. The same compound showed 19.2 mg/g dye adsorption capacity against the cationic MB dye in a pH 6 environment in our previous work. From the results, it can be said that the compound has a higher ability to adsorb against MB dye than RhB.

4. Conclusion

In this study, it was investigated whether **Hg-CP**, which we synthesised in our previous study, could adsorb or not RhB dye. Adsorption studies were performed in two different pH environments: pH = 6, which is the natural pH of **Hg-CP** in water, and pH = 3, which is a more acidic medium. The results show that the dye adsorption capacity of **Hg-CP** increases from 4.89 mg/g to 18.14 mg/g when the pH value decreases from 6 to 3. 81% of the RhB is removed from the solution of **Hg-CP** in pH 3 media. Also, it was found that **Hg-CP** could selectively adsorb RhB dye with an adsorption capacity of 15.45 mg/g from the RhB/MO dye mixture. This experiment was carried out under these conditions because the adsorption result for RhB was higher in the pH = 3 medium. The surface charge values of **Hg-Cp** (before adsorption and after adsorption) obtained from zeta potential measurements support the adsorption experiment results. According to the PXRD results, Hg-CP used as an adsorbent saved its structure after the adsorption. As a result, the pH change increased the adsorption of the cationic RhB dye, and the surface charges played an important role on the adsorption phenomena.

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Author's Contributions

Afranur Pendar: Synthesing and UV Vis Experiments

Derya Davarcı: Supervised the progress of the experiment, the interpretation of the results, drafted the manuscript.

Ethics

There is no ethical problem regarding the publication of this manuscript.

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