

# The Adsorption of Coexisting Heavy Metal Ions by Modified Chinese Walnut Shell

Chunguang Yu<sup>a</sup>, Xuena Han

Harbin Commercial University, Harbin 150028, China.

<sup>a</sup>spring\_sun2015@qq.com

**Keywords:** coexisting metal ions, Wastewater; Chinese Walnut Shell

**Abstract:** This study using modified Chinese Walnut Shell (MCWS) to contain  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cr}^{6+}$  mixed solution for processing. The result through coexisting metal ions adsorption experiment confirmed the MCWS adsorption  $\text{Cr}^{6+}$ ,  $\text{Cu}^{2+}$ , the optimal condition of  $\text{Hg}^{2+}$  and  $\text{Cd}^{2+}$ : pH between 5.0 to 7.0; The best initial concentration of 25 mg/L; The best mixed metal adsorption temperature 30°C; The best adsorbent mass is 3 g/L.

## Introduction

It is reported that removing single heavy metal ion in aqueous solution has been a lot of research<sup>[1-4]</sup>. But for the coexistence of two or more than two kinds of heavy metal ion solution is studied less. In actual wastewater, it is mostly in the coexistence of a variety of metal ions. Mixed metal ions adsorption between condition is more complex, have promote interaction between adsorption and inhibitory effect of adsorption, no effect<sup>[5; 6]</sup>. Promote adsorption refers to the presence of other metals is better than a single metal adsorption effect, inhibition refers to the existence of a variety of metal adsorption effect than single metal adsorption effect is poor; No action refers to a variety of metal is little influence on the effect of the adsorption<sup>[7; 8]</sup>.

The influence of metal ion coexist basically has the following kinds<sup>[9]</sup>: (1) promoting effect: after mixing the adsorption quantity is greater than the single component adsorption of mixed before; (2) brake: after mixing the adsorption quantity of adsorption amount is less than before the hybrid components; (3) zero (not the role): after adsorption and mix before the adsorption quantity of the same. So the coexistence of a variety of metal ion state biological adsorption performance is very necessary<sup>[10; 11]</sup>. The adsorption mechanism of mixed metal complex, adsorption behavior by the initial concentration of metal ions, the form of the metal ions, pH of solution and influence factors such as physical and chemical characteristics of adsorbent<sup>[12; 13]</sup>. It is only for some factors were studied.

This experiment using MCWS for agent adsorption to simulate the water absorption of four kinds of heavy metal ions  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cr}^{6+}$ . The influential factors of the effect of mixed metal adsorption were studied, such as pH, initial concentration, temperature, modification of pecan shell mass, etc.

## Material and Methods

The Chinese Walnut Shell (CWS) was obtained from market in Harbin, China. CWS was modified by mixed HCl and  $\text{HNO}_3$  to 3:1, was washed by deionized water to remove dust and soluble material and then dried at 110°C for 2 hours. The dried CWS was crushed into a fine powder in a still mill. The resulting material was sifted through the 80-mesh standard sieve.

The concentration of ions in solution was determined by the Atomic Absorption Spectrometer. Fourier Transform Infrared experiment was conducted to determine the surface functional groups of MCWS that might be relevant to ions adsorption. The pH of solution was measured with a Sartorius pH meter.

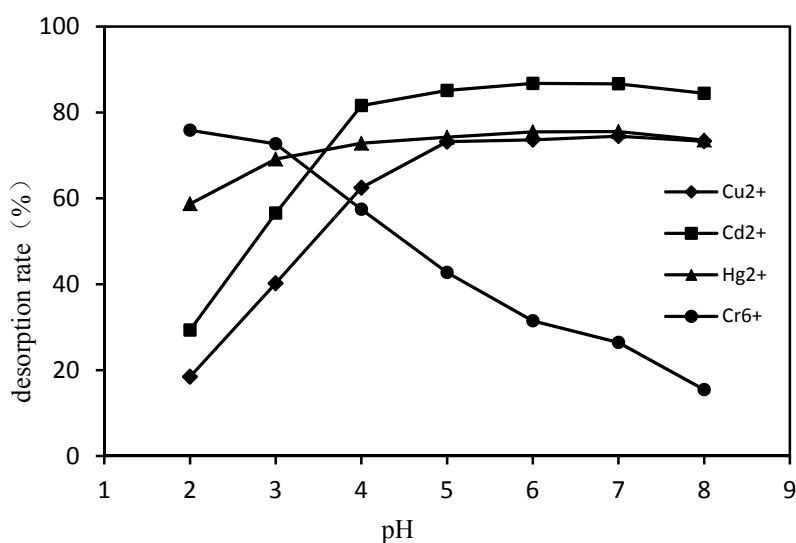
## Result and Discussion

### The effect of pH

In the process of adsorption, pH is one of the important influence factors<sup>[14; 15]</sup>. In general, metal removal is increased with the increase of pH. PH can affect the degree of protonation of adsorbent and the adsorbent surface features, and the precipitation of metals can be determined. Solution of ionization degree affected by pH, adsorbent surface charge, there are a lot of hydroxyl groups on the chemical reactions will cause the change of the charge.

The form of Heavy metal ions existed in solution depending on pH. It is reported pH can affect the reactive group on the modified pecan shell. Take  $\text{Cr}^{6+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$  concentration are 25 mg/L, the solution with HCL and NaOH solution pH adjustment were 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, under 30°C, the adsorption of 90 min, adsorption results as shown in figure 1.

Fig.1 Effect of pH on the adsorption of mixed metal solution



It can be seen from the table, the pH between 5.0, 7.0, adsorption rate of  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$  is higher than  $\text{Cr}^{6+}$ , and the change is not big, the maximum adsorption rate were 74.48%, 74.56% and 84.48% respectively. Relative to the single metal  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Cd}^{2+}$  the biggest adsorption rate (80.44%, 92.39%, 95.64%), and fell. And the adsorption rate of  $\text{Cr}^{6+}$  ions with pH increase and decrease, the adsorption rate of the presence of  $\text{Cr}^{6+}$  ions adsorption rate also fell, the adsorption rate was between 15.46% and 75.86%. In the pH = 5.0, the adsorption rate was 42.74%. Mixed metal solution between the adsorption rate of decline may be the cause of metal ions have mutual inhibition effect, reduces the adsorption sites. Another solution of  $\text{H}^+$  and under the condition of the acid active group - COOH, - OH, will also hinder the  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Cd}^{2+}$ ,  $\text{Cr}^{6+}$  adsorption. Because in the case of high pH,  $\text{H}_3\text{O}^+$  ions and metal ions, less competition, modification of pecan shell more provided to metal ions adsorption sites. In the actual wastewater, as a result of a pH fluctuations

### The effect of initial concentration

Metal ions removal and closely related to the initial concentration of metal ions. Take  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cr}^{6+}$ ,  $\text{Cd}^{2+}$  metal ions mixed solution, four kinds of metal concentration in the same 25 mg/L, respectively, 50 mg/L, 100 mg/L, 120 mg/L, 150 mg/L. Experimental results as shown in figure 6 to 11, along with the increase of the initial concentration of the metal ions, the adsorption rate is reduced,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Cd}^{2+}$  ions in the initial concentration of 25 mg/L, the adsorption rate is maximum, division of 72.13%, 74.98%, 85.26%.  $\text{Cr}^{6+}$  adsorption rate increased with the increase of initial concentration decreased the amplitude of the previous three metals much more, the rather than a single metal under the condition of adsorption rate has a similar trend. Among them, when the initial concentration of 25 mg/L, the adsorption rate is only 45.24%, but considering comprehensive adsorption rate of four kinds of metal, so make sure  $\text{Cr}^{6+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$  mixed

ion initial concentration of 25 mg/L for the study of the reasonable conditions. When the initial metal ion concentration increases, the  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Cd}^{2+}$  metal ions adsorption rate has dropped sharply, possible reason is four

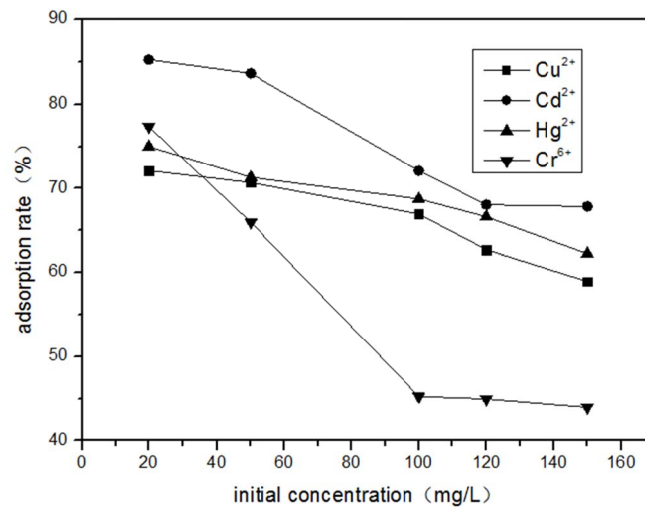


Fig.2 Effect of initial concentration on adsorption efficiency of mixed metal

### The effect of temperature

Temperature is one of the factors affecting the adsorption effect, but its influence is not obvious. This experiment within the temperature range of 15-35 °C, with different  $\text{Cr}^{6+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$  mixed ion initial concentration (10-100 mg/L, pH5.0, adsorbent dosage is 3 g/L, in 150 r/min under oscillation adsorption 120 min) were studied. After the adsorption Modified pecan shell of  $\text{Cr}^{6+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$  mixed ion adsorption rate changing with temperature is shown in figure 6 and 12. It can be seen that mixed metal ions adsorption rate increases with temperature rise,  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  ions adsorption curve in 35°C maximum adsorption rate and adsorption rate of the relative single metal solution, maximum adsorption rate is less,  $\text{Cu}^{2+}$  ions adsorption rate from 88.75% to 86.26%,  $\text{Cd}^{2+}$  ions adsorption rate from 81.15% to 80.4%, while  $\text{Hg}^{2+}$  maximum adsorption rate in 30°C, larger decline, from 82.75% to 82.75%. Three metal adsorption process of coexistence, may exist between ion competition, inhibited the adsorption of various kinds of metal

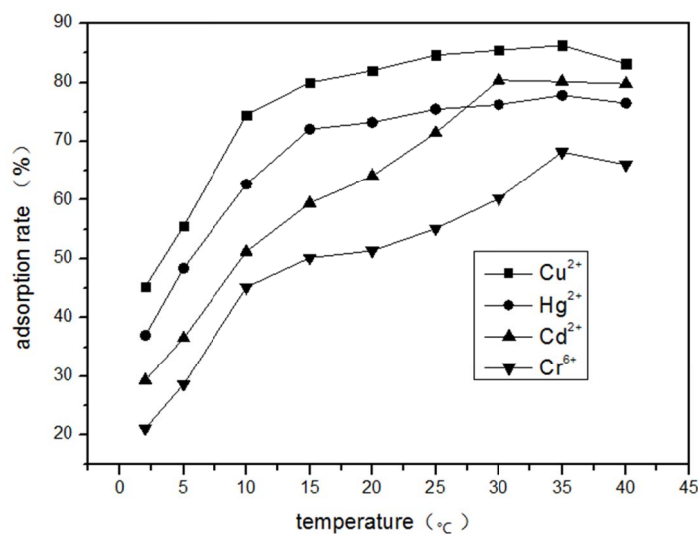


Fig.3 Effect of temperature on adsorption of mixed metal

## The effect of dose

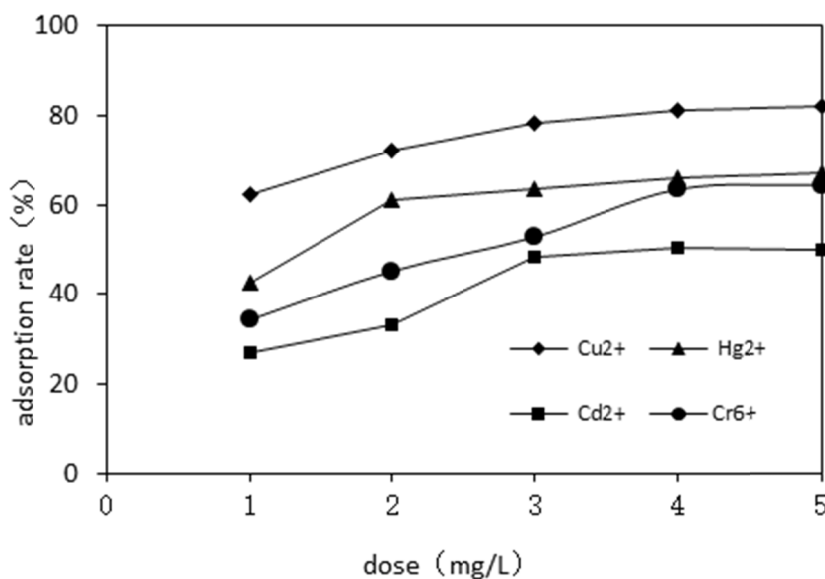


Fig.4 Effect of dosage of MCWS on adsorption of mixed metal solution

It is shown that  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$  ions of initial concentration of 25, 100 mg/L respectively, pH 5.0. Experimental results of the different modified pecan shell mass as shown in figure 4. Results show that with the increment of adding performance-altered pecan shell, all kinds of modified pecan shell with initial concentration, the adsorption of  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$  efficiency with increased. But increase the amplitude of slow, especially when the amount of modified pecan shell reaches 3 g/L, the adsorption rate is almost no growth. So make sure the 3 g/L for modification of the best mass pecan shell adsorption  $\text{Hg}^{2+}$  ions.

## Conclusion

The coexisting metal ions adsorption experiment confirmed the MCWS adsorption  $\text{Cr}^{6+}$ ,  $\text{Cu}^{2+}$ , the optimal condition of  $\text{Hg}^{2+}$  and  $\text{Cd}^{2+}$ : pH between 5.0 to 7.0; The best initial concentration of 25 mg/L; The best mixed metal adsorption temperature 30°C; The best adsorbent mass is 3 g/L.

## Acknowledgements

The authors thank The Doctor Research Projects of Harbin commercial university (Project Number: 13DL009) for the financial support to this project.

## References

- [1] Graillot A, Cojocariu C, Bouyer D, et al. Thermosensitive polymer Enhanced Filtration (TEF) process: An innovative process for heavy metals removal and recovery from industrial wastewaters[J]. Separation and Purification Technology, 2015, 141(0): 17-24.
- [2] Al-Harashsheh M S, Al Zboon K, Al-Makhadmeh L, et al. Fly ash based geopolymer for heavy metal removal: A case study on copper removal[J]. Journal of Environmental Chemical Engineering, 2015, 3(3): 1669-1677.
- [3] Bi N, Yang Z, Wang H, et al. Impact of artificial water and sediment discharge regulation in the Huanghe (Yellow River) on the transport of particulate heavy metals to the sea[J]. CATENA, 2014, 121(0): 232-240.
- [4] Mizzouri N S, Shaaban M G. Individual and combined effects of organic, toxic, and hydraulic shocks on sequencing batch reactor in treating petroleum refinery wastewater[J]. Journal of hazardous materials, 2013, 250-251(0): 333-344.

- [5]Aldor I, Fourest E, Volesky B. Desorption of Cadmium from Algal Biosorbent[J]. Canadian Journal of Chemical Engineering, 1995, 73(4): 516-522.
- [6]Kaewsarn P, Yu Q M, Ma W D. Interference of co-ions in biosorption of  $\text{Cu}^{2+}$  by biosorbent from marine alga *Durvillaea potatorum*[J]. Environmental Engineering Science, 2001, 18(2): 99-104.
- [7]Kratochvil D, Pimentel P, Volesky B. Removal of trivalent and hexavalent chromium by seaweed biosorbent[J]. Environmental Science & Technology, 1998, 32(18): 2693-2698.
- [8]Gupta V K, Gupta M, Sharma S. Process development for the removal of lead and chromium from aqueous solutions using red mud - an aluminium industry waste[J]. Water Research, 2001, 35(5): 1125-1134.
- [9]Tamilselvan N, Saurav K, Kannabiran K. Biosorption of Cr(IV),Cr(III),Pb( II ) and Cd( II ) from Aqueous Solutions by *Sargassum wightii* and *Caulerpa racemosa* Algal Biomass[J]. Journal of Ocean University of China, 2012, v.11(01): 52-58.
- [10]Salinas E, De Orellano M E, Rezza I, et al. Removal of cadmium and lead from dilute aqueous solutions by *Rhodotorula rubra*[J]. Bioresource Technology, 2000, 72(2): 107-112.
- [11]Bandosz T J, Bagreev A, Bashkova S, et al. Sewage sludge-derived materials as efficient adsorbents for removal of hydrogen sulfide[J]. Environmental Science & Technology, 2001, 35(7): 1537-1543.
- [12]Zheng H, Geng T M, Hu L M. Selective Solid-phase Extraction of Hg(II) Using Silica Gel Surface - Imprinting Technique[J]. Chemia Analityczna, 2008, 53(5): 673-687.
- [13]Han R P, Zhu L, Zou W H, et al. Removal of copper(II) and lead(II) from aqueous solution by manganese oxide coated sand - II. Equilibrium study and competitive adsorption[J]. Journal of Hazardous Materials, 2006, 137(1): 480-488.
- [14]Lee S M, Kim W G, Laldawngliana C, et al. Removal Behavior of Surface Modified Sand for Cd(II) and Cr(VI) from Aqueous Solutions[J]. Journal of Chemical and Engineering Data, 2010, 55(9): 3089-3094.
- [15]Chen B L, Yuan M X, Liu H. Removal of polycyclic aromatic hydrocarbons from aqueous solution using plant residue materials as a biosorbent[J]. Journal of hazardous materials, 2011, 188(1-3): 436-442.