

# Ultrafiltration treatment of wastewater contained heavy metals complexed with palygorskite

Jun Ren<sup>1, 2, 3, \*</sup>, Tianyi Cao<sup>1</sup>, Xin Yang<sup>1</sup>, Ling Tao<sup>1, 2, 3</sup>

<sup>1</sup>School of Environmental and Municipal Engineering, Lanzhou Jiaotong University, Lanzhou 730070, P. R. China

<sup>2</sup>Gansu Hanxing Environmental Protection Co. Ltd., Lanzhou 730070, China

<sup>3</sup>Key Laboratory of Yellow River Water Environment in Gansu Province, Lanzhou Jiaotong University, Lanzhou 730070

\*Corresponding author: e-mail: renjun@mail.lzjtu.cn

Palygorskite was applied in complexation-ultrafiltration treatment of heavy metals in wastewater under different pH and ionic strength. The results indicated that the rejection of heavy metals increased significantly with pH value, and decreased slightly with an increase of ionic strength of Na<sup>+</sup> and Cl<sup>-</sup>. A certain concentration of NaCl significantly reduced the rejection rate of Cu<sup>2+</sup>. The rejection of Cu<sup>2+</sup>, Zn<sup>2+</sup> and Cd<sup>2+</sup> could reach over 86.8%, 93.6% and 93.7% at pH of 7 and 0.1 mol/L NaCl. The rejection of heavy metals was severely affected by low molecular weight competing complexing agents and the effect of sodium tartrate was greater than triethanolamine. In the presence of sodium tartrate, the rejection of Cu<sup>2+</sup>, Zn<sup>2+</sup> and Cd<sup>2+</sup> could arrive over 81.4%, 57.6% and 60.5% at pH of 7 in 20 min. Palygorskite was offered a potential complexing agent for the removal of heavy metals in wastewater at the complexation-ultrafiltration process.

**Keywords:** palygorskite; heavy metals; ultrafiltration; complexation; pH; ionic strength.

## INTRODUCTION

Over the past decade, researchers have increasingly focused on so-called the modified technique of micellar enhanced ultrafiltration (MEUF) and it is found that by adding an appropriate surfactant in solution, the efficiency of ultrafiltration can be further improved<sup>1, 2</sup>. At present, MEUF is seen as one of the potential techniques for the surfactant-based removal of heavy metal ions from wastewater<sup>3, 4</sup>. It is especially important to select the appropriate surfactant, which depends on the nature of the fomite to be eliminated in MEUF process. Surfactant molecules rejoin each other, toward critical micelle concentration (CMC)<sup>5, 6</sup>. These micelles are highly ionic (anionic) on which metal ion (cationic) adsorbs, therefore, true solution of heavy metals ions is converted to colloidal solution<sup>7, 8</sup>. The permeate passes through membrane pores along with the traces of surfactant monomers and non-solubilized metal ions. This colloidal-sized metal complex is big enough in size to retain on ultra membranes of suitable molecular weight cutoff (MWCO)<sup>9–11</sup>.

The treatment of wastewater containing kinds of metal ions such as Co<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup> and Hg<sup>2+</sup> has been successfully implemented by complexation-ultrafiltration process<sup>12–14</sup>. The natural character of a water-soluble polymer directly determines the operating conditions and the efficiency of combination with target heavy metal ions, and its selection is of significance in complexation-ultrafiltration process<sup>15, 16</sup>. A copolymer with abundant carboxyl functional groups, the copolymer of acrylic acid and maleic acid (PMA-100), can be used as a complexing agent in the complexation-ultrafiltration process but has not been deeply studied as water-soluble polymer in counterpart<sup>17, 18</sup>. Many studies also have reported that some living biomaterials have the potential to adsorb heavy metal ions from the environment, for instance, fungus, bacteria and algae<sup>19, 20</sup>. Nevertheless, organic materials can easily cause exogenous pollution in wastewater. It is crucial for wastewater treatment to develop inorganic materials, for example, palygorskite,

which increases the efficiency of complexing in complexation-ultrafiltration process<sup>21, 22</sup>. Palygorskite is an aquiferous chain-layer magnesium-aluminum silicate, which has a special structure and characters. According to the mineralogical classification, it belongs to the sepiolite of the group. The ideal structure formula is [(OH)<sub>2</sub>]<sub>4</sub>(Mg,Al, Fe)<sub>5</sub>(OH) · 2Si<sub>8</sub>O<sub>20</sub>] · 4H<sub>2</sub>O with Mg preferentially located in octahedral sites, but some of Mg<sup>2+</sup> cations have been already replaced by Al<sup>3+</sup> and Fe<sup>3+</sup> cations. The palygorskite is famous for their ion-exchange properties, but palygorskite has advanced to incorporate the formation of nanoscale crystals with precisely tailored physical-chemical properties recently. Hence, the potential effectiveness was improved significantly in an assortment of biomedical, chemical and environmental applications<sup>23–25</sup>.

The threat of a high concentration of toxic heavy metal to human health and the water environment is difficult to estimate. It is proceeding more efficiently, the nanoparticles for complexation with heavy metal ions have to retain following specific characteristics: (1) chemical and mechanical stability, (2) the high affinity toward the target metal ions and the low affinity toward nontarget ions<sup>26</sup>, (3) low toxicity, (4) low cost and the possibility of regeneration. The key process is the nanoparticle separation, which could be achieved by low-pressure membrane processes in a manner resembling polymer enhanced ultrafiltration (PEUF)<sup>27–30</sup>. The membrane characteristics like MWCO, physical-chemical properties (material type, hydrophilicity and hydrophobicity, pore size, charge, etc.), and fouling resistance, as well as energy consumption, play an important role in the nanoparticle-enhanced ultrafiltration (NEUF)<sup>31–33</sup>.

The current study concentrated on elucidating the relative abilities of nanoscale materials to bind metal ions, and subsequently, to be removed from water by ultrafiltration<sup>34–36</sup>. In this study, separation of micelles metal complex was investigated using ultrafiltration membranes with MWCO ranging from 6 to 100 kDa. Effects of pH, ionic strength and competitive complexing agent in the

treatment of model wastewater containing  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  by heavy metals with palygorskite nanomaterials on complexation-ultrafiltration were investigated. The binding capacity of palygorskite dendrimers was evaluated at several experimental conditions. The discussion reveals some light on the fundamental physical-chemical influencing factors governing nanoparticle-enhanced filtration and its potential for practical application.

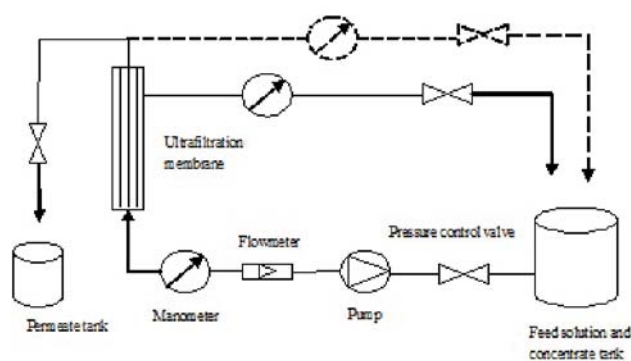
## MATERIAL AND METHODS

### Materials

All the chemicals were of maximum purity and used as received without any further purification. Palygorskite is provided by Lanzhou Kunlun environmental protection & Technology Co., Ltd., from Tianshui of Gansu province. It is broken, crushed and grinded, and then 200 mesh sieves. Palygorskite rock was from Tianshui, Gansu province, China. The constitution of palygorskite is supplied by the specification of the product. The main composition were  $\text{SiO}_2$  63.47%,  $\text{MgO}$  20%,  $\text{Al}_2\text{O}_3$  18.01%,  $\text{Fe}_2\text{O}_3$  5.16% and  $\text{K}_2\text{O}$  3.64%. The micrographs obtained the form of palygorskite bundles from scanning electron microscopy (SEM) (Fig. 1). These individual fibers often form long bundles that are 5 to 10  $\mu\text{m}$  long and fibers shown as individual well separated fibers or as elongated bundles of many fibers aggregation. It contains impurity minerals such as palygorskite, quartz and montmorillonite. The preparation of simulated heavy metal wastewater is called proper  $\text{CdCl}_2$ ,  $\text{CuCl}_2$ ,  $\text{ZnCl}_2$  adding a certain amount of water, and the concentration of  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  is 10, 40 and 30  $\text{mg/L}$ , respectively.

### Apparatus

The ultrafiltration experiment for laboratory scale was carried out with the apparatus shown in Fig. 2 and considerable mass transfer is achievable which membrane module is operated with reflux<sup>37</sup>. The membrane module

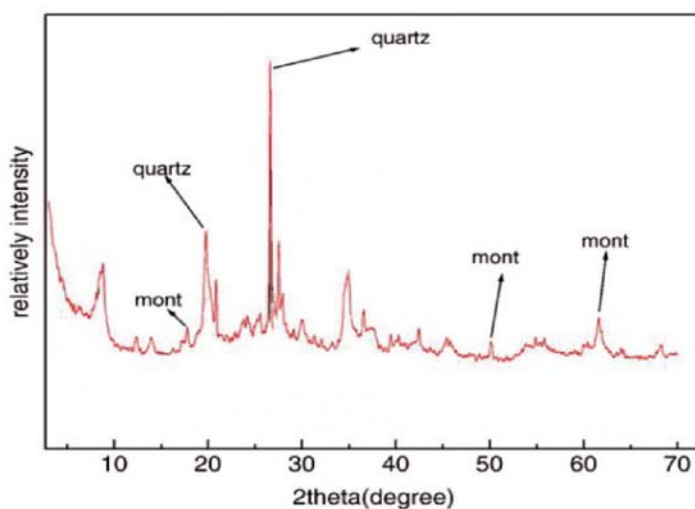
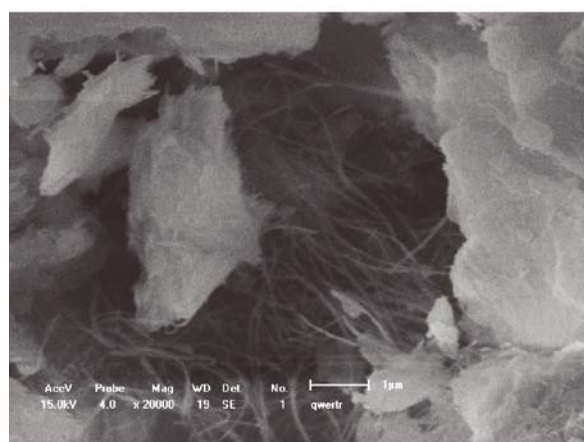


**Figure 2.** Schematic diagram of ultrafiltration treatment of wastewater contained heavy metals complexed by palygorskite

is hollow fiber ultrafiltration membrane and purchased from Tianjin Motian membrane Engineering Technology Co., Ltd. The main parameters are shown in Table 1<sup>38,39</sup>. Key ultrafiltration process consists of the concentrate tank with feed solution, membrane module and permeate tank, which has been connected with tubing and pressure control valves, manometer, a flow meter with a digital panel meter/display, a peristaltic pump, a stirrer for mixing and a power supply.

### Experimental procedure

In this work, the amount of complexing agent used was 5  $\text{g/L}$  of palygorskite with an overall concentration at a pH of 7. The concentrate tank immitted 30 L initial feed which was circulated through the apparatus. Operative pressure of 0.1  $\text{mpa}$  and flow rate of 25  $\text{L/h}$  were controlled in the whole process. The thermostatic water bath was utilized to keep the temperature at 293 K. In the total recirculation phase, both the permeation and retentate stream were returned to the concentrate tank so that the concentration of feed was constant. The sample of permeate was provided for analysis. The permeate flux was measured by weighing the per-



**Figure 1.** 1 SEM and XRD pattern of palygorskite

**Table 1.** Main parameters of hollow fiber ultrafiltration membrane

Model	Material	Relative molecular mass cutoff	Membrane area/ $\text{m}^2$	Inside diameter/ $\text{m}^2$	Outside diameter/ $\text{mm}$	Effective length/ $\text{mm}$
UEIP-503	PES*	$20 \times 10^3$	0.3	0.8	1.2	260

\* Polyethersulfone

meate volume produced in a certain quantity of time and the concentration of the permeation was analyzed by atomic absorption spectroscopy.

### Statistical analysis

Membrane flux is the seepage volume of unit membrane area per unit time under certain temperature and pressure. Membrane flux is a parameter that represents the permeability of ultrafiltration membrane, and is related to factors such as pore size, internal structure and viscosity of slurry. The membrane flux was measured by measuring the quality of osmotic fluid per unit time. The quality of osmotic fluid was measured by electronic balance, and the sampling time was determined by the stopwatch. The calculation formula is as follows:

$$J_V = \frac{V}{S \times t} \quad (1)$$

where:

$J_V$  – ultrafiltration membrane permeation flux, L/m<sup>2</sup>·h;

$V$  – The volume of permeation fluid, L;

$S$  – ultrafiltration membrane area, m<sup>2</sup>;

$t$  – running time, h.

The rejection rate  $R$ , which measures the membrane's separating capabilities is defined as:

$$R(\%) = \left(1 - \frac{c_p}{c_0}\right) \times 100 \quad (2)$$

where:

$c_0$  – the concentration of solute upstream of the membrane.

$c_p$  – the concentration of solute downstream from the membrane.

The membrane specific flux (defined as the ratio of the pure water flux of the cleaned membranes ( $J_c$ ) to that of the virgin membrane ( $J_0$ )).

$$r = \frac{J_c}{J_0} \quad (3)$$

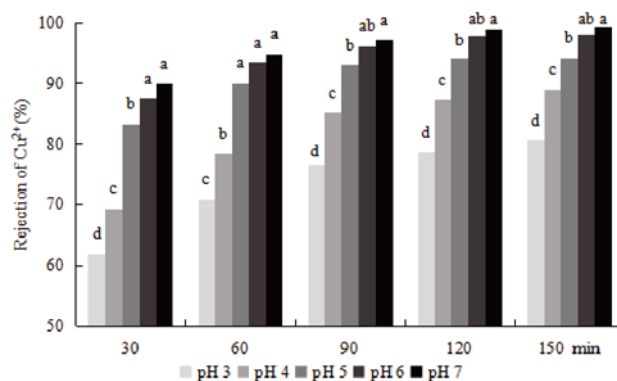
Statistical analysis was performed based on STATISTICA. The data were analyzed through one-way analysis of variance (ANOVA) to determine the effect of membrane molecular weight cutoff and rejection coefficients. Besides, the Duncan's multiple comparison tests were performed to determine the statistical significance of the differences in different membrane molecular weight cutoff and permeate flux. The  $F$  is the ratio of the mean square between groups and means square within groups. The larger the ratio is, the greater the difference between groups is. The  $P$  is the calculated confidence interval of test statistic  $F$ . The a, b, c and d indicate whether there is a significant difference between groups.

## RESULTS AND ANALYSIS

### Effect of pH on rejection coefficients of heavy metal

Rejection coefficient of Cu<sup>2+</sup> increases strongly with the increase of pH (Fig. 3). At 30 min, it was found that the rejection of Cu<sup>2+</sup> was significantly different in the five kinds of pH ( $F_{4,10} = 178.72$ ,  $p < 0.001$ ). The rejection coefficient of several pH were 61.9%, 69.3%, 83.3%, 87.5%, and 90.0%, respectively. There was no significant difference in the rejection coefficients of Cu<sup>2+</sup>

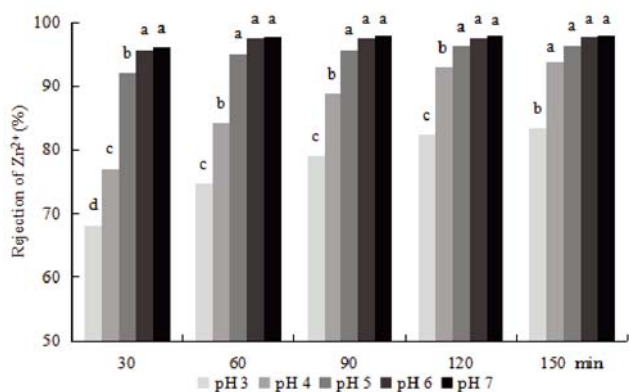
between pH 6 and pH 7. Then the testing showed that the rejection of Cu<sup>2+</sup> was significantly different in the five kinds of pH at 60 min ( $F_{4,10} = 26.50$ ,  $p < 0.001$ ). The rejection coefficient of five pH were 70.8%, 78.4%, 90.1%, 93.4%, and 94.9%, respectively. As well as, there was no significant difference in the rejection coefficients of Cu<sup>2+</sup> among pH 5, pH 6 and pH 7. At 90 min, the rejection coefficient of several pH were 76.4%, 85.1%, 93.0%, 96.2%, and 97.2%, respectively. It was indicated that the rejection of Cu<sup>2+</sup> was significantly different in the five kinds of pH ( $F_{4,10} = 48.28$ ,  $p < 0.001$ ). There was no significant difference in the rejection coefficients of Cu<sup>2+</sup> between pH 6 and pH 7. The results are the same as pH 5 and pH 6. At 120 min, it was concluded that the rejection of Cu<sup>2+</sup> was significantly different in the 5 kinds of pH ( $F_{4,10} = 35.74$ ,  $p < 0.001$ ). The rejection coefficient of five pH were 78.6%, 87.3%, 94.1%, 97.9%, and 98.9%, respectively. There was no significant difference in the rejection coefficients of Cu<sup>2+</sup> between pH 6 and pH 7. There was no significant difference in Cu<sup>2+</sup> rejection between pH 5 and pH 6. At 150 min, the rejection coefficient of five pH were 80.5%, 89.0%, 94.2%, 98.0%, and 99.4%, respectively. It was seen that the rejection of Cu<sup>2+</sup> was significantly different in the five kinds of pH ( $F_{4,10} = 28.37$ ,  $p < 0.001$ ).



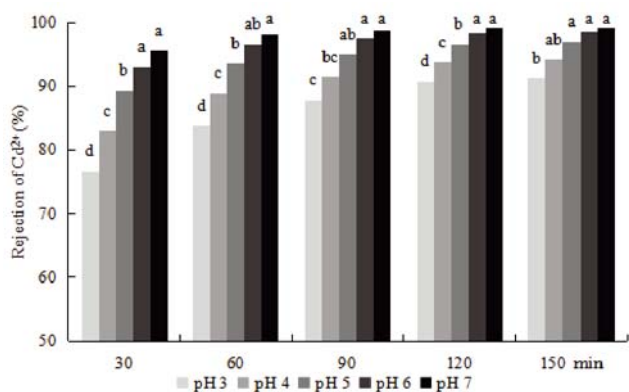
**Figure 3.** The rejection coefficients of ultrafiltration treatment under different pH for wastewater contained Cu<sup>2+</sup> complexed by palygorskite

Coincidentally, the rejection coefficient of Zn<sup>2+</sup> also increases strongly with the increase of pH (Fig. 4). At 30 min, it was indicated that the rejection of Zn<sup>2+</sup> was significantly different in the five kinds of pH ( $F_{4,10} = 157.57$ ,  $p < 0.001$ ). The rejection coefficient of five pH were 68.2%, 77.0%, 92.1%, 95.7%, and 96.0%, respectively. There was no significant difference in the rejection coefficients of Zn<sup>2+</sup> between pH 6 and pH 7. Then at 60 min, it was found that the rejection of Zn<sup>2+</sup> was significantly different in the five kinds of pH ( $F_{4,10} = 60.43$ ,  $p < 0.001$ ). The rejection coefficient of five pH were 74.7%, 84.3%, 95.1%, 97.5%, and 97.8%, respectively. There was no significant difference in the rejection coefficients of Zn<sup>2+</sup> among pH 5, pH 6 and pH 7. At 90 min, it was concluded that the rejection of Zn<sup>2+</sup> was significantly different in the five kinds of pH ( $F_{4,10} = 29.09$ ,  $p < 0.001$ ). The rejection coefficient of five pH were 79.1%, 88.9%, 95.7%, 97.6%, and 98.0%, respectively. There was no significant difference in the

rejection coefficients of  $Zn^{2+}$  among pH 5, pH 6 and pH 7. In the following, it was shown that the rejection of  $Zn^{2+}$  was significantly different in the five kinds of pH, at 120 min ( $F_{4,10} = 146.48, p < 0.001$ ). The rejection coefficient of five pH were 82.3%, 92.9%, 96.3%, 97.6% and 98.0%, respectively. There was no significant difference in the rejection coefficients of  $Zn^{2+}$  among pH 5, pH 6 and pH 7. At 150 min, it was seen that the rejection of  $Zn^{2+}$  was significantly different in the five kinds of pH ( $F_{4,10} = 17.23, p < 0.001$ ). The rejection coefficient of five pH were 83.4%, 93.8%, 96.4%, 97.7% and 98.0%, respectively. There was no significant difference in the rejection coefficients of  $Zn^{2+}$  among pH 4, pH 5, pH 6 and pH 7.



**Figure 4.** The rejection coefficients of ultrafiltration treatment under different pH for wastewater contained  $Zn^{2+}$  complexed by palygorskite



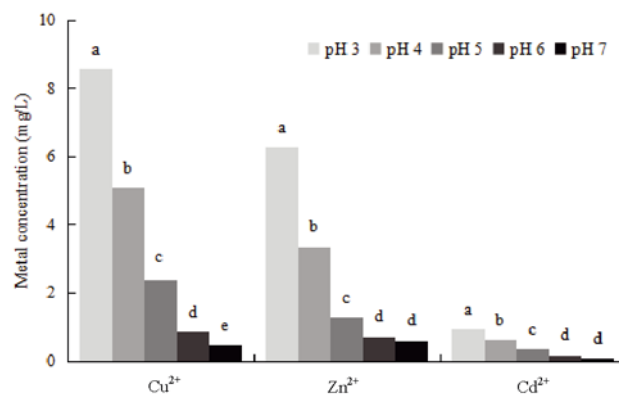
**Figure 5.** The rejection coefficients of ultrafiltration treatment under different pH for wastewater contained  $Cd^{2+}$  complexed by palygorskite

Finally, the rejection coefficient of  $Cd^{2+}$  also increases strongly with the increase of pH (Fig. 5). It was concluded that the rejection of  $Cd^{2+}$  was significantly different in the five kinds of pH, at 30 min ( $F_{4,10} = 57.69, p < 0.001$ ). The rejection coefficient of five pH were 76.7%, 83.0%, 89.3%, 93.1%, and 95.6%, respectively. There was no significant difference in the rejection coefficients of  $Cd^{2+}$  between pH 6 and pH 7. At 60 min, it was seen that the rejection of  $Cd^{2+}$  was significantly different in the five kinds of pH ( $F_{4,10} = 19.46, p < 0.001$ ). The rejection coefficient of five pH were 83.8%, 88.9%, 93.6%, 96.6%, and 98.1%, respectively. There was no significant difference in the rejection coefficients of  $Cd^{2+}$  between pH 6 and pH 7. At 90 min, it was shown that the rejection of  $Cd^{2+}$  was significantly different in the five kinds of

pH ( $F_{4,10} = 8.73, p < 0.01$ ). The rejection coefficient of five pH were 87.8%, 91.5%, 95.0%, 97.6% and 98.7%, respectively. There was no significant difference in the rejection coefficients of  $Cd^{2+}$  among pH 5, pH 6 and pH 7. At 120 min, it was indicated that the rejection of  $Cd^{2+}$  was significantly different in the five kinds of pH, ( $F_{4,10} = 39.07, p < 0.001$ ). The rejection coefficient of five pH were 90.7%, 93.8%, 96.6%, 98.4%, and 99.1%, respectively. There was no significant difference in the rejection coefficients of  $Cd^{2+}$  between pH 6 and pH 7. At 150 min, it was found that the rejection of  $Cd^{2+}$  was significantly different in the five kinds of pH ( $F_{4,10} = 4.73, p < 0.05$ ). The rejection coefficient of five pH were 91.3%, 94.2%, 97.0%, 98.5%, and 99.1%, respectively. There was no significant difference in the rejection coefficients of  $Cd^{2+}$  among pH 4, pH 5, pH 6 and pH 7.

In conclusion, variance analysis and multiple comparisons of the heavy metal concentrations of  $Cu^{2+}$ ,  $Zn^{2+}$ , and  $Cd^{2+}$  in five pH were performed at the operating time of 120, 90, and 120 min, respectively. There were significantly different in the concentration of heavy metal  $Cu^{2+}$  in the permeation between different pH ( $F_{4,10} = 4058.71, p < 0.001$ ). There were significantly different in the concentration of heavy metal  $Zn^{2+}$  in permeate between different pH ( $F_{4,10} = 335.63, p < 0.001$ ). There were significantly different in the concentration of heavy metal  $Cd^{2+}$  in the permeation between different pH ( $F_{4,10} = 56.24, p < 0.001$ ). Under five pH conditions, the stable permeate concentration of heavy metals  $Cu^{2+}$ ,  $Zn^{2+}$  and  $Cd^{2+}$  increased with decreasing pH (Fig. 6).

In palygorskite and heavy metal aqueous solution systems, because the pH of the surface of the palygorskite was higher than the pH value of the heavy metal solution, it was preferred that hydrolysis and precipitation occurred first on the surface of the palygorskite. In addition, the heavy metal ion hydroxide colloidal particles had a positive charge, and the surface of the palygorskite was negatively charged. The action of positive and negative colloidal particles promotes the adhesion of the colloidal particles on the surface of the palygorskite. Therefore, the hydrolytic precipitation of colloidal silica and the interaction of colloidal particles on palygorskite were the main mechanisms for removing heavy metals from palygorskite. The increase of pH value in the aqueous solution system was beneficial to the hydrolytic precipitation of heavy metals and the mutual adhesion of colloidal particles.

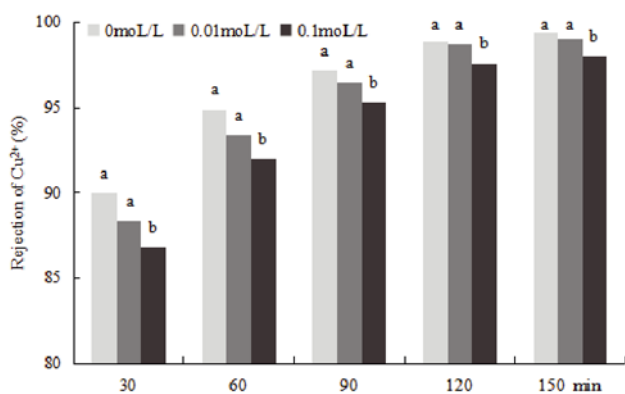


**Figure 6.** The concentration of heavy metals after ultrafiltration treatment under different for wastewater contained heavy metals complexed by palygorskite

### Effect of ionic strength on rejection coefficients of heavy metal

The effect of ionic strength on the rejection coefficient was investigated at different times (30, 60, 90, 120, and 150 min) while the other conditions such as pH, metal initial concentration, pore membrane and transmembrane pressure were constant during the test.

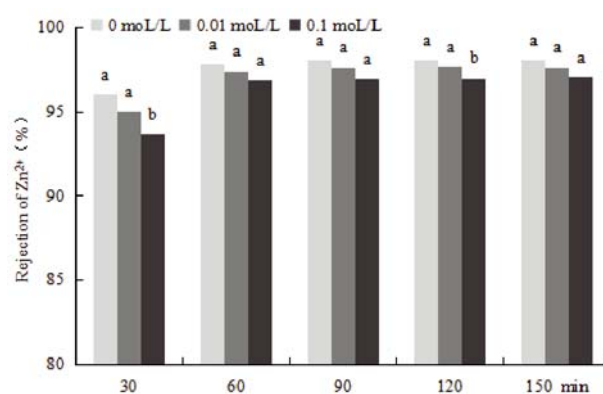
Rejection coefficient of  $\text{Cu}^{2+}$  increases slightly with the increase of the concentrations of NaCl (Fig. 7). At 30 min, it was concluded that the rejection of  $\text{Cu}^{2+}$  was significantly different in the different concentrations of NaCl ( $F_{2,6} = 4.08, p < 0.05$ ). The rejection coefficient of three different concentrations of NaCl was 89.9%, 88.4%, and 86.8%, respectively. Then, it was found that the rejection of  $\text{Cu}^{2+}$  was significantly different in the different concentrations of NaCl at 60 min ( $F_{2,6} = 8.92, p < 0.05$ ). The rejection coefficient of three different concentrations of NaCl were 94.9%, 93.5% and 92.0%, respectively. At 90 min, it was shown that the rejection of  $\text{Cu}^{2+}$  was significantly different in the different concentrations of NaCl ( $F_{2,6} = 7.76, p < 0.05$ ). The rejection coefficient of three different concentrations of NaCl was 97.1%, 94.5% and 95.3%, respectively. It was found that the rejection of  $\text{Cu}^{2+}$  was significantly different in the different concentrations of NaCl at 120 min ( $F_{2,6} = 16.42, p < 0.01$ ). The rejection coefficient of three different concentrations of NaCl was 98.9%, 98.7% and 97.6%, respectively. It was indicated that the rejection of  $\text{Cu}^{2+}$  was significantly different in the different concentrations of NaCl at 150 min ( $F_{2,6} = 9.68, p < 0.05$ ). The rejection coefficient of three different concentrations of NaCl were 99.4%, 99.0% and 98.0%, respectively. At five time points, there was no difference in  $\text{Cu}^{2+}$  interception rate between 0.01 mol/L sodium chloride and 0.1 mol/L sodium chloride rejection.



**Figure 7.** The rejection coefficients of ultrafiltration treatment under different ionic strength for wastewater contained  $\text{Cu}^{2+}$  complexed by palygorskite. Condition: the concentration of NaCl was 0 mol/L, 0.01 mol/L and 0.1 mol/L, respectively

Coincidentally, the rejection coefficient of  $\text{Zn}^{2+}$  also increases slightly with the increase of the concentrations of NaCl (Fig. 8). It was indicated that the rejection of  $\text{Zn}^{2+}$  was significantly different in the different concentrations of NaCl at 30 min ( $F_{2,6} = 9.08, p < 0.05$ ). The rejection coefficient of three different concentrations of NaCl were 96.0%, 95.0% and 93.7%, respectively. It was seen that the rejection of  $\text{Zn}^{2+}$  was significantly different in the

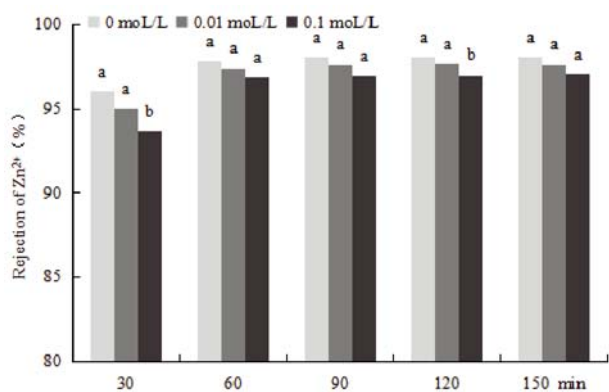
different concentrations of NaCl at 60 min ( $F_{2,6} = 0.86, p > 0.05$ ). The rejection coefficient of three different concentrations of NaCl was 97.8%, 97.4% and 96.9%, respectively. At 90 min, it was shown that the rejection of  $\text{Zn}^{2+}$  was significantly different in the different concentrations of NaCl ( $F_{2,6} = 2.56, p > 0.05$ ). The rejection coefficient of three different concentrations of NaCl were 98.0%, 97.6% and 97.0%, respectively. Then, it was found that the rejection of  $\text{Zn}^{2+}$  was significantly different in the different concentrations of NaCl at 120 min ( $F_{2,6} = 9.83, p < 0.05$ ). The rejection coefficient of three different concentrations of NaCl were 98.1%, 97.6% and 97.0%, respectively. It was concluded that the rejection of  $\text{Zn}^{2+}$  was significantly different in the different concentrations of NaCl at 150 min ( $F_{2,6} = 5.09, p > 0.05$ ). The rejection coefficient of three different concentrations of NaCl were 98.0%, 97.6% and 97.0%, respectively.



**Figure 8.** The rejection coefficients of ultrafiltration treatment under different ionic strength for wastewater contained  $\text{Zn}^{2+}$  complexed by palygorskite. Condition: the concentration of NaCl was 0 mol/L, 0.01 mol/L and 0.1 mol/L, respectively

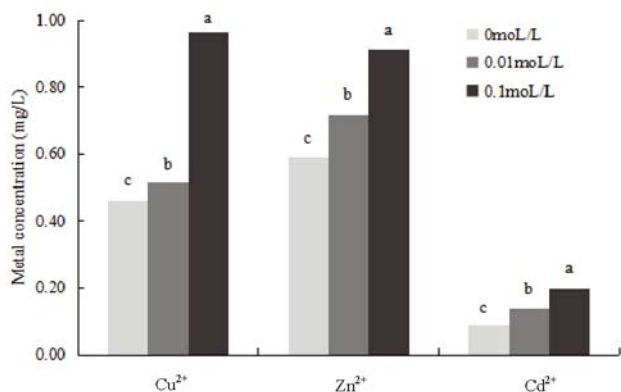
At last, the rejection coefficient of  $\text{Cd}^{2+}$  also increases slightly with the increase of the concentrations of NaCl (Fig. 9). It was concluded that the rejection of  $\text{Cd}^{2+}$  was significantly different in the different concentrations of NaCl at 30 min ( $F_{2,6} = 5.37, p < 0.05$ ). The rejection coefficient of three different concentrations of NaCl were 95.6%, 95.1% and 93.7%, respectively. It was indicated that the rejection of  $\text{Cd}^{2+}$  was significantly different in the different concentrations of NaCl at 60 min ( $F_{2,6} = 1.57, p > 0.05$ ). The rejection coefficient of three different concentrations of NaCl were 98.1%, 97.6% and 96.9%, respectively. It was seen that the rejection of  $\text{Cd}^{2+}$  was significantly different in the different concentrations of NaCl at 90 min ( $F_{2,6} = 2.48, p > 0.05$ ). The rejection coefficient of three different concentrations of NaCl was 98.7%, 98.3% and 97.7%, respectively. It was found that the rejection of  $\text{Cd}^{2+}$  was significantly different in the different concentrations of NaCl at 120 min ( $F_{2,6} = 10.80, p < 0.05$ ). The rejection coefficient of three different concentrations of NaCl was 99.1%, 98.6% and 98.0%, respectively. It was shown that the rejection of  $\text{Cd}^{2+}$  was significantly different in the different concentrations of NaCl, at 150 min ( $F_{2,6} = 6.19, p < 0.05$ ). The rejection coefficient of three different concentrations of NaCl was 99.1%, 98.6% and 98.0%, respectively. At 30 and 120 min, there was no significant difference in the rejection coefficients of  $\text{Cd}^{2+}$  between 0.01 and 0.1 mol/L

sodium chloride. For the rejection coefficients, there was no significant difference in the rejection of  $\text{Cd}^{2+}$  between the concentrations of NaCl at the 60 and 90 min.



**Figure 9.** The rejection coefficients of ultrafiltration treatment under different ionic strength for wastewater contained  $\text{Cd}^{2+}$  complexed by palygorskite. Condition: the concentration of NaCl was 0 mol/L, 0.01 mol/L and 0.1 mol/L, respectively

Conclusions there were significantly different in the concentration of heavy metal  $\text{Cu}^{2+}$  in the permeation between different concentrations of ionic strength ( $F_{2,6} = 220.17$ ,  $p < 0.001$ ). There were significantly different in the concentration of heavy metal  $\text{Zn}^{2+}$  in permeate between different concentrations of ionic strength ( $F_{2,6} = 155.43$ ,  $p < 0.001$ ). There were significantly different in the concentration of heavy metal  $\text{Cd}^{2+}$  in the permeation between different concentrations of ionic strength ( $F_{2,6} = 252.26$ ,  $p < 0.001$ ). Under there different concentrations of ionic strength, the stable permeate concentration of heavy metals  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  decreased with decreasing ionic strength (Fig. 10). The ionic strength will change the thickness of the double electric layer on the surface of the complexing agent and promote the agglomeration of the complexing agent in the form of particles; it will also compete with the heavy metal ions for ion exchange and affect the complexation effect.

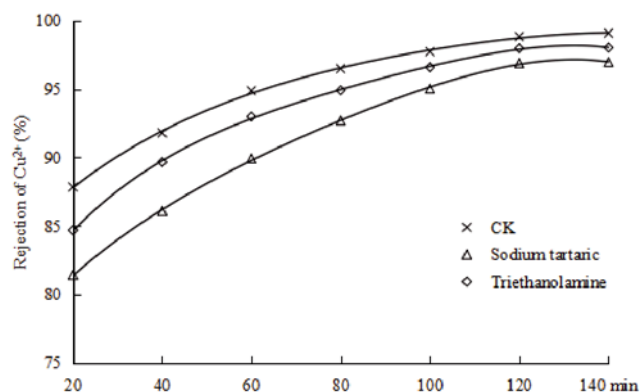


**Figure 10.** The concentration of heavy metals after ultrafiltration treatment under different ionic strength for wastewater contained heavy metals complexed by palygorskite. Condition: the concentration of NaCl was 0 mol/L, 0.01 mol/L and 0.1 mol/L, respectively

#### Effect of competitive complexing agent on rejection coefficients of heavy metal

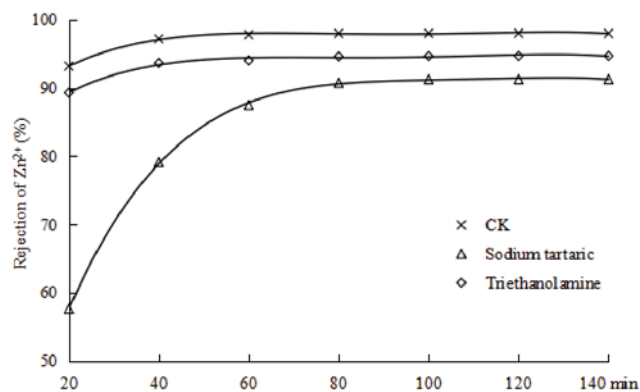
Rejection coefficient of  $\text{Cu}^{2+}$  increased slightly with the adding of sodium tartaric and triethanolamine (Fig. 11). The permeate concentration of  $\text{Cu}^{2+}$  decreased with complexation time, and it changes little after about

120 min. The rejection coefficient increased significantly in 20 min. The rejection coefficient of three competitive complexing agents was 87.84%, 84.40% and 81.40%, respectively. The differences between the 140 and 20 min rejection coefficient for  $\text{Cu}^{2+}$  at different competitive complexing agents were 11.01%, 13.31% and 15.31%, respectively. The retention coefficient of three competitive complexing agents was stable at 98.85%, 97.99% and 96.91%, respectively, and the  $\text{Cu}^{2+}$  concentration in the permeate was stable at 0.46, 0.80 and 1.24 mg/L, respectively.



**Figure 11.** The rejection coefficients of ultrafiltration treatment under different competitive complexing agent for wastewater contained  $\text{Cu}^{2+}$  complexed by palygorskite

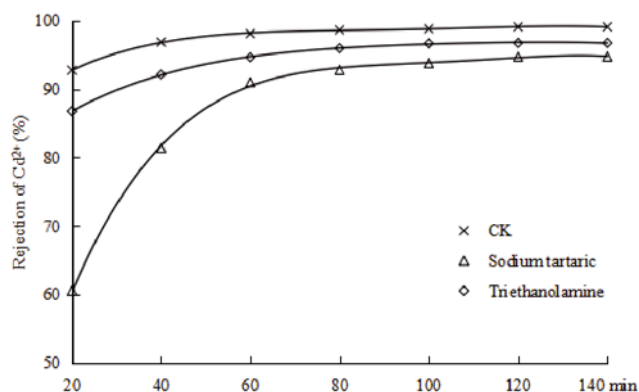
Rejection coefficient of  $\text{Zn}^{2+}$  increased strongly with the adding of sodium tartaric and triethanolamine (Fig. 12). The permeate concentration of  $\text{Zn}^{2+}$  decreased with complexation time, and it changes little after about 100 min. The rejection coefficient increased significantly in 20 min. The rejection coefficient of three competitive complexing agents was 93.21%, 89.31% and 57.62%, respectively. The differences between the 100 and 20 min rejection coefficient for  $\text{Zn}^{2+}$  at different competitive complexing agents were 4.82%, 5.38% and 33.66%, respectively. The retention coefficient of three competitive complexing agents was stable at 98.03%, 94.69% and 91.28%, respectively, and the  $\text{Zn}^{2+}$  concentration in the permeate was stable at 0.59, 1.59 and 2.62 mg/L, respectively.



**Figure 12.** The rejection coefficients of ultrafiltration treatment under different competitive complexing agent for wastewater contained  $\text{Zn}^{2+}$  complexed by palygorskite

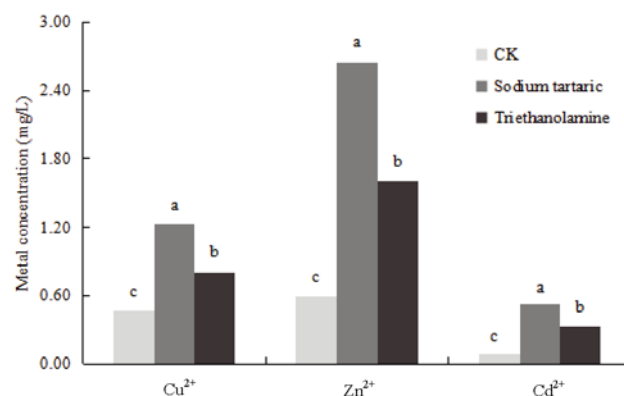
Coincidentally, the rejection coefficient of  $\text{Cd}^{2+}$  increased strongly with the adding of sodium tartaric and triethanolamine (Fig. 13). The permeate concentration of

$\text{Cd}^{2+}$  decreased with complexation time, and it changes little after about 120 min. The rejection coefficient increases significantly in 20 min. The rejection coefficient of three competitive complexing agents was 92.78%, 86.79% and 60.51%, respectively. The differences between the 120 and 20 min rejection coefficient for  $\text{Cd}^{2+}$  at different competitive complexing agents were 6.34%, 9.98% and 34.24%, respectively. The retention coefficient of three competitive complexing agents was stable at 99.12%, 96.77% and 94.75%, respectively, and the  $\text{Cd}^{2+}$  concentration in the permeate was stable at 0.09, 0.32 and 0.53 mg/L, respectively.



**Figure 13.** The rejection coefficients of ultrafiltration treatment under different competitive complexing agent for wastewater contained  $\text{Cd}^{2+}$  complexed by palygorskite

Analysis of variance and multiple comparisons of heavy metal concentrations in the wastewater of heavy metals  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  under different competing complexing agents were performed, at the system operating time was 120, 90 and 120 min, respectively. It was shown that there was a significant difference in the concentration of heavy metal  $\text{Cu}^{2+}$  in the permeate between different competing complexing agents ( $F_{2,6} = 425.89, p < 0.001$ ). There was a significant difference in the concentration of heavy metal  $\text{Zn}^{2+}$  in the permeation between different competing complexing agents ( $F_{2,6} = 68.96, p < 0.001$ ). There was a significant difference in the concentration of heavy metal  $\text{Cd}^{2+}$  in the permeation between different competing complexing agents ( $F_{2,6} = 624.39, p < 0.001$ ). The wastewater concentrations of the three heavy metal permeates varied similarly with competing complexing agents. The order of the concentration of the wastewater was sodium tartrate > triethanolamine > control (Fig. 14).



**Figure 14.** The concentration of heavy metals after ultrafiltration treatment under different competitive complexing agent for wastewater contained heavy metals complexed by palygorskite

Jawor et al. evaluate the removal of cadmium ions from water by nanoparticle-enhanced ultrafiltration using polymer and zeolite nanoparticles, when the ionic strength is relatively low, the rejection coefficients increase almost linearly with the ionic strength concentration (Jawor and Hoek 2010). Canizares et al. examined the treatment of metal plating wastewater by MEUF attaining complete removal of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  using PAA as different pH. It can be seen lead rejection is greater than cadmium for the majority of pH values due to the higher affinity of lead for PAA previously reported (Cañizares et al. 2008). Moreover, the similar results of ultrafiltration treatment of wastewater contained heavy metals have been reported in Table. 2. The palygorskite could improve the rejection of heavy metals by comparing with other studies and significantly offer potential material for ultrafiltration treatment of wastewater.

## CONCLUSIONS

With the increase of pH value, the rejection of three heavy metals increased significantly. In the pH range of 3–5, the pH value increased by one unit, the  $\text{Cu}^{2+}$  rejection rate increased 8.91% on average, and the pH value was 6–7. The  $\text{Cu}^{2+}$  rejection rate did not increase significantly; the pH value ranged from 3 to 4, the pH increased by one unit, and the rejection of heavy metal  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  increased by 9.42% and 4.40% on average. At pH values of 5–7, the pH value increased, and the interception rates of heavy metals  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  increased slightly. As the concentration of NaCl increased, the rejection of three heavy metals decreased

**Table 2.** Interception effect of different materials on heavy metals in the previous study

Materials	heavy metals	Experimental conditions	Rejection rate (%)	Ref.
Rhamnolipid	$\text{Cr}^{6+}$	Hollow fiber cartridge, pH 6 23°C, TMP 70 kPa	98.7%	5
	$\text{Cr}^{3+}$		96.2%	
Starch and polyethyleneimine	$\text{Zn}^{2+}$	Polysulfone hollow fibre, 26 ± 1°C, pH 7	96%	3
	$\text{Pb}^{2+}$		87%	
Anionic polyacrylamide	$\text{Ag}^+$	Polyethersulphone UF membrane, 30 ± 1°C, pH 7	Close to 100%	4
	$\text{Cr}^{6+}$		Close to 94%	
Poly acrylic acid	$\text{Cd}^{2+}$	Micelles Enhanced Ultra Filtration, pH 4.5, 50°C, 0.15 M $\text{NaNO}_3$	93%	27
	$\text{Ni}^{2+}$		79%	
palygorskite	$\text{Cu}^{2+}$	Hollow fiber ultrafiltration Membrane, pH 7, 0.1 mol/L NaCl	86.8%	This work
	$\text{Zn}^{2+}$		93.6%	
	$\text{Cd}^{2+}$		93.7%	

slightly. 0.01 mol/L NaCl had no significant effect on the interception rate of three heavy metals, 0.1 mol/L NaCl significantly reduced the retention rate of heavy metal  $\text{Cu}^{2+}$ , and had little effect on the rejection of  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$ . Low-molecular-weight competitive complexing agents have serious effects on the rejection rate of three heavy metals. The effect of sodium tartrate on three heavy metals is greater than that of triethanolamine, and the effect on  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  is much greater than that of  $\text{Cu}^{2+}$ . The effect of triethanolamine on  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  is much greater than that of  $\text{Cu}^{2+}$ . Under the condition of stable concentrations of three heavy metal permeates,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Cd}^{2+}$  decreased by 0.86%, 3.36%, and 2.35%, respectively, in the presence of triethanolamine. Under the conditions of sodium tartrate,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Cd}^{2+}$  decreased by 5.07%, 6.87%, and 4.37%, respectively. The order of the impact of competing complexing agents on ions was  $\text{Zn}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+}$ . Compared to other complexing agents, the rejection coefficient of palygorskite decreased because the organic complexing agent had almost no rejection coefficient for  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$ . However, considering the simple fabrication and easy handle of palygorskite, they are very promising to be used as a high-performance complexing agent for heavy metal removal.

#### ACKNOWLEDGEMENTS

This research was supported by the National Natural Science Foundation of China (No.5166803).

#### LITERATURE CITED

- Zeng, J.X., Ye, H.Q., Huang, N.D., Liu, J.F. & Zheng, L.F. (2009). Selective separation of Hg(II) and Cd(II) from aqueous solutions by complexation-ultrafiltration process. *Chemosphere* 76(5), 706–710. DOI: 10.1016/j.chemosphere.2009.05.019.
- Chew, C.M., Aroua, M.K. & Hussain, M.A. (2018). Advanced process control for ultrafiltration membrane water treatment system. *J. Cleaner Prod.* 179, 63–80. DOI: 10.1016/j.jclepro. 2018.01.075.
- Baharuddin, N.H., Sulaiman, N.M.N. & Aroua, M.K. (2015). Removal of zinc and lead ions by polymer-enhanced ultrafiltration using unmodified starch as novel binding polymer. *Internat. J. Environ. Science Technol.* 12(6), 1825–1834. DOI: 10.1007/s13762-014-0549-4.
- Desai, K.R. & Murthy, Z.V.P. (2014). Removal of Ag(I) and Cr(VI) by Complexation-Ultrafiltration and Characterization of the Membrane by CFSK Model. *Separ. Sci. Technol.* 49(17), 2620–2629. DOI: 10.1080/01496395.2012.690486.
- Abbasi-Garravand, E. & Mulligan, C.N. (2014). Using micellar enhanced ultrafiltration and reduction techniques for removal of Cr(VI) and Cr(III) from water. *Separ. Purific. Technol.* 132(34), 505–512. DOI: 10.1016/j.seppur.2014.06.010.
- Zhou, S., Xue, A., Zhao, Y., Wang, Q.W., Chen, Y., Li, M.S. & Xing, W.H. (2011). Competitive adsorption of  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Co}^{2+}$  ions on polyacrylamide/attapulgitite. *Desalination* 270(1), 269–274. DOI: 10.1016/j.desal.2010.11.055.
- Qiu, Y.R., Mao, L.J. & Wang, W.H. (2014). Removal of manganese from waste water by complexation-ultrafiltration using copolymer of maleic acid and acrylic acid. *Transactions of Nonferrous Metals Society of China*, 24(4), 1196–1201. DOI: 10.1016/S1003-6326(14)63179-4.
- Huang, Y., Wu, D., Wang, X., Huang, W., Lawless, D. & Feng, X.S. (2016). Removal of heavy metals from water using polyvinylamine by polymer-enhanced ultrafiltration and flocculation. *Separ. Purific. Technol.* 158(6), 124–136. DOI: 10.1016/j.seppur.2015.12.008.
- Malamis, S., Katsou, E., Kosanovic, T. & Haralambous, K.J. (2012). Combined adsorption and ultrafiltration processes employed for the removal of pollutants from metal plating wastewater. *Separ. Sci. Technol.* 47(7), 983–996. DOI: 10.1080/01496395.2011.645983.
- Chavan, M. (2015). Mathematical modelling for removal of mixture of heavy metal ions from waste-water using micellar enhanced ultrafiltration (MEUF) process. *Separ. Sci. Technol.* 50(3), 365–372. DOI: 10.1080/01496395.2014.973515.
- Fenelon, V.C., Miyoshi, J.H., Mangolim, C.S., Noce, A.S., Koga, L.N. & Matioliet, G. (2018). Different strategies for cyclodextrin production: Ultrafiltration systems, CGTase immobilization and use of a complexing agent. *Carbohydr. Polym.* 192, 19–27. DOI: 10.1016/j.carbpol.2018.03.035.
- Khosa, M.A., Shah, S.S. & Feng, X. (2014). Thermodynamic functions of metal-sericin complexation in ultrafiltration study. *J. Membrane Sci.* 470(23), 1–8. DOI: 10.1016/j.memsci.2014.06.056.
- Zhou, S., Xue, A., Zhang, Y., Li, M.S., Li, K., Zhao, Y.J. & Xing, W.H. (2015). Novel polyamidoamine dendrimer-functionalized palygorskite adsorbents with high adsorption capacity for  $\text{Pb}^{2+}$ , and reactive dyes. *Appl. Clay Sci.* 107, 220–229. DOI: 10.1016/j.clay.2015.01.032.
- Khalid, M., Usman, M., Siddiq, M., Rasool, N., Saif, M.J., Imran, M. & Rana, U.A. (2015). Removal of Ni(II) from aqueous solution by using micellar enhanced ultrafiltration. *Water Sci. Technol. A: J. Internat. Associ. Water Pollut. Res.* 72(6), 946–951. DOI: 10.2166/wst.2015.216.
- Chavan, M. (2015). Mathematical modelling for removal of mixture of heavy metal ions from waste-water using micellar enhanced ultrafiltration (MEUF) process. *Separ. Sci. Technol.* 50(3), 365–372. DOI: 10.1080/01496395.2014.973515.
- Jana, S., Saikia, A., Purkait, M.K. & Mohantya, K. (2011). Chitosan based ceramic ultrafiltration membrane: Preparation, characterization and application to remove Hg(II) and As(III) using polymer enhanced ultrafiltration. *Chem. Engin. J.* 170(1), 209–219. DOI: 10.1016/j.cej. 2011.03.056.
- Karate, V.D. & Marathe, K.V. (2008). Simultaneous removal of nickel and cobalt from aqueous stream by cross flow micellar enhanced ultrafiltration. *J. Hazard. Mater.* 157(2), 464–471. DOI: 10.1016/j.jhazmat.2008.01.013.
- Korus, I. & Loska, K. (2009). Removal of Cr(III) and Cr(VI) ions from aqueous solutions by means of polyelectrolyte-enhanced ultrafiltration. *Desalination* 247(1–3), 390–395. DOI: 10.1016/j.desal. 2008.12.036.
- Khosa, M.A., Shah, S.S. & Feng, X. (2014). Metal sericin complexation and ultrafiltration of heavy metals from aqueous solution. *Chem. Engin. J.* 244(10), 446–456. DOI: 10.1016/j.cej. 2014.01.091.
- Jawor, A. & Hoek, E.M. (2010). Removing cadmium ions from water via nanoparticle-enhanced ultrafiltration. *Environ. Sci. Technol.* 44(7), 2570–2576. DOI: 10.1021/es902310e.
- Feng, Y., Wang, Y., Wang, Y., Liu, S.C., Jiang, J.L., Cao, C.G. & Yao, J.F. (2017). Simple fabrication of easy handling millimeter-sized porous attapulgitite/polymer beads for heavy metal removal. *J. Colloid Interf. Sci.* 502, 52–58. DOI: 10.1016/j.jcis.2017.04.086.
- Liu, Y., Xu, J.X., Wang, W.B. & Wang, A.Q. (2014). Effects of sodium salts organic acids modification on the microstructure and dispersion behavior of palygorskite nanopowder via high-pressure homogenization process. *J. Disper. Sci. Technol.* 35(6), 840–847. DOI: 10.1080/01932691.2013.818547.
- Wang, W. & Wang, A. (2010). Nanocomposite of carboxymethyl cellulose and attapulgitite as a novel pH-sensitive superabsorbent: Synthesis, characterization and properties. *Carbohydr. Polym.* 82(1), 83–91. DOI: 10.1016/j.carbpol.2010.04.026.
- Zhou, S., Xue, A., Zhao, Y., Wang, Q.W., Chen, Y., Li, M.S. & Xing, W.H. (2011). Competitive adsorption of  $\text{Hg}^{2+}$ ,



- Pb<sup>2+</sup> and Co<sup>2+</sup> ions on polyacrylamide/attapulgit. *Desalination* 270(1), 269–274. DOI: 10.1016/j.desal.2010.11.055.
25. Lam, B., Déon, S., Morin-Crini, N., Crini, G. & Fievet, P. (2018). Polymer-enhanced ultrafiltration for heavy metal removal: Influence of chitosan and carboxymethyl cellulose on filtration performances. *J. Cleaner Prod.* 171, 927–933. DOI: 10.1007/s10311-018-00818-0.
26. Niu, Y.N., Yuan, Y., Gao, W.X., Qian, S. & Sun, W. (2018). Adsorption of Cu(II) from aqueous solution on sulfuric acid treated palygorskite. *IOP Conference Series: Mater. Sci. Engin.* 322(4), 2021–2027. DOI: 10.1088/1757-899X/322/4/042021.
27. Cañizares, P., Pérez, A., Camarillo, R. & Mazarrob, R. (2008). Simultaneous recovery of cadmium and lead from aqueous effluents by a semi-continuous laboratory-scale polymer enhanced ultrafiltration process. *J. Membrane Sci.* 320(1–2), 520–527. DOI: 10.1016/j.memsci.2008.04.043.
28. Chakraborty, S., Dasgupta, J., Farooq, U., Sikder, J., Drioli, E. & Curcio, E. (2014). Experimental analysis, modeling and optimization of chromium(VI) removal from aqueous solutions by polymer-enhanced ultrafiltration. *J. Membrane Sci.* 456(c), 139–154. DOI: 10.1016/j.memsci.2014.01.016.
29. Yu, J.H., Chou, Y.H., Liang, Y.M. & Li, C.W. (2015). Integration of polyelectrolyte enhanced ultrafiltration and chemical reduction for metal-containing wastewater treatment and metal recovery. *Water Sci. Technol.* 72(7), 1096–101. DOI: 10.2166/wst.2015.315.
30. El-Sonbati, A.Z., Diab, M.A., El-Bindary, A.A., Eldesoky, A.M. & Morgan, Sh.M. (2015). Correlation between ionic radii of metals and thermal decomposition of supramolecular structure of azodye complexes. *Spectrochim. Acta Part A: Molec. Biomol. Spectrosc.* 135, 774–791. DOI: 10.1016/j.saa.2014.07.055.
31. Huang, J., Lei, P., Zeng, G., Li, X., Zhao, Y., Liu, L. X., Li, F. & Chai, Q. (2014). Evaluation of micellar enhanced ultrafiltration for removing methylene blue and cadmium ion simultaneously with mixed surfactants. *Separ. Purific. Technol.* 125(14), 83–89. DOI: 10.1016/j.seppur.2014.01.020.
32. Zamariotto, D., Lakard, B., Fievet, P. & Fatin-Rouge, N. (2010). Retention of Cu(II)-and Ni(II)-polyaminocarboxylate complexes by ultrafiltration assisted with polyamines. *Desalination* 258(1), 87–92. DOI: 10.1016/j.desal.2010.03.040.
33. Mbareck, C., Nguyen, Q.T., Alaoui, O.T. & Barillier, D. (2009). Elaboration, characterization and application of polysulfone and polyacrylic acid blends as ultrafiltration membranes for removal of some heavy metals from water. *J. Hazard. Mater.* 171(1), 93–101. DOI: 10.1016/j.jhazmat.2009.05.123.
34. Goh, P.S., Ng, B.C., Lau, W.J. & Ismail, A.F. (2015). Inorganic Nanomaterials in Polymeric Ultrafiltration Membranes for Water Treatment. *Separ. Purific. Rev.* 44(3), 216–249. DOI: 10.1080/15422119.2014.926274.
35. Huang, J.H., Zeng, G.M., Zhou, C.F., Li, X., Shi, L.J. & He, S.B. (2010). Adsorption of surfactant micelles and Cd<sup>2+</sup>/Zn<sup>2+</sup> in micellar-enhanced ultrafiltration. *J. Hazard. Mater.* 183(1–3), 287–293. DOI: 10.1016/j.jhazmat.2010.07.022.
36. Sekulić, Z., Antanasijević, D., Stevanović, S. & Trivunac, K. (2019). The prediction of heavy metal permeate flux in complexation-microfiltration process: polynomial neural network approach. *Water Air Soil Pollution* 230(1), 23–45. DOI: 10.1007/s11270-018-4072-y.
37. Yeh, H.M., (2013), Mass transfer in cross-flow parallel-plate dialyzer with internal recycle for improved performance. *Membrane Water Treatment.* 4(4), 251–263. DOI: 10.1080/00986445.2011.560517.
38. Wan, P., Zhang, Z. & Deng, B. (2019). Photocatalytic polysulfone hollow fiber membrane with self-cleaning and antifouling property for water treatment. *Industrial Engin. Chem. Res.* 58(8), 3339–3348. DOI: 10.1021/acs.iecr.8b05783.
39. Ho, C.D., Sung, Y.J., Chen, W.T. & Tsai, F.C. (2017). Performance improvement of countercurrent-flow membrane gas absorption in a hollow fiber gas-liquid membrane contactor. *Membrane Water Treatment* 8(1), 35–50. DOI: 10.12989/mwt.2017.8.1.035.