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# C–3,4–Dimethoxyphenylcalix[4]resorcinarene Triphenylphosphonium Chloride Adsorbent for Hexavalent Chromium Removal

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**Abstract :** Synthesis of positively–charged C–3,4–dimethoxyphenylcalix[4]resorcinarene triphenylphosphonium chloride (CMPCRP) has been conducted. The synthesis was carried out from vaniline via methylation, aromatic electrophilic substitution–cyclization, chloromethylation, and bimolecular nucleophylic substitution reaction. Structural elucidation of products was performed using FT–IR and NMR spectrometer. CMPCRP is an orange solid with a 97.14% yield and melting point of 296°C. The removal of hexavalent chromium (Cr(VI)) from aqueous solution was investigated in this study. Adsorption studies were carried out using the batch methods at different acidity, contact time, and initial Cr(VI) concentration. The initial and final Cr(VI) concentration were determined using AAS spectrometer. The result showed that the optimum condition of Cr(VI) adsorption was at pH 4, contact time 30 min, and concentration of 25 mg/L. The maximum adsorption capacity for the adsorption process is 15.71 mg/g. The rate of adsorption was found to follow the pseudo–second–order kinetic model. Cr(VI) adsorption equilibrium fitted the Langmuir isotherm model most and the mechanism is a chemisorption (Gibb's energy = 36.24 kJ/mol) that occurs in the monolayer.

**Key Words:** Adsorption, C–3,4–dimethoxyphenylcalix[4]resorcinarene triphenylphosphonium chloride, Cr(VI), Chemisorption.

## Introduction

Chromium exists in the environment in two main oxidation states Cr(III) and C (VI). Cr(III) is an essential element for humans and is much less toxic than Cr(VI), it is required to otentiate insulin and for normal glucose metabolism. Cr(III) is poorly adsorbed by any route so the toxicity of chromium is attributed to the Cr(VI) form[1]. Hexavalent chromium Cr(VI) is of particular environmental concern due to its toxicity, mobility, and challenging removal from industrial wastewater[1]. In general, Cr(VI) compounds are generally more soluble and bioavailable than Cr(III) compounds[2]. It is a strong oxidizing agent and diffuses quickly through soil and aquatic environments[3]. Cr(VI) can be absorbed by the lung and gastrointestinal tract, and even to a certain extent by intact skin. If Cr(VI) is reduced to Cr (III) extracellularly, the toxicity is not observed. Cr (VI) can be reduced intracellularly by hydrogen peroxide, glutathione reductase and ascorbic acid to produce reactive intermediates. Any of these species could attack DNA, proteins and membrane lipids thereby disrupting cellular integrity and functions. Exposure to chromium (VI) can cause respiratory, renal, hepatic, gastrointestinal, cardiovascular and hematological problems. Also Cr (VI) is considered to be carcinogenic. Hexavalent Chromium is 500 times more toxic than the trivalent Chromium[4]. Cr (VI) is introduced into natural waters by a variety of industrial processes including textile, dyes and pigment production, film and photography, galvanometry, leather tanning, electroplating and metal finishing industries[1,] .

A number of treatment methods for the removal of chromium from aqueous solutions have been reported. These include coagulation/precipitation[5], membrane filtration[6], ion exchange[7], and adsorption [1,8–13] . Among these methods, adsorption is a widely used, promising technique, and feasible alternatives to remove the hexavalent chromium from the industrial effluents because of its high efficiency and advantages in simple operation and cost–effective[14]. Cr(VI) removal from wastewater has been highlighted recently by the use of various sorbent material such as activated carbon[9,10], chitosan[11], C–4–ethoxy–3–methoxyphenylcalix[4] resorcinarene triphenylphosphonium chloride[12], spongeous[15], magnetite[16], aminated wheat straw[17], and plant material[18]. In recent developments, calixarene is able to be used as an absorbent[12,13]. However, little information is available in the literature on the removal of Cr(VI) using calix[4]resorcinarene compounds.

The overall objective of this study was to determine chromium Cr(VI) adsorption behaviour onto C–3,4–dimethoxyphenylcalix[4]resorcinarene triphenylphosphonium chloride (CMPCRP).

## Material and Methods

### Apparatus

Apparatus used in this experiment were laboratory glassware, pH meter, magnetic stirrer, and UV–Visible spectrophotometer, FT–IR and NMR spectrometer.

### Reagents and solutions

All chemical used in this experiment were of analytical grade and purchased from Merck (Germany). Vaniline, DMF, HCl, ethanol, dichloromethane, asetone, $ZnCl_2$, Cr(VI), triphenylphosphine (Aldrich), paraformaldehyde, hexane, NaOH, TLC plates, Whatman filter paper 42, aquabidest.

### Adsorbent preparation

Synthesis of positively–charged C–3,4–dimethoxyphenylcalix[4]resorcinarene triphenylphosphonium chloride (CMPCRP) has been conducted. The synthesis was carried out from (1) vaniline via methylation produce 3,4-dimethoxybenzaldehyde, (2) aromatic electrophilic substitution with resorcinol and acid catalyst-cyclization produce C–3,4–dimethoxyphenycalix[4]resorcinarene, (3) chloromethylation with paraformaldehyde, HCl, and $ZnCl_2$ catalysts produce chloromethyl–C–3,4–dimethoxyphenylcalix[4] resorcinarene and (4) bimolecular nucleophylic substitution reaction produce CMPCRP. Synthesis of CMPCRP carried out from chloromethyl–C–3,4–dimethoxyphenylcalix[4] resorcinarene (1.5 mmol) while stirred for 30 minutes in a 100 mL flask and then added triphenylphosphine (7.5 mmol) and refluxed for 48 hours[12]. The precipitate formed was filtered and washed several times with water, hexane, and dichloromethane and dried.

### Characterization of the adsorbent

The structural characteristics of the adsorbent, inculding Fourier Transform Infrared (FTIR) spectroscopes of the carbon before adsorption were recorded in the range 4000–400 $cm^{-1}$, using FT–IR spectrometer (IR Shimadzu 8201 PC). Chemical shift of proton and carbon were determined by $^1H$ and $^{13}C$ NMR spectrometer ($^1H$ NMR, JEOL–MY60 and $^{13}C$ NMR, JEOL–MY500).

### Adsorption studies

Adsorption study of Cr(VI) on CMPCRP was carried out at different acidity, contact time, and initial Cr(VI) concentration. The acidity effect was studied within the range of 1.0–6.0 with the initial Cr(VI) concentration of 10 mg/L and the contact time of 180 min at 298 K. Effect of contact time was carried out at 0.5; 1; 1.5; 2; 2.5; 3; 5; 10; 30; 60; 120; and 180 minute with the initial Cr(VI) concentration of 10 mg/L and the optimum pH at 298K. The initial and final Cr(VI) concentration were determined using AAS spectrometer. Adsorption isotherms were conducted within initial Cr(VI) concentration of 5, 10, 15, 20, 25, 30, and 35 mg/L at 298K in optimum pH and contact time. All experiments using 10 mL Cr(VI) solution and the adsorbent dose of 0.01 g[12,13].

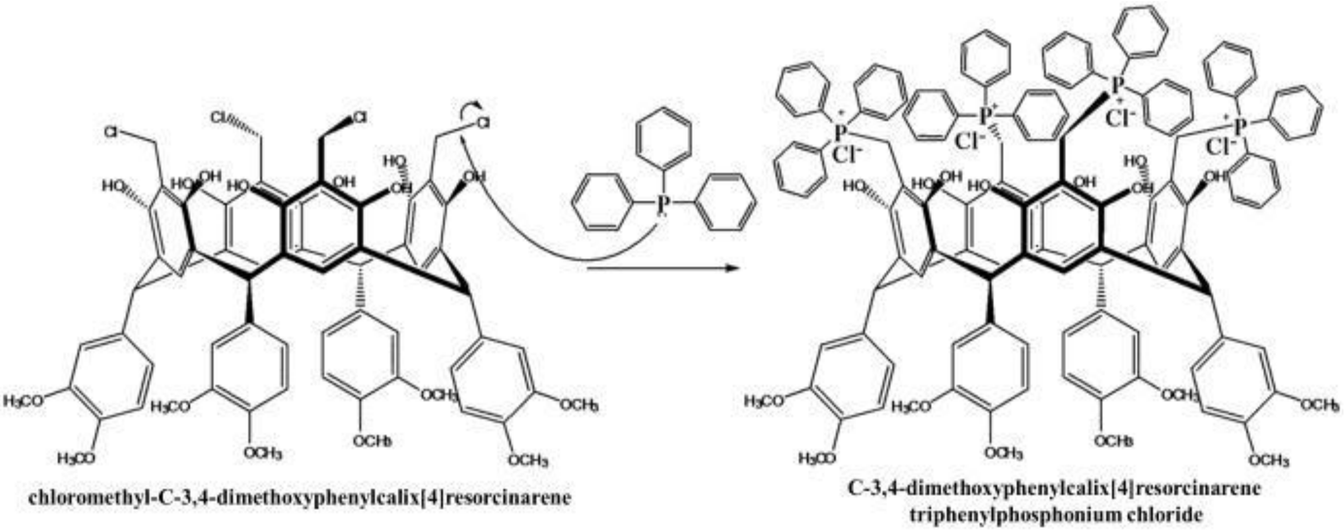


**Figure 1. Synthesis of CMPCRP**

## Result and Discussion

### Characterisation

In this research, nucleophile of triphenylphosphine was employed to produce positively–charge calix[4]resorcinarene. The reaction was carried out by refluxing both chloromethylated C–3,4–dimethoxy–phenylcalix[4]resorcinarene and triphenylphosphine in ethanol for 48 hour. The product as obtained as an orange solid with m.p 296 ºC in 97.14% yield. Structural elucidation of the product was performed with IR spectrometer, $^1$H and $^{13}$C NMR spectrometer.

Based on IR spectrum displayed in Fig.2, it could be seen that the hydroxyl groups on the CMPCRP gave broad adsorption band at 3425 cm$^{-1}$. Then, absorption at 1604 cm$^{-1}$ was indicated to come from the aromatic double bond. The medium bands at 1435 cm$^{-1}$ were characteristic band for P–$C_6H_5$ group. The peak around 1604 and 1512 cm$^{-1}$ is due to the C=C aromatic and the peak around 1134–1265 cm$^{-1}$ indicated the methoxy group (–OCH3) . The peaks in the range of δ 6.12–7.23 ppm in $^1$H NMR spectrum indicated the presence of Ar3P group. The methine bridge (Ar3CH) indicated at 5.41–5.64 ppm (Table 1 ). While, the $^{13}$C NMR spectrum indicates Ar3P group at 128.76–129.03 ppm and the methine bridge around 40.50 ppm ( Fig.3) [12,19].

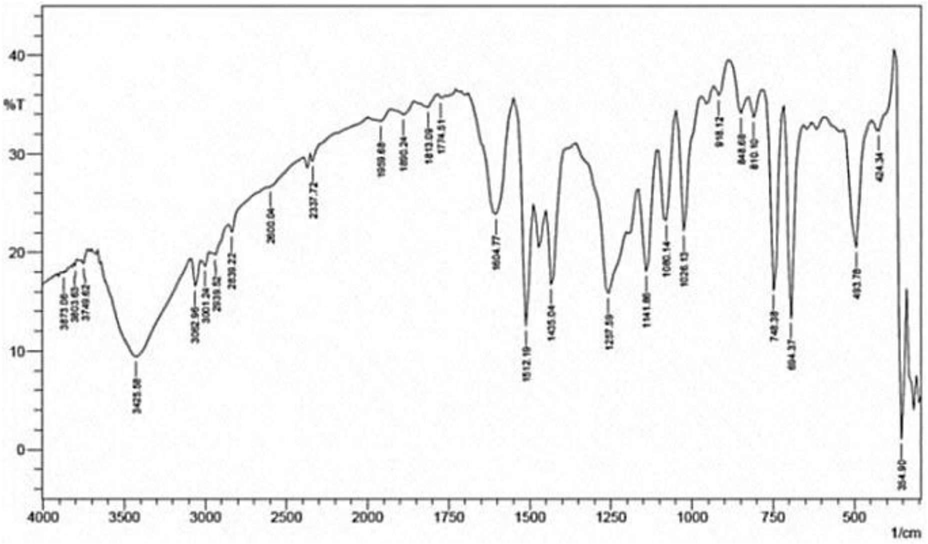
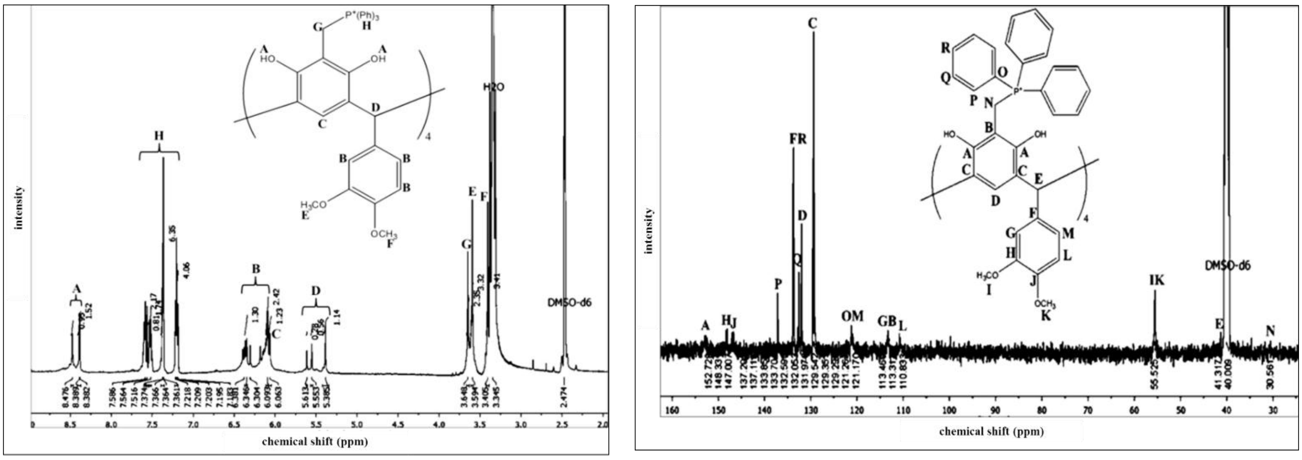


Figure 2. FT–IR spectra of CMPCRP



A B

Figure 3. $^{1}$H NMR (A) and $^{13}$C NMR (B) spectra of CMPCRP

Table 1 $^{1}$H NMR spectrum of CMPCRP

| Group | Chemical shift (ppm) | Proton |
|---|---|---|
| A | 8.38; 8.48 | hydroxyl |
| B, C | 6.06–6.38 | aryl methine |
| D | 5.39–5.61 | methine bridge |
| E, F | 3.34–3.59 | methoxy |
| G | 3.64 | methylene |
| H | 7.18–7.59 | aryl(–P(Ph)$_3$) |

Adsorption studies were carried out using the batch methods at different acidity, contact time, and initial Cr(VI) concentration. The effect of initial pH on the Cr(VI) removal was studied at initial pH value 1–6. Figure 5a shows the concentration removal of the Cr(VI) was high at pH 4 but decreased at pH

5–6. The highest concentration of Cr(VI) removal was 93.39 µmmol/g. The level of acidity (pH) in the adsorption of Cr(VI) obviously affects the ionization of molecules Cr(VI) and determines the Cr(VI) ionic charge. In this adsorption, occurred interaction between the $Cr_2O_7^{2-}$ (negatively–charge) of Cr(VI) with adsorbent CMPCRP surface (–$P^+Ar_3$, positively–charged). Therefore, the acidity degree in the Cr(VI) adsorption process would determine of ion charged. In acid conditions, Cr(VI) will negatively–charge.

Adsorption of Cr(VI) by CMPCRP in the range of contact time (Fig. 4 b) shows that at the first stage of 30 minutes, the adsorption of Cr(VI) was fast due to the availability of a large number of surface sites. However, the adsorption gradually became slower until it reached the equilibrium where no more Cr(VI) can be adsorbed from the solution. At this point, the remaining surface of sites was difficult to be filled. While, Fig. 4c shows that the adsorption uptakes of Cr(VI) increase with increase in Cr(VI) concentration. This phenomenon was due to increase in the driving force of concentration gradient as an increase in the initial dye concentration. The Cr(VI) adsorption at equilibrium increased from 24.96 to 73.49 µmol/g as the initial Cr(VI) concentration increased from 5 to 25 mg/L.

Kinetics adsorption data of Cr(VI) on CMPCRP was analyzed using two kinetic models: pseudo–first–order and pseudo–second–order. The pseudo–first–order kinetic model is shown by the following equation:

$$\log(q_e - q_t) = \log\, q_e - kt$$

where $q_e$ and $q_t$ (mg/g) are the amount of adsorbate adsorbed at equilibrium and at any time, $t$ (h), respectively, and $k$ (1/h) is the adsorption rate constant. Figure 5a shows that the linear plot of $\log(q_e - q_t)$ versus $t$ gives a gradient of $k$ and intercept at $\ln q_e$. Table 2 shows the values of $k$ and $R^2$ obtained from the plots at 25□C. The adsorption of Cr(VI) on CMPCRP was following pseudo–second–order model.

The pseudo–second–order model predicts the performance over the total range adsorption and is expressed as:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t$$

where $k$ (g/mg h) is the rate constant of second-order adsorption. Figure 5 b shows that the linear plot of ${}^{t}/_{q_t}$ versus $t$ gave $\frac{1}{kq_e^2}$ as the intercept and ${}^{1}/_{q_e}$ as the gradient. From Table 2, the $R^2$ for the pseudo–second–order adsorption shows the highest value mostly 0.99 which indicated that this kinetic model has a good relation and is consistent between the experimental and the calculated $q_e$ values. It also shows that pseudo–second–order model adsorption is predominant.

The adsorption isotherm used to show the adsorption molecules distribute between the solid phase and liquid phase at adsorption equilibrium state. The Langmuir and Freundlich isotherms are the most frequently employed models. The linear regression is used to determine the best–fitting isotherm and the pertinence of isotherm equation is compared by evaluating the correlation coefficients, $R^2$.

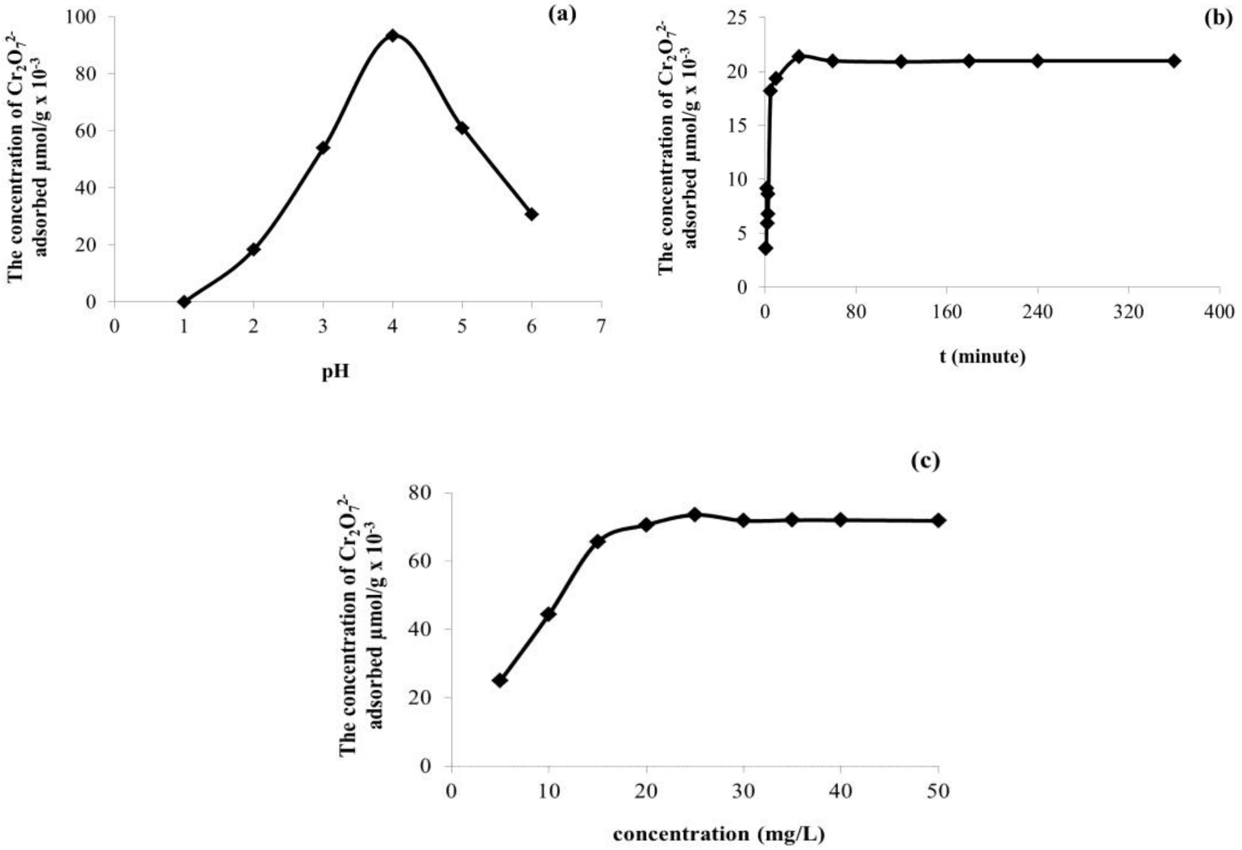


**Figure 4.Adsorption of Cr(VI) by CMPCRP at different pH (a), contact time (b), and initial Cr(VI) concentration (c)**

Langmuir's isotherm model is based on the theory that adsorption energy is constant and uptake occurs on a homogeneous surface by monolayer sorption. When the surface is covered by a monolayer of adsorbate, the adsorption goes on localized sites with no interaction between adsorbate molecules and that maximum adsorption occurs. The linear from of Langmuir isotherm equation is given as:

$$\frac{1}{q_e} = \frac{1}{(Q_m . K_L . C_e)} + \frac{1}{Q_m}$$

where $C_e$ (mg/L) is the Cr(VI) equilibrium concentration and $q_e$(mg/g) is the amount of Cr(VI) adsorbed per unit mass of adsorbent. $Q_m$ (mg/g) is the Langmuir constants related to adsorption capacity and $K_L$ (L/mg) is the rate of adsorption[19,20,21]. The value of $Q_m$ and $K_L$ were calculated from the intercept and slope of the linear plot and are presented in Table 3.

Freundlich model is an empirical expression that is the earliest known relationship describing the sorption equation. This isotherm that takes into account a heterogeneous surface and multilayer adsorption to the binding sites located on the surface and multilayer adsorption to the binding sites located on the surface of the sorbent. The Freundlich model is expressed by the following equation:

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

where $K_F$ and $n$ are indicative isotherm parameters of adsorption capacity and adsorption intensity, respectively[20,21]. Generally, n > 1 illustrates the adsorbate is favorably adsorbed on the adsorbent. The higher the number of n, the more favorable the adsorption and stronger the adsorption intensity[22].

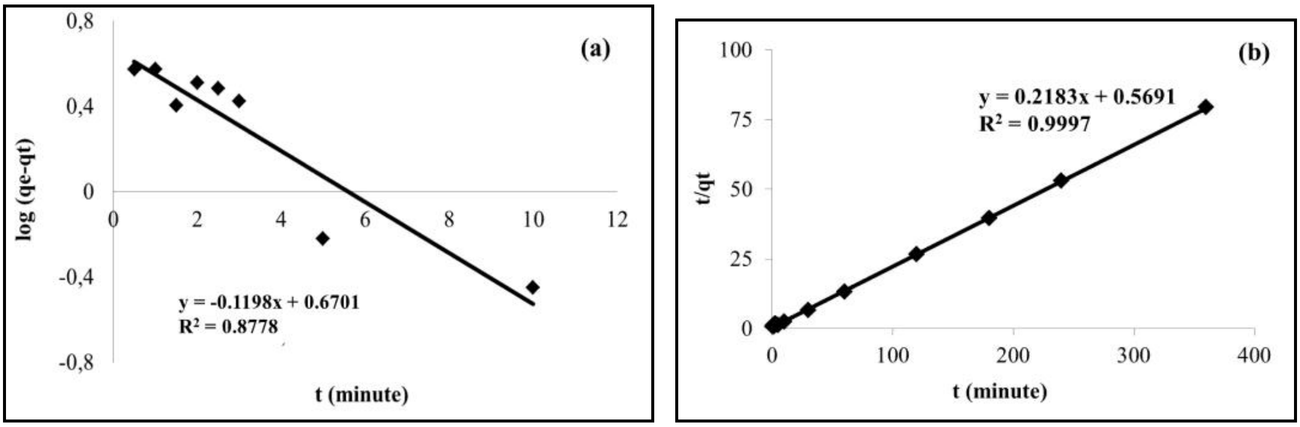


**Figure 5. Adsorption Kinetics Models of Cr(VI) by CMPCRP: Lagergren (a); Ho and McKay (b)**

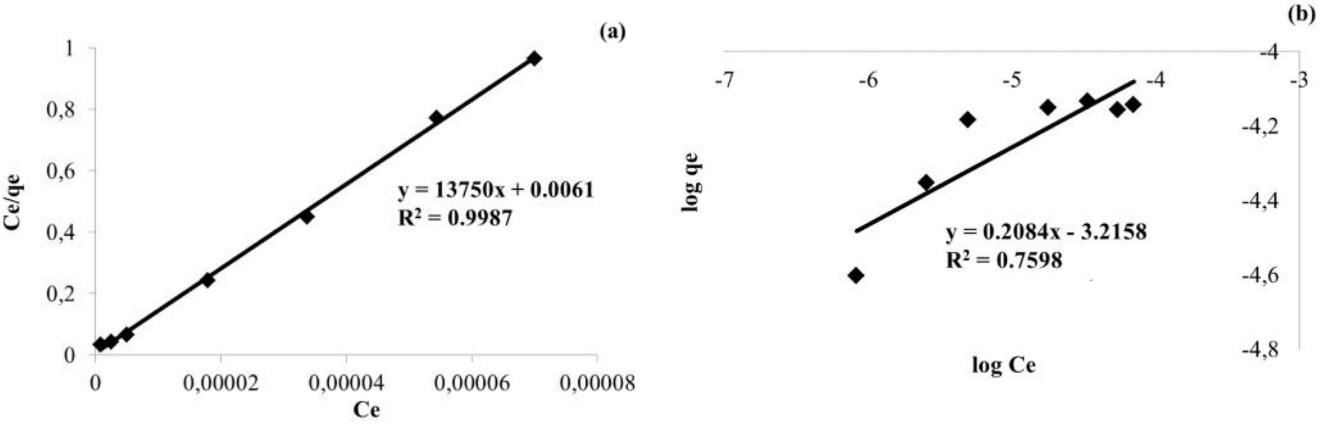


**Figure 6. Adsorption Isotherm Models of Cr(VI) by CMPCRP: Langmuir (a) and Freundlich (b)**

**Table 2 Kinetic adsorption models of CMPCRP**

| **Pseudo–first–order** | | | **Pseudo–second–order** | | |
|---|---|---|---|---|---|
| **Equation** | **$R^2$** | ***k* x $10^{-1}$ (g.mmol$^{-1}$.min$^{-1}$)** | **Equation** | **$R^2$** | ***k* x $10^{-1}$ (g.mmol$^{-1}$.min$^{-1}$)** |
| y = –0.1198x + 0.6701 | 0.8778 | 1.198 | y = 0.2183x + 0.5691 | 0.9997 | 8.374 |

**Table 3 The adsorption isotherm models of CMPCRP**

| **Langmuir** | | | | | | **Freundlich** | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Slope ($1/q_m$)** | **$q_m$ (mg/g)** | **$R^2$** | **Intercept $1/(q_m.K)$** | **$K_L$ (L/mol)** | ΔG°Ads (kJ/mol) | **slope** | **$R^2$** | **intercept** | **$K_F$ x$10^{-4}$** | **n** |
| 13750 | 15.71 | 0.9617 | 0.006 | 2254098.36 | –36.24 | 0.2084 | 0.7598 | –3.2158 | 6.08 | 4.79 |

Adsorption energy of CMPCRP determined by the Gibbs free energy equation (ΔG°Ads = –RTlnK). CMPCRP adsorption energy of 36.24 kJ/mol Thus, the adsorption of Cr(VI) on the CMPCRP can be classified as chemisorption[22]. Chemisorption process that occurs due to the hydroxyl group (OH) and the active sites (quaternary phosphonium group) on CMPCRP that can interact with Cr(VI). The adsorption of Cr(VI) by CMPCRP effectively only occurs under alkaline conditions. This indicates that the mechanism of interaction CMPCRP with Cr(VI) must be preceded by the protonation Cr(VI).

## Conclusion

In this study, CMPCRP was found to be suitable for Cr(VI) removal. The adsorption of Cr(VI) was found to increase with the increase in acidity, contact time, and Cr(VI) initial concentration. The Langmuir isotherm model and the pseudo–second–order kinetic model were proved to fit the adsorption equilibrium and kinetic data, respectively. From the Gibbs free energy equation, CMPCRP adsorption energy of 36.24 kJ/mol The adsorption of Cr(VI) on the CMPCRP can be classified as chemisorption and occur in monolayer.

## Acknowledgements

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