ADSORPTION PROPERTIES OF POMS/CTS COMPOSITE MATERIALS ON Pb^{2+} IN WATER ANALYZED BY T TEST AND NONPARAMETRIC TEST

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The preparation and the adsorption properties of two kinds of Polyoxometalates-Chitosan (POMs/CTS) composite materials used in adsorbing lead ion in water were reported. IR spectroscopy was used to characterize these two kinds of POMs/CTS composites, which proved that the POMs were successfully wrapped by CTS to form POMs/CTS composites. The adsorption experiment was carried out in $Pb(NO_3)_2$ solution. The adsorption capacity (Q_t), removal rate (r) and distribution adsorption coefficient (K_d) have been obtained and analyzed by t test and nonparametric test. The P values of r and K_d were both less than 0.05, while the P value of Q_t was higher than 0.05, suggesting two kinds of POMs/CTS composite materials have some effect on Pb^{2+} absorption. Considering the initial concentration of Pb^{2+}, the P values of Q_t, r and K_d were all less than 0.05 at an initial concentration of 100 mg/L. The adsorption performance of PW_9/CTS composite material is better than that of PW_{12}/CTS composite material for Pb^{2+} at an initial concentration of 100 mg/L.

Keywords Polyoxometalates-Chitosan Composite Material; Absorption; Pb^{2+}; T Test; Nonparametric Test

1. Introduction

Heavy metal pollution is the main source of water pollution in China. Lead is one of the most concerned heavy metal pollutants, which is not easy to be degraded in the environment. By biological enrichment and biological amplification effect, lead seriously harms the water environment and the human health. It is difficult to eliminate once it enters the human body in the form of ions, which can accumulate in a variety of tissues and organs, including the nervous system, blood system, digestive system, cardiovascular system and kidney. Lead can cause the body to be teratogenic, carcinogenic, causing mutations. Some may cause poisoning and even death. Lead can also affect offspring by entering the fetus through the placenta through milk and blood,

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especially to the fetal nervous system, resulting in children's innate intelligence. Therefore, it is very important to treat lead ions in water.

At present, there are many ways to treat heavy metal ions in water, such as adsorption separation, chemical precipitation and ion exchange [1]. Among them, adsorption separation method is the most popular, including activated carbon (AC) adsorption, biological adsorption, and chitosan adsorption, etc [2-8]. Chitosan (CTS) as a biological macromolecule is a kind of basic linear polysaccharide. It contains a lot of reactive groups, such as hydroxyl and amidogen, which have strong binding ability to heavy metal ions [9]. CTS can combine with a variety of metals, forming metal chelate. Chitosan as a kind of natural macromolecular material, which is non-toxic and non-irritating, can be found in animals, plants and organisms without secondary pollution to water. However, it is easy to protonate and reduce the selectivity of metal ions that affects the adsorption effect under acid conditions [10-11]. Compared with the above three materials, CTS can be modified as raw material, which is expected to produce new environment-friendly adsorbents.

Polyoxometalates (POMs) are metal-oxygen compounds formed by interactions with counter ions and polyanions possessing various structures and functions formed by tetrahedron $\{MO_4\}$ or octahedron $\{MO_6\}$ bonded by transition metal and oxygen. POMs have a lot of advantages, which can be widely used in many fields, due to a strong oxidation-reduction ability, good thermal stability, and low toxic side effects. Recently, Li et al. reported a novel metal-organic framework (MOF) material HKUST-1-MW@$H_3PW_{12}O_{40}$ [12], which has high selective adsorption performance on Pb^{2+} in aqueous solution. The introduction of tungsten phosphate acts as a template for the synthesis of materials, which makes the materials have large specific surface area. Meanwhile, the nucleophilic property of the tungsten phosphate polyanion increases the density of metal ion adsorption points.

At present, the research of adsorption performance of adsorbent materials is limited to the direct judgment from the data. Although this method is intuitive, it lacks scientific accuracy that the adsorption experiment can only be carried out with a few points of conditions. Statistics is a branch of applied mathematics, which mainly builds mathematical models by using probability theory, collects data of observed systems, conducts quantitative analysis and summary, and then makes inferences and predictions to provide basis and reference for relevant decisions. It is more scientific and effective to apply statistical methods to the research and evaluation of material properties, and this also provides a new idea for the study of material science.

Based on the above, two polyoxometalates-chitosan (POMs/CTS) composites were prepared from CTS and phosphotungstic acid, which can adsorb Pb^{2+} quickly and efficiently at room temperature. Statistical methods were used for the first time to compare the adsorption performance of heavy metal ions in two POMs/CTS composites, which opens up a new idea for the study of adsorbent materials.

2. Experimental

All chemicals were commercially purchased and used without further purification.

Preparation of $H_3PW_{12}O_{40}\cdot 12H_2O$ and $Na_9[A\text{-}PW_9O_{34}]\cdot 7H_2O$. Dissolve 100 g $Na_2WO_4\cdot 2H_2O$ in 100 mL hot water and heat to boiling until the solution is clarified. Add 10 mL 85% H_3PO_4, and then add 80 mL concentrated HCl solution drop by drop. The addition speed should not be too fast. After cooling, the crystal product $H_3PW_{12}O_{40}\cdot 12H_2O$ is obtained. Dissolve 60 g $Na_2WO_4\cdot 2H_2O$ (0.36 mol) in 75 mL water and stir until solid is completely dissolved. Add 2 mL 0.06 mol (85%) of phosphoric acid per drop, until the solution pH is 8.9~9.0. Under severe stirring, 11.25 mL 0.40 mol of glacial acetic acid was added into the solution drop by drop, resulting in a large amount of white precipitate, and the final solution pH was 7.5±0.3. After stirring for 1 h, the precipitated $Na_9[A\text{-}PW_9O_{34}]\cdot 7H_2O$ was obtained. The above two POMs were prepared and ground into powder.

Preparation of PW_{12}/CTS and PW_9/CTS composite materials. 1 g CTS was dissolved in 50 mL 2% acetic acid solution for filtration, and then the clear and permeable layer of mucus was retained. 1.7 g $H_3PW_{12}O_{40}\cdot 12H_2O$ was dissolved in 100 mL deionized water. 0.1 mol/L hydrochloric acid regulates pH to 6.0. The CTS solution was extracted with a syringe and added drop-by-drop to the $H_3PW_{12}O_{40}\cdot 12H_2O$ solution with slight stirring for ion crosslinking reaction. After 4 h, several well-formed PW_{12}/CTS gel balls could be obtained. They were removed from the same ionic solution after 1 day of stasis, washed to neutral, and placed in a cool and ventilated place. The PW_{12}/CTS composite materials are kept till they are completely dry. The preparation method of PW_9/CTS is basically the same as that of PW_{12}/CTS, except that the dosage of $Na_9[A\text{-}PW_9O_{34}]\cdot 7H_2O$ is 1.51 g.

Adsorption experiment. The adsorption experiment was carried out in the $Pb(NO_3)_2$ solution, with initial concentrations of: 50 mg/L, 100 mg/L, 150 mg/L, and 200 mg/L, respectively. 0.05 g POMs/CTS composite material was taken into 50 mL numbered beaker. 15 mL solutions of different concentrations were respectively removed and sealed with plastic wraps. The standard solutions were placed on the oscillator at room temperature (pH=7). The adsorption times were set to 20 min, 40 min, 60 min, 80 min, 100 min and 120 min, respectively.

Physical Measurements. The infrared spectrum of the solid sample was obtained on a BRUKER Model Vertex 70 FTIR spectrometer in the 400-4000 cm^{-1} region with a KBr pellet. The heavy metal ion concentration in the residual solution was determined by atomic absorption spectrometry.

Statistical analysis. Excel was used to establish the database and SPSS17.0 was used for statistical analysis. The normality Test was conducted for the measurement data. T test was applied when the data was subject to normal distribution. Otherwise, nonparametric test (Marginal Homogeneity Test) was applied. The difference of $P < 0.05$ was statistically significant.

3. Results and Discussion

Synthesis. The droplet acceleration and mixing speed have great influence on the crosslinking of POMs/CTS composite materials. Through experimental exploration and literature review [8], the stable gels with smooth and transparent appearance are easy to form under the condition of 20 d/min drop acceleration and 200 rpm stirring speed. If the droplet acceleration is too fast, it is easy to form agglomeration. The appearance of the gel ball is irregular and uneven. If the mixing speed is too fast, the gel ball will break easily.

IR Spectroscopy Analysis. The Infrared spectra shows that $H_3PW_{12}O_{40}\cdot 12H_2O$ had four characteristic peaks. The characteristic peak of 1079 nm^{-1} is formed by anti-symmetrical P-O_a stretching vibration. The peak of 983 nm^{-1} is the characteristic peak of W-O_d anti-symmetrical stretching vibration. The peak of 895-850 nm^{-1} is the characteristic peak of the anti-symmetrical stretching vibration of the W-O_d-W bridge oxygen bond. The peak of 800-760 nm^{-1} is the anti-symmetrical stretching vibration of the W-O_c-W bridge oxygen bond. As shown in Fig. 1, the four characteristic absorption peaks mentioned above still existed in PW_{12}/CTS composites, meanwhile, the characteristic peaks of chitosan also appeared. It showed that $H_3PW_{12}O_{40}\cdot 12H_2O$ and CTS are connected successfully. Analogously, the characteristic peaks of $Na_9[A\text{-}PW_9O_{34}]\cdot 7H_2O$ and CTS can be found in the IR spectrum of PW_9/CTS, proving that $Na_9[A\text{-}PW_9O_{34}]\cdot 7H_2O$ and CTS are connected successfully.

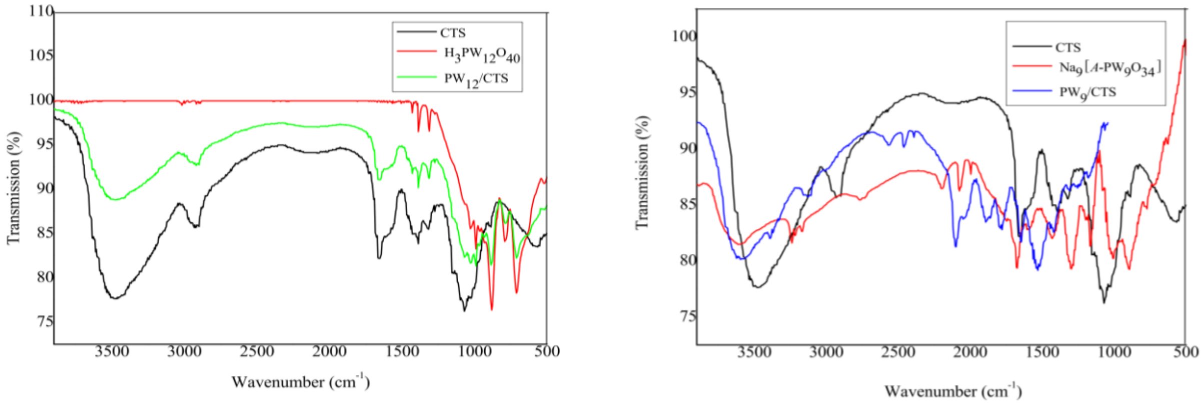

Fig. 1. Infrared spectrogram of POMs/CTS

Adsorption performance. Pb^{2+} was selected to investigate the adsorption performance of the prepared PW_{12}/CTS and PW_9/CTS. The adsorption performance of the two POMs/CTS was evaluated by adsorption quantity (Q_t, mg/g), removal rate (r), and distribution adsorption coefficient (K_d).

$$Q_t = \frac{(C_0 - C_e)\times V}{W} \qquad r = \frac{C_o - C_e}{C_0}$$

where C_0 is the initial concentration of lead in the solution [mg/L], C_e is the concentration of lead ions in the adsorbed solution [mg/L], V is the volume of the lead nitrate solution [mL], W is the mass of POMs/CTS for adsorption [g].

$$K_d = \frac{1000\,Q_t}{C_e}$$

As shown in Fig. 2-4, the Q_t, r and K_d of the two POMs/CTS composite materials with different adsorption times and initial concentration of Pb^{2+} were obtained.

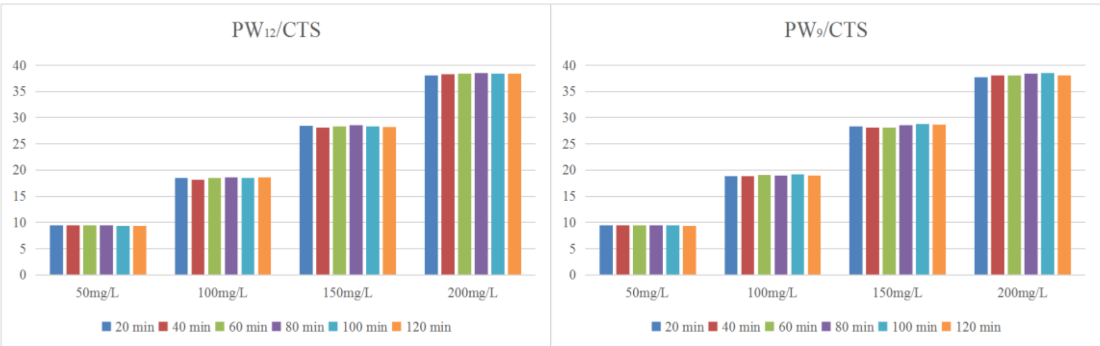

Fig. 2. Adsorption quantities (Q_t, mg/g) of the two POMs/CTS composite materials with different adsorption times and initial concentration of Pb^{2+}

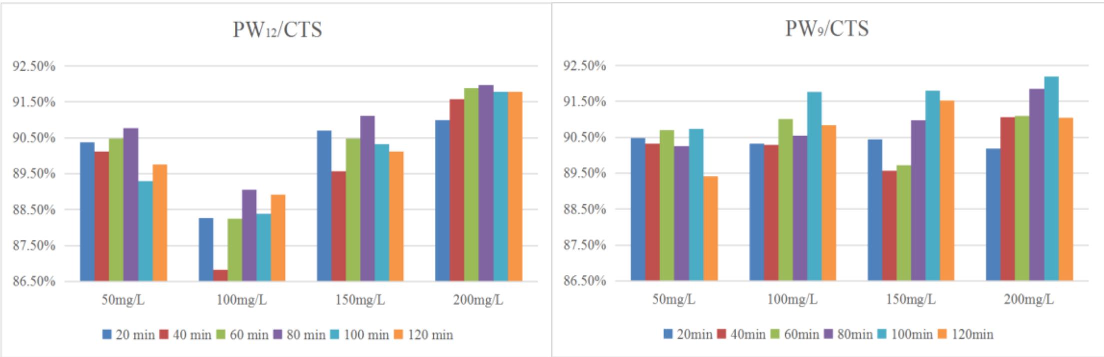

Fig. 3. Removal rates (r) of the two POMs/CTS composite materials with different adsorption times and initial concentration of Pb^{2+}

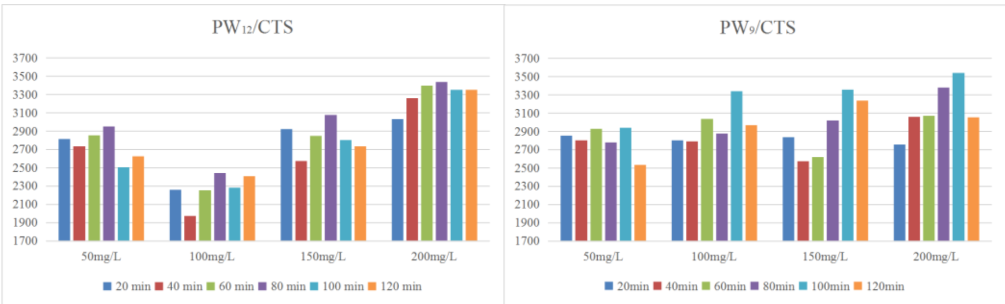

Fig. 4. Distribution adsorption coefficients (K_d) of the two POMs/CTS composite materials with different adsorption times and initial concentration of Pb^{2+}

Through the normal test of the difference values of Q_t, r and K_d between the two materials, it was found that P values of Q_t, r and K_d were all less than 0.05 (Table 1).

Table 1

Lilliefors Significance Correction of Normal Test

	Statistic	*df*	*P*
d(Q_t)[a]	0.187	24	0.030
d(r)[b]	0.207	24	0.009
d(K_d)[c]	0.185	24	0.032

a. Q_t of PW_{12}/CTS minus Q_t of PW_9/CTS;
b. r of PW_{12}/CTS minus r of PW_9/CTS;
c. K_d of PW_{12}/CTS minus K_d of PW_9/CTS.

At the test level of $\alpha = 0.05$, the above samples were considered to be non-normal distribution. Therefore, the rank test of two independent samples was used to compare the Q_t, r and K_d values of the two POMs/CTS composite materials. The P values of r and K_d were both less than 0.05 (Table 2). At the test level of α

= 0.05, the r and K_d of the two POMs/CTS composite materials were significantly different, suggesting that the adsorption properties of the two materials may be different.

Table 2

Marginal Homogeneity Test

	Distinct Values	Off-Diagonal Cases	Std. MH Statistic	P
Q_t	43	24	-1.674	0.094
r	42	24	-2.161	0.031
K_d	47	24	-2.033	0.042

However, the P value of Q_t was higher than 0.05. The values for Q_t of the two POMs/CTS composite materials were not significantly different, at the test level of α = 0.05. Since the initial concentration of Pb^{2+} was not considered in the above data analysis, the data were analyzed according to four initial concentration segments in order to further study the adsorption properties of the two materials at different initial concentrations. Through the normal test of the difference values of sectional data of Q_t, r and K_d between the two materials at different initial concentrations, it was found that P values were all higher than 0.05 (Table 3).

Table 3

Lilliefors Significance Correction of Normal Test for segment data

	C_0 (mg/L)	Statistic	df	P
d(Q_t)[a]	50	0.286	6	0.137
	100	0.208	6	0.200
	150	0.302	6	0.093
	200	0.242	6	0.200
d(r)[b]	50	0.316	6	0.062
	100	0.211	6	0.200
	150	0.292	6	0.121
	200	0.240	6	0.200
d(K_d)[c]	50	0.302	6	0.092
	100	0.223	6	0.200
	150	0.305	6	0.084
	200	0.249	6	0.200

a. Q_t of PW_{12}/CTS minus Q_t of PW_9/CTS;
b. r of PW_{12}/CTS minus r of PW_9/CTS;
c. K_d of PW_{12}/CTS minus K_d of PW_9/CTS.

At the test level of α = 0.05, the sectional data was considered to be normal distribution. Therefore, the t test of two independent samples was used to compare the sectional data of Q_t, r and K_d values of the two POMs/CTS composite materials at different initial concentrations. The P values of Q_t, r and K_d were all less than 0.05 at an initial concentration of 100 mg/L (Table 4).

Table 4

Paired Samples Test

	C_0 (mg/L)	Paired Differences: 95% Confidence Interval of the Difference, Lower	Upper	t	df	P
Q_t	50	-0.09510	0.05177	-0.758	5	0.482
	100	-0.70213	-0.34454	-7.524	5	0.001
	150	-0.39329	0.21329	-0.763	5	0.480
	200	-0.03431	0.39097	2.156	5	0.084
r	50	-0.90817	0.52817	-0.680	5	0.527
	100	-3.37001	-1.65665	-7.542	5	0.001
	150	-1.25632	0.68632	-0.754	5	0.485
	200	-0.08317	0.92651	2.147	5	0.085
K_d	50	-277.55878	160.37878	-0.688	5	0.522
	100	-941.53386	-458.70947	-7.455	5	0.001
	150	-460.94572	233.05905	-0.844	5	0.437
	200	-44.89271	366.22271	2.009	5	0.101

At the test level of $\alpha = 0.05$, the Q_t, r and K_d of the two POMs/CTS composite materials were significantly different, suggesting that the adsorption properties of the two materials are different at an initial concentration of 100 mg/L. At other concentrations, the P values were higher than 0.05. Therefore, the adsorption performance of the two materials showed no difference under other initial concentration conditions. The values of Q_t, r and K_d of PW_9/CTS are significantly higher than those of PW_{12}/CTS at an initial concentration of 100 mg/L (Fig. 5), which is due to the fact that PW_{12}/CTS composite material is saturated, while the PW_9/CTS composite material is trivacant in chemical configuration. Compared with saturated composite, the number of adsorption sites of trivacant composite is relatively large. The adsorption performance of PW_9/CTS composite material is better than that of PW_{12}/CTS composite material for Pb^{2+}.

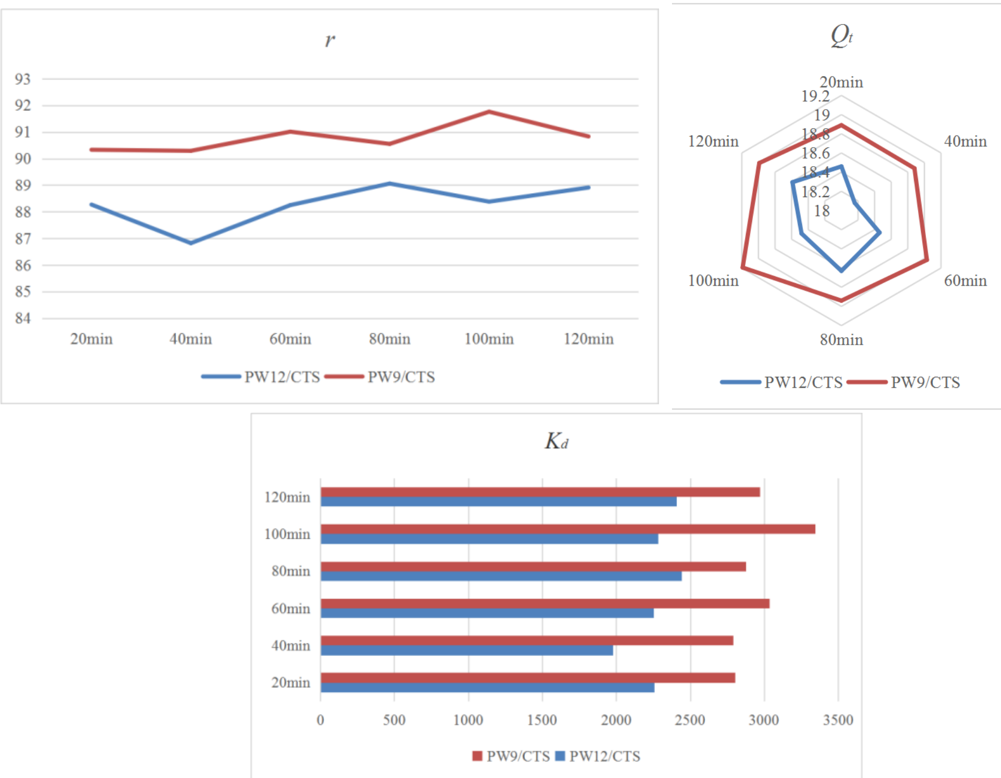

Fig. 5. Comparison diagram of the two POMs/CTS composite materials at an initial concentration of 100 mg/L

4. Conclusion

Two composite materials PW_{12}/CTS and PW_9/CTS were successfully synthesized and used to adsorb lead ions in water. The adsorption properties of the two materials were studied by statistical methods for the first time, which provides a new route to design and research of adsorption materials. In our primary studies, statistical results showed that the adsorption properties of the two materials are different. The application of statistical methods to the study of adsorption kinetics of materials needs further study. Such work is ongoing in our laboratory.

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