

New Approach to Elimination of Chlorophenol Compounds from Water

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Keywords	Abstract
Chlorophenols, Cd ²⁺ , Nano-porous, Xerogel.	Contamination of natural water with organic pollutants is a problem of major concern and the demand for effective adsorbents for the removal of toxic compounds is increasing. At present work tetramethoxy orthosilane (TMOS) xerogel were synthesized. Xerogels are nano-porous materials obtained from drying the sol-gels of tetraalkoxy silanes such as TMOS. They carry negative surface charges in water where the pH is higher than the Point of Zero Charge. This feature was employed to load divalent metal cations on the surfaces of these materials. Although xerogels do not show affinity for adsorption of chlorophenols from aqueous medium, TMOS xerogel loaded with Cd ²⁺ (TMOS-Cd) showed a 291 percent increase in 2,4,6-trichlorophenol (TCP) adsorption compared to that of neat TMOS xerogel. TMOS-Cd adsorbent is stable and follows a chemisorption mechanism for adsorption of TCP.

1. Introduction

Extremely growing urban life has exposed water resources to various kinds of pollutants including organic and inorganic compounds. The lack of sewage collection and treatment plants leaves opens the way for organic compounds to contaminate clean water sources. Chlorination, which is the classic method of water disinfection, can react with water containing aromatic pollutants such as phenolic compounds, increasing the concentration of chloroaromatic compounds [1, 2]. Some of these substances give water unpleasant taste.

Chlorophenols are a widespread class of water pollutants that are known to cause serious human health problems; hence these chemicals are found in the list of priority pollutants of the Environmental Protection Agency (EPA) [3]. Results of numerous risk assessment studies suggest meaningful correlation between the chloroaromatic concentrations and some specific health problems [4].

A number of methods such as coagulation, filtration with coagulation, precipitation, ozonation, adsorption, ion exchange, reverse osmosis and advanced oxidation processes have been used for the removal of chlorophenol and organic pollutants from polluted water and wastewater. Adsorption Technology is the cost-effective method and can efficiently remove toxic materials from the liquid phase, and chemical surface treatments of adsorbents can significantly enhance the selectivity and capacity of substrates. Many reliable adsorbents are used for removal all types of pollutants including chlorophenols (CP) from water resources of and

advances in this field have been reviewed [5-9]. The new adsorbents developed in this work are modified silica-based xerogel. Classical xerogels are prepared from acid/base hydrolysis of tetra-alkoxy silanes such as tetramethoxy silane (TMOS). The products of the hydrolysis are readily polymerized at neutral pH and room temperature. The polymeric material, at this stage, called a sol-gel, can be dried to produce a xerogel. Xerogel can be shaped or powdered with considerable surface area, ranging from 200 to 1500 m² g⁻¹. Xerogels are robust, inexpensive, non-toxic and recyclable materials. Silica based materials have attractive physical and mechanical properties, Manipulating the conditions at any step of this process can change the mechanical, physical and chemical properties of the final xerogel. Due to these advantages of xerogel in comparison to other adsorbents, various silica-based materials have been prepared and examined for various adsorption applications [10, 11]. It has been demonstrated that classic xerogels do not adsorb phenolic compounds, especially CP. Compared to phenol, CP are stronger acids so they produce more anions at normal drinking water pH. When the particles are neutral or have not any charge at a pH, this pH is called the point of zero charge (PZC). At pHs higher than PZC, the surface is negatively charged [12]. The opposite is observed at pHs lower than PZC. The typical values of PZC for the silica based materials are between 2.4 and 3.5 [13]. Therefore, in aqueous mediums with pHs close to neutral, the classical xerogels carry a net negative charge due to the hydrolysis of the unpolymerized silnols [14]. Therefore, adsorption of CP

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on TMOS xerogel is electrostatically prohibited at pH(s) close to neutral [15].

To improve the applicability of xerogel for adsorption, several techniques have been developed [15-18]. Surface of TMOS xerogel due to the outward oxygen atoms in the molecular structure, is negatively charged, so this solid, shows good ability to adsorb metal ions. But because of the negative charge on the surface of the adsorbent, the anions, particularly organic anion compounds are not absorbed. To fix this problem, it can set the metal ions on the surface of the solid. By placing Cd ions on the xerogel, a positive charge on the surface of TMOS is made, which increases the ability of the adsorbent to attract organic compound.

In this study, the surface charges of TMOS xerogel was modified with Cd²⁺. These xerogels carrying modified surface charges (TMOS-M) were examined for their ability to adsorb TCP. Then influences parameters in adsorption process such as pH, contact time, adsorbent dose and initial TCP concentration were investigated. The kinetic study, thermodynamic study and adsorption isotherms (Langmuir, Freundlich and Dubinin-Radushkevich) for before and after the modification were compared with each other.

2. Material and Methods

2.1. Chemicals and Instrumentation

TMOS and another chemical reagents used in this work including HCl, NaOH, TCP, Cd(NO₃)₂ .4H₂O were purchased from Sigma Aldrich. Standard solution of TCP, and Cd(NO₃)₂ were prepared by dissolving the appropriate amounts of the compounds in deionized water. Cadmium concentration (Standard Con: 0-5 mg L⁻¹, $y=0.0208x + 0.006$, $R^2=0.9995$) was measured using a Shimadzu (Tokyo, Japan) flame atomic absorption (AA) spectrometer (Model AA680) equipped with an air-acetylene flame. The concentration of TCP was determined using a UV-Visible spectrophotometer (Shimadzu, UV-1650PC) at its corresponding λ_{max} (294 nm at pH=6, $\epsilon = 2410 \text{ cm}^{-1} \text{ m}^{-1} \text{ L}$). Pore size analysis was performed on a Micromeritics Gemini VII2390 Surface Area Analyzer. Fine-sized powder xerogels (about 10 mg) were used for this analysis without any additional treatment. The pressure was measured as nitrogen was adsorbed or desorbed at a constant temperature controlled by liquid nitrogen.

The specific surface area of xerogel was calculated by the Brunauer-Emmett-Teller (BET) method [19].

$$q_e = q_m K_{BET} X / (1 - X) [1 + (K_{BET} - 1) X] \quad (1)$$

$X = C_e/C_s$ and C_s is the concentration (mg L⁻¹) of solute at saturation and q_m is saturation capacity (mol g⁻¹) of adsorbent for solute.

2.2. Adsorption of Cadmium Ion

To assess the adsorption characteristics of metal ion Cd²⁺, a fixed amount of the xerogel powder (20 mg), was added to a glass bottle containing 5 ml of the desired ion solution (known concentration taken from a stock solution containing 1000 mg L⁻¹ of the corresponding compound) and the resulting mixture was agitated (200 rpm) for the 75 min time

period at room temperature. The solution was then allowed to sit at room temperature for one h to allow the particles to gravity settle. Then the supernatant was separated and filtered before AA analysis.

2.3. Synthesis of Nanoporous Xerogel

1 mole of TMOS, 4 mole of H₂O and 0.0015 moles of HCl were mixed in a beaker and sonicated in a water bath at room temperature until a clear one-phase solution was obtained. An equivalent volume of phosphate buffer solution (10 ml, 0.1 mol L⁻¹, pH 7) was added to these solutions. The resulting mixtures were shed in a glass dish and stirred until the sol-gel formed. Then aged at room temperature for 15 days, until its weight was constant (Figure1). Obtained Xerogel then was sieved pass through a 250 μm Standard Sieve. For the loaded xerogel experiments, the xerogel was first exposed to the desirable cation solution then the loaded xerogel (Ex-M) was employed in the adsorption studies.

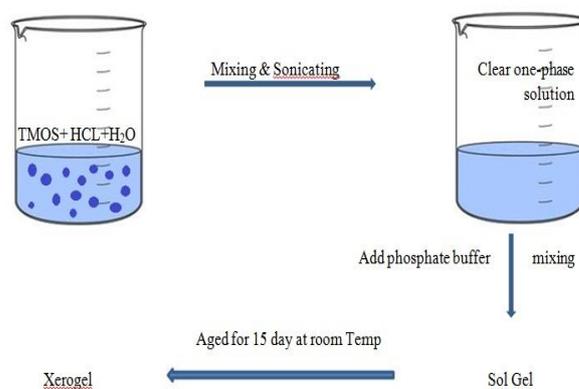


Figure 1. Synthesis of TMOS xerogel

3. Results and Discussion

3.1. Adsorption of Chlorophenols

The desired xerogel (20 mg) was added to a glass bottle containing 5 ml of the appropriate chlorophenol solution with known concentration (taken from the stock solution containing 1000 mg L⁻¹ of the corresponding compound). The resulting mixture was agitated for 120 min at the desired pH and room temperature. The solution was then allowed to gravity settle at the same temperature. The supernatant was filtered through a filter paper before AA analysis. The adsorption of the 2, 4, 6-trichlorophenol on the preloaded xerogel (TMOS-M) was studied in the same way except that the xerogel had been loaded with the appropriate cadmium at the optimal pH and room temperatures. The Ex-M was separated from the cation solution and used for the CP adsorption without drying. The effect of various parameters such as contact time, Initial concentration, amount of the adsorbent and pH was examined. All reported data are the average of at least triplicate measurements.

3.2. Equilibrium Isothermal Adsorption

Using the batch equilibrium method and the optimum conditions for the adsorption of Cd²⁺ (Table 1), the

isothermal adsorption of Cd²⁺ on the appropriate xerogel was studied at RT in flasks containing 5 ml of the aqueous solution of the ion from 5 to 100 mg L⁻¹.

To obtain the equilibrium isothermal adsorption curves for the adsorption of TCP on Ex-M, experiments were repeated using 10-80 mg L⁻¹ solutions of TCP in the presence of TMOS-Cd. A blank containing 5 ml of the desired TCP and no xerogel was tested under the optimized conditions of the adsorbent amount, pH, and contact time.

The percent removal and the amount of the adsorbed metal ion per gram of xerogel at equilibrium (q_e mg g⁻¹) were calculated using Eqs. (2) and (3), respectively.

$$\text{Removal efficiency(\%)} = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

$$q_e = \frac{V}{M} (C_i - C_e) \quad (3)$$

C_i and C_e are the initial and equilibrium concentrations of the metal ion in the solution (mg L⁻¹), respectively. V is the volume of solution (L) and M is the amount of the xerogel used in the experiment (g).

3.3. Kinetic and Thermodynamic Studies

The effect of time on the removal of TCP from the aqueous solutions was investigated under optimal conditions at room temperature by determining the amount of the adsorbed chlorophenol at different time intervals (1-120 min). The experiments were carried out in total volume of 5 ml aqueous solution containing 20 mg of the adsorbent with 30 mg L⁻¹ initial concentration of TCP. Thermodynamic experiments were performed at various temperatures of 288, 298, 303, 313, 328 K. Thermodynamic parameters were calculated from the slope and intercept of the plot of $\ln K_C$ versus $1/T$ at five different temperatures using the Eq. (4) as

$$\Delta G^\circ = -RT \ln K_C = \Delta H^\circ - T \Delta S^\circ \quad (4)$$

where R is universal gas constant (8.314 J mol⁻¹ K⁻¹). T is the absolute temperature in K. The standard enthalpy and entropy are designated by ΔH° and ΔS° , respectively. The equilibrium constant K_C was calculated using the Eq. (5) [20]

$$K_C = \frac{q_e}{C_e} \quad (5)$$

where q_e and C_e are the equilibrium concentration of the adsorbate on adsorbent and in the solution (mg L⁻¹), respectively.

The negative ΔG° value (-2.2), indicate the feasibility and spontaneous nature of TCP adsorption on TMOS-Cd. The positive value of ΔH° (2.24) reveal that the adsorption process is endothermic in nature and the positive ΔS° (78.94) suggests an increased randomness at the solid-liquid interface during the removal of TCP using the TMOS-Cd. During the segregation of chlorophenol anions, the solvent molecules, which are displaced by the incoming anions, gain more translational entropy than is lost by the anions, thus allowing for the prevalence of randomness in the system.

3.4. Adsorption of Cadmium

There are numerous reports on the use of various silane-based materials for adsorption of metal cations, especially

hazardous ones such as Cu²⁺, and Pb²⁺, but few of them contain information about the adsorption of divalent cations on the classic TMOS xerogel, especially from an adsorption point of view. To modify the xerogel surface charge for assisted adsorption of TCP, adsorption of Cd²⁺ on TMOS xerogel was examined first. The optimal values of the parameters that would affect adsorption including the initial concentration of the adsorbate (C_i), the adsorbent dose, pH and contact time were obtained. Then, the equilibrium adsorption isotherm (EAI) for Cd²⁺ on the xerogel was studied (Table 1).

The percent of removal can be used as a rough approximation for evaluation of the adsorption ability of an adsorbent for different sorbate species, although the proposed order is not based exclusively on this criterion. The analysis of the EAI experiments revealed that the adsorption data reasonably fits into the linear forms of both the Langmuir and Freundlich isotherm models Eq. (6) and (7), respectively.

$$\frac{C_e}{q_e} = \frac{C_e}{Q^\circ} + \frac{1}{bQ^\circ} \quad (6)$$

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_f \quad (7)$$

Q° is the maximum mass of solute adsorbed per mass of adsorbent for complete monolayer. K_f and b are constants. The Langmuir model suggests that uptake occurs on a homogeneous surface by monolayer adsorption of the sorbate particles on the equal, non-cooperative adsorbing sites. In contrast, the Freundlich equation is based on the adsorption data collected for heterogeneous surfaces [20]. So, it is assumed that a monolayer of the divalent cation is adsorbed on the heterogeneous surface of the classical xerogel. The $1/n$ parameter is extracted from the linear form of the Freundlich equation, Eq. (7), and is considered as an index of the adsorbent surface heterogeneity. The closer the heterogeneity parameter is to unity, the more homogeneous the adsorbent surface. Values of n in range of 2 to 10, 1 to 2, and 0 represents good, poor, and difficult adsorption characteristics, respectively. The value of n was 1.88 and 2.28 for Cd (II) and TCP respectively, which means that TCP was adsorbed on the surface of TMOS-Cd. This is interpreted as good adsorption.

In Langmuir isotherm the degree of appropriate of adsorbent drawn toward adsorbate is predicted from the values of separation factor constant (R_L), which is shown as Eq. (8)

$$R_L = \frac{1}{(1+bC_o)} \quad (8)$$

where C_o (mg L⁻¹) is initial concentration of adsorbate. The Langmuir isotherm constant is represented by b . The value of R_L revealed that the adsorption of adsorbate onto the adsorbent is favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$), and linear ($R_L = 1$) and unfavorable ($R_L > 1$). In this study, the values of R_L were 0.34 and 0.23 for Cd (II) and TCP respectively, signifying favorable adsorption. Data shows that the R^2 values of the Langmuir model are higher than in Freundlich model.

The structure of evolving silicates is a consequence of the successive polymerization, gelation, aging and drying, steps

and gives pores various sizes and accessibility. The analysis of the gas adsorption results using the BET equation, Eq (1) suggests an average surface area of 411.60 m² g⁻¹ and pore size values of 20.60 Å for TMOS xerogel. It is known that the structural heterogeneity is further increased during sol-gel drying as more unbond silanols cross-link and shrink the xerogel skeleton [21]. Table 1 indicates that the heterogeneity of the xerogel surface is more obvious for the interaction between Cd²⁺ and the xerogel with 1/n value of 0.532 for TMOS xerogel. The Langmuir coefficient, b in Eq. (6), is the ratio of the adsorption to desorption rate and is considered as adsorption intensity of the sorbate on the sorbent.

K_f [Freundlich constant (mg g⁻¹)] in Eq. (7) is usually stand for adsorption capacity. Values of these parameters, b and K_f in Table 1 are similar to what was concluded based on the percent removal. This result was further supported by examination of the adsorption at different temperatures and the calculated ΔG values at 293 K are summarized in Table 1. It is possible gain an understanding of the adsorption mechanism by the analysis of the EAI data using the Dubinin-Radushkevich (D-R) model. The ϵ parameter in the D-R equation, Eq. (9), is the Polyani potential which can be correlated to C_e be Eq. (10)

$$\ln q_e = \ln q_m - B\epsilon^2 \quad (9)$$

$$\epsilon = RT \ln(1 + 1/C_e) \quad (10)$$

Here, R is the gas constant in kJ mol⁻¹ and T is the absolute temperature in Kelvin. The advantage of the D-R method is that the B constant obtained from the Eq. (9) can be used for calculating the mean free energy (E) of sorption per mole of the solute after it is adsorbed onto the surface by the Eq. (11) [22]

$$E = 1/(-2B)^{\frac{1}{2}} \quad (11)$$

It has been shown that E values >8 kJ mol⁻¹ represent adsorption behavior characterized by ionexchange interactions and that E values <8 kJ mol⁻¹ are representative of non-ionic intermolecular interactions [23]. Although the adsorption data for the cadmium on the TMOS xerogel did not fitted well in the D-R equation (R² about 0.75), this analysis produced E values larger than 8 kJ mol⁻¹ (data are not shown). This indicates that the adsorption of these cadmium on the classic xerogel can be explained by considering an ionic interaction between Cd²⁺ and the negative charges on the xerogel surface. Cd²⁺ has a higher charge density because of its smaller ionic radius; hence, it has a stronger ionic interaction [24].

3.5. Adsorption of TCP

Figure 2 shows the results of TCP adsorption on TMOS and TMOS preloaded with cadmium. It is clear that loading TMOS with cadmium has enhanced TCP adsorption. It is assumed that the adsorption of cadmium on the xerogel surface changes the overall surface charge negative to positive. This facilitates the adsorption of the TCP anions onto the xerogel surface and the acid-base equilibrium of TCP in the solution shifts towards the basic side.

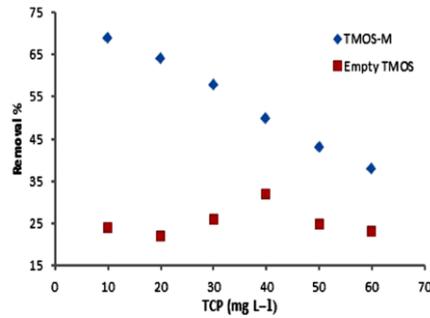


Figure 2. Adsorption of TCP on TMOS and TMOS-Cd²⁺ at pH 6 and 298K

3.6. Influential Parameters

3.6.1. Contact time

Figure 3 shows the removal of TCP with contact time. It is clear that the removal efficiency of TCP reached a maximum value after 80 min and then no further significant increase was observed. This may be due to the fact that initially all adsorbent sites were vacant and the solute concentration gradient was high. Therefore based on these results, a contact time of 80 was selected in subsequent isotherm studies.

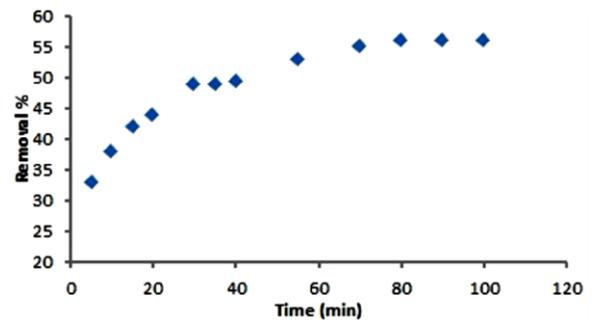


Figure 3. Effect of contact on the adsorption of TCP on TMOS-Cd at 298 K

3.6.2. Adsorbent Dose

The surface area available increase as more adsorbent is used. This, in turn, enhances the uptake of TCP as illustrated in Figure 4. Adsorption reaches a plateau for a fixed volume of solution containing a defined amount of CP due to the competition of the solvent molecules with the adsorbing sites and the adsorbate molecules (Figure 4).

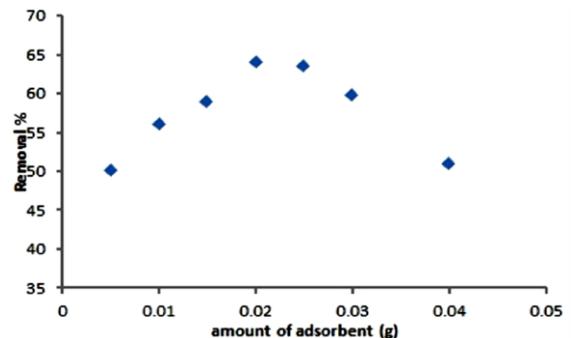


Figure 4. Effect of Adsorbent dose on the adsorption of TCP on TMOS-Cd at 298 K

3.6.3. pH

Based on pH studies (Table 1) the optimal pH for Cd²⁺ adsorption onto TMOS is 5.6. The opportunity for the cadmium hydroxide formation is increased at higher pH(s). On the other hand, the ionization of 2,4,6-trichlorophenol is increased at pH(s) above 5.6. To examine how these two factors are balanced, the adsorption of TCP on TMOS-Cd was studied over a pH range from 2 to 10. Figure 5 shows the best adsorption of TCP at pH 4.

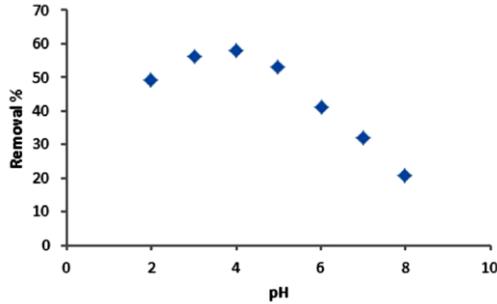


Figure 5. Effect of pH on the adsorption of TCP on TMOS-Cd at 298 K.

3.6.4. Initial Chlorophenol Concentration

Figure 2 shows that the adsorption of TCP on TMOS-Cd decreases as the chlorophenol concentration increases. By increasing the concentration of the chlorophenol in the presence of a constant number of adsorbing sites, the average number of the adsorption sites per molecule of the adsorbate is decreased.

3.6.5. Equilibrium Adsorption Isotherms

EAI experiments were carried out to identify the possible mechanism of adsorption operating with the TCP and TMOS-Cd. The data was analyzed using the linear form of the Langmuir, Freundlich, and D-R isotherm equations. The results in Table 2 show that the data was best fit by the Langmuir equation. This indicates that an ionic mechanism rules over the adsorption of TCP on TMOS-Cd.

3.6.6. Kinetics and Thermodynamics of the Assisted Adsorption of TCP

The results obtained from the kinetic studies on the adsorption of TCP on TMOS-Cd were analyzed using pseudo-first Eq. (11), pseudo-second order Eq. (12), and intraparticle diffusion Eq. (13) kinetic equations.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{11}$$

$$\frac{t}{q_t} = \frac{1}{k_2(q_2^2)} + \left(\frac{1}{q_2}\right) t \tag{12}$$

$$q_t = C + k_{dif} t^{\frac{1}{2}} \tag{13}$$

The result showed in Table 3. That clearly showed data fitted with pseudo-second order.

It has been shown that the pseudo-second order equation can be applied in cases where chemisorption processes could be rate limiting for the sorption step [19].

Table 1. Cadmium adsorption on TMOS xerogel

Ion	Ci mg L ⁻¹	TMOS mg	pH	time min	%R	EAI	R ²	Q ⁰ mg g ⁻¹	b L mg ⁻¹	K _f L mg ⁻¹	n	ΔG kJ mol ⁻¹
Cd ²⁺	20	20	5.6	75	87	Lan	0.99	18.2	0.094	---	---	-5.98
						Fre	0.98			2.21	1.88	
						D-R	0.75					

Table 2. Analysis of the results of EAI experiments of TCP on TMOS-Cd

EAI	parameters	Calculated
Langmuir	q _{max}	7.9
	k _L	0.11
	R ²	0.99
Freundlich	n	2.28
	K _f	1.36
	R ²	0.94
Dubinin-Radushkevich	q _m	5.54
	K _{D-R}	-2*10 ⁻⁶
	R ²	0.90

Table 3. Pseudo-first-order, Pseudo-second-order and Intra-particle diffusion values

Kinetic Models	parameters	Calculated
Pseudo-first-order	q ₁	1.37
	k ₁	0.002
	R ²	0.949

Pseudo-second-order	q_2	3
	k_2	0.051
	R^2	0.998
Intra-particle diffusion	K_{dir}	0.156
	C	1.49
	R^2	0.985

10. Conclusions

A new Nano adsorbent was prepared by a simple, cost-effective and environmental friendly technique and applied for the removal of TCP in this work. The resulted adsorbent is non-toxic material and has high surface area. They carry negative surface charges in water streams with $pH(s) > 4$. Hence the surface charge of the TMOS xerogel works as a strong driving force for stable loading divalent metal cations such as cadmium on their surfaces. As a result of the cation adsorption, the surface charge of the loaded xerogel is modified and helps it to adsorb organic molecules carrying negative charges at $pH(s) > 4$ such as TCP. The adsorption capacity of the loaded TMOS Xerogel for TCP is higher than many low-cost adsorbents and follows a chemisorption mechanism.

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