

# The Effect of Coexisted Cu(II), Ni(II), Zn(II) on the Removal of Cr(VI) in Wastewater by Tetraethylenepentamine-Functionalized Fe<sub>3</sub>O<sub>4</sub> Magnetic Polymers

H. Y. Shen<sup>1,\*</sup>, Y. Zhang<sup>1,2</sup>, Q. F. Mao<sup>1</sup>, Y. G. Zhao<sup>1</sup>, S. D. Pan<sup>1,2</sup>

**Abstract** – In this study, the tetraethylenepentamine (TEPA) functionalized, core-shell structured, nano magnetic polymer adsorbents (TEPA-NMPs) have been used for the removal of Cr(VI) from aqueous solution in the presence of Cu(II), or Ni(II), or Zn(II) ions. Batch adsorption studies were carried out to evaluate the effect of the co-existing ions on its adsorption properties to Cr(VI). The results showed that the maximum adsorption capacity ( $q_m$ ) of Cr(VI) was found to be 263 mg·g<sup>-1</sup>, 333 mg·g<sup>-1</sup>, 354 mg·g<sup>-1</sup> at temperature of 35°C and pH value at 2.0, when 50 mg·L<sup>-1</sup> Cu(II), or Ni(II), or Zn(II) was added to Cr(VI) solutions, which was ~29%, ~10%, and 4.4% decreased than that free of these ions ( $q_m = 370.4$  mg·g<sup>-1</sup>).

The adsorption mechanism of adsorbents to Cr(VI) coexisted with Cu(II) was deeply studied via FTIR. Presumed mechanism of the competition of Cu(II), or Ni(II), or Zn(II) with Cr(VI) was proposed. Copyright © 2012 Praise Worthy Prize S.r.l. - All rights reserved.

**Keywords:** Adsorption Mechanism, Coexisting Ions, Cr(VI), Maximum Adsorption Capacity, Tetraethylenepentamine-Functionalized Magnetic Polymers (TEPA-Nmps)

## I. Introduction

Wastewater generated from industries, including electroplating, printed circuit, metal finishing, and dye manufacturing, et al., always contains variable levels of Cr(VI), Cu(II), Zn(II), or Ni(II), etc [1]. Most of these metal ions have been placed on the top of the priority list of toxic pollutants by the U. S. EPA. Some of them act as carcinogens, mutagens and teratogens in biological systems [2], [3], [4]. Therefore, treatment of industry wastewater containing these metal ions prior to discharge is essential [5], [6], [7], [8].

Recently, magnetic adsorption was found to be a conventional but efficient technique to remove metal ions from wastewater [9].

The magnetic nano-particles possess the advantages of large surface area, high number of surface active sites, and favorable magnetic properties, which lead to high adsorption efficiency and high removal rate of contaminants.

The incomparable rapid separation of adsorbent from solution property can be easily realized via magnetic field, which can overcome the separation difficulties in industry wastewater treatment. Moreover, the adsorbents can be reusable after magnetic separation by the external magnetic field [9], [10], [11]. In our previous work, we reported a kind of core-shell structured tetraethylenepentamine (TEPA)-functionalized nano magnetic polymer adsorbents, named as TEPA-NMPs with maximum adsorption capacity of TEPA-NMPs to Cr(VI) at 370.4 mg·g<sup>-1</sup> [12].

Since there are unavoidable some coexisted ions, e.g., Cu(II), Zn(II), and Ni(II) ions, et al. in wastewater system, whether or not the adsorption properties of TEPA-NMPs would be affected by these coexisting ions should be taken into account prior to apply in real sample system. In this work, the effect of coexisting Cu(II), Zn(II), and Ni(II) ions on the removal of Cr(VI) from wastewater were studied by laboratory batch tests. Some promising results were obtained.

## II. Experiments

### II.1. Synthesis and Characterization of TEPA-NMPs

The tetraethylenepentamine (TEPA) functionalized magnetic polymers (TEPA-NMPs) have been prepared via suspension polymerization according to our previous reported procedures [12], [13], named as TEPA-NMPs *infra*. The preparation procedure was illustrated in Fig. 1.

The TEM revealed that the TEPA-NMPs were multi-dispersed with an average diameter of around 30 nm [14]. The saturation moment was found to be 3.79 emu·g<sup>-1</sup> by VSM studies. The XRD patterns of TEPA-NMPs showed six characteristic peaks of Fe<sub>3</sub>O<sub>4</sub> at  $2\theta$  of 30.1°, 35.5°, 43.1°, 53.4°, 57.0° and 62.6° corresponding to their indices (220), (311), (400), (422), (511) and (400). It revealed that chemical modification of the magnetic cores did not make significant changes in the phase property of Fe<sub>3</sub>O<sub>4</sub> cores [15]. In the IR spectra of TEPA-NMPs, the characteristic absorptions of C=O groups at ~1730 cm<sup>-1</sup>, C-O-C groups at ~1265 cm<sup>-1</sup> and ~1149 cm<sup>-1</sup> and -NH-

and  $\text{-NH}_2$  groups at  $\sim 1576\text{ cm}^{-1}$  and  $\sim 3365\text{ cm}^{-1}$  appeared. This revealed that the epoxy- of co-poly (MMA-GMA) had been functionalized successfully with the amino groups *via* ring-opening reaction. The nitrogen percentage of TEPA-NMPs obtained from EA was 10.9%.

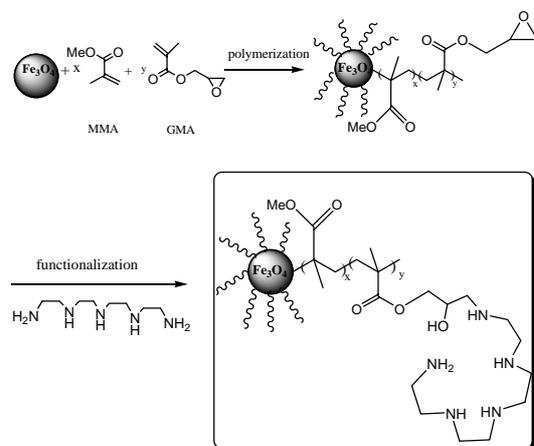


Fig. 1. Preparation procedure of TEPA-NMPs

## II.2. Adsorption Studies

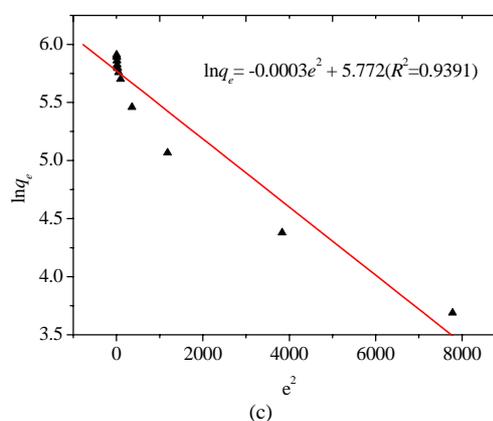
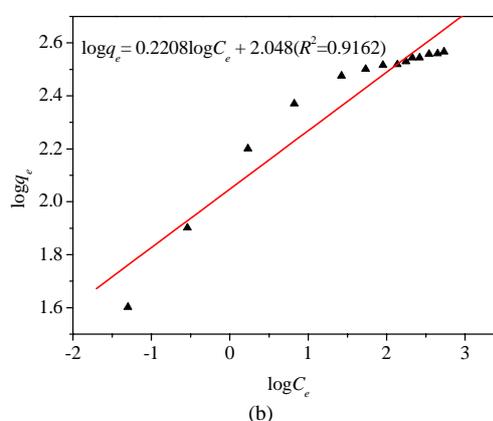
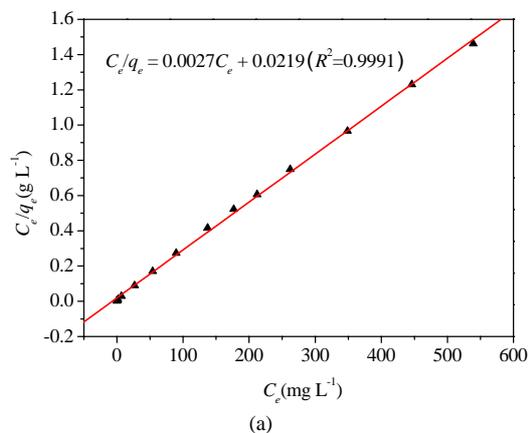
A stock solution of Cr(VI) at concentration range of  $50\text{--}1000\text{ mg}\cdot\text{L}^{-1}$  coexisted with  $50\text{ mg}\cdot\text{L}^{-1}$  Cu(II), Zn(II), Ni(II) was prepared by dissolving a known quantity of  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ , or  $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ ,  $\text{ZnCl}_2$  and  $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$  in ultrapure water.  $0.1\text{ M HCl}$  and  $0.1\text{ M NaOH}$  solutions were used for pH adjustment. Batch adsorption studies were performed by mixing  $0.05\text{ g}$  TEPA-NMPs with  $40\text{ mL}$  stock solution of varying concentration from  $50$  to  $1000\text{ mg}\cdot\text{L}^{-1}$  in a  $100\text{ mL}$  stopper conical flask with temperature of  $35\text{ }^\circ\text{C}$  and pH value at  $2.0$  for  $24\text{ h}$  to reach equilibrium. The concentration of Cr(VI) ions in the aqueous solution was analyzed with a spectrophotometer according to the standard method [16] at a wavelength of  $540\text{ nm}$  after acidification of samples with  $1\text{ N H}_2\text{SO}_4$  and reaction with 1, 5-diphenyl carbazide to produce a purple colour complex for colorimetric measurement. The concentration of Cu(II), Zn(II) and Ni(II) ions in the aqueous solution was analyzed with an atomic absorption spectrometer (AAS).

## III. Results and Discussion

### III.1. Equilibrium Adsorption Isotherms

Adsorption isotherms of TEPA-NMPs were obtained at temperature of  $35\text{ }^\circ\text{C}$  and pH value at  $2.0$  [12] by varying the initial concentration of Cr(VI) from  $50$  to  $1000\text{ mg}\cdot\text{L}^{-1}$ . Three kinds of models, e.g. Langumir [17], Freundlich and D-R [18] were used to fit the experimental data, shown in Figs. 2, (a) for Langumir, (b) for Freundlich and (c) for D-R mode, respectively. As it can be seen, the experimental data on adsorption from a liquid-phase fit the Langumir equation well, with  $R^2 = 0.9991$ , while fit unsatisfied with Freundlich ( $R^2 = 0.9162$ ) and D-R mode

( $R^2 = 0.9391$ ). This result showed that the adsorption of Cr(VI) ions occurs on a homogeneous surface by monolayer adsorption with  $q_m$  of Cr(VI) at  $370.4\text{ mg}\cdot\text{g}^{-1}$ .



Figs. 2. Langmuir adsorption isotherm (a), Freundlich adsorption isotherm (b), and Dubinin-Radushkevich adsorption isotherm (c) for Cr(VI) adsorption on TEPA-NMPs (pH at  $2.0$  and temperature at  $35\text{ }^\circ\text{C}$ )

### III.2. The Effect of the Coexisting Ions on the Adsorption of Cr(VI) on TEPA-NMPs

$40\text{ mL}$  of the initial concentration of Cr(VI) from  $50$  to  $1000\text{ mg}\cdot\text{L}^{-1}$  with coexisting Cu(II), or Zn(II), or Ni(II) ions, and all the three metal ions with pH value at  $2.0$  and

temperature of 35 °C were mixed with 0.05 g TEPA-NMPs, and the results were shown in Fig. 3.

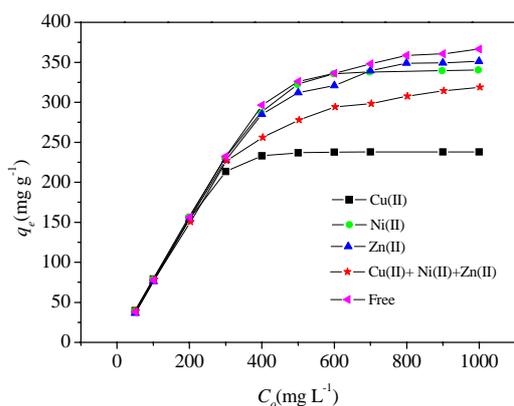


Fig. 3. The effect of coexisted metal ions on the adsorption of Cr(VI) on TEPA-NMPs

As shown in the Fig. 3, the adsorption capacity was highly affected by the coexisting ions. The suppression effect tendency of coexisting ions on the adsorption of Cr(VI) on TEPA-NMPs was in the order of Cu(II) > Ni(II) > Zn(II). The adsorption behaviors of the TEPA-NMPs to Cr(VI) was evaluated by Langmuir mode. The  $q_m$  of TEPA-NMPs to Cr(VI) was found to be 263  $\text{mg}\cdot\text{g}^{-1}$  (~29% decreased), 333  $\text{mg}\cdot\text{g}^{-1}$  (~10% decreased), 354  $\text{mg}\cdot\text{g}^{-1}$  (~4.4% decreased), when 50  $\text{mg}\cdot\text{L}^{-1}$  of Cu(II), or Ni(II), or Zn(II) coexisted, respectively, while the suppression percentage reached to ~13% when all the three kinds of the ions coexisted simultaneously.

This phenomenon could be attributed to the fact that the coordination formation constants of the complication between Cu(II), or Ni(II), or Zn(II) and amino group (-NH<sub>2</sub>) were  $K_f$  [Cu(II)-NH<sub>2</sub>] >  $K_f$  [Ni(II)-NH<sub>2</sub>] >  $K_f$  [Zn(II)-NH<sub>2</sub>]. It was reported that the logarithm of the coordination formation constants between Cu(II), or Ni(II), or Zn(II) and ethylenediamine (en) (lgK) were 10.67, 7.52 and 5.77, respectively [19]. Thus, the complication ability of Cu(II) to amino group was much stronger than those of Ni(II) and Zn(II), which resulted in the suppression effect of Cu(II) ions on the adsorption of Cr(VI) on TEPA-NMPs was much higher than those of Ni(II) and Zn(II) ions. According to the discussion above, the conclusion in our previous study of the adsorption mechanism of Cr(VI) on TEPA-NMPs related with coordination interactions could be proved [13], [20]. In the case of the initial concentration of Cr(VI) coexisted with all the three kinds of ions, the competition among the coexisting ions for the limited available adsorption sites would result in the adsorption of Cr(VI) on TEPA-NMPs were suppressed.

### III.3. The Effect of the Initial Concentration of Cu(II) on the Adsorption of Cr(VI) on TEPA-NMPs

Since the adsorption efficiency was highly affected by the coexisting Cu(II) ions, the effect of the initial

concentration of Cu(II) on the adsorption of Cr(VI) on TEPA-NMPs was intensively investigated at temperature of 35 °C and pH value at 2.0 by varying the initial concentration of Cr(VI) from 50 to 1000  $\text{mg}\cdot\text{L}^{-1}$  with the coexisting concentration of Cu(II) varied as 0, 10, 50, 100, 500  $\text{mg}\cdot\text{L}^{-1}$ , respectively.

The results were shown in Fig. 4. The adsorption behaviors of the TEPA-NMPs to Cr(VI) was evaluated by Langmuir mode. The  $q_m$  of TEPA-NMPs to Cr(VI) was found to be decreased from 370.4  $\text{mg}\cdot\text{g}^{-1}$  to 232.6  $\text{mg}\cdot\text{g}^{-1}$  with the increasing of the initial Cu(II) concentration. This is expected due to the fact that for a fixed adsorbent dosage, the total available adsorption sites are limited thus leading a decrease in the removal percentage of Cr(VI) (from ~21% to ~37%) with an increasing of the initial Cu(II) concentration from 10 to 500  $\text{mg}\cdot\text{L}^{-1}$ .

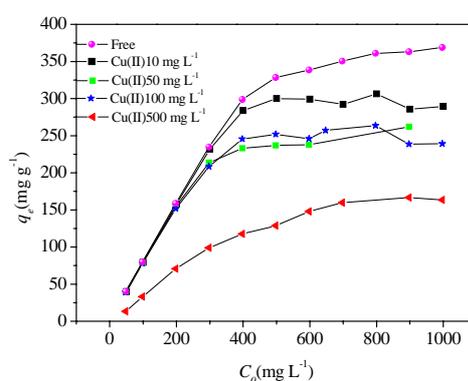


Fig. 4. The effect of the initial concentration of Cu(II) on the adsorption of Cr(VI) on TEPA-NMPs

### III.4. The FTIR of TEPA-NMPs Adsorbed with Cr(VI) and Coexisting Cu(II) Ions

To get further understanding of the adsorption mechanism, the FTIR (shown in Fig. 5) of TEPA-NMPs after adsorption to Cu(II) 500  $\text{mg}\cdot\text{L}^{-1}$  (a), Cu(II) 500  $\text{mg}\cdot\text{L}^{-1}$  and Cr(VI) 200  $\text{mg}\cdot\text{L}^{-1}$  (b), Cu(II) 500  $\text{mg}\cdot\text{L}^{-1}$  and Cr(VI) 800  $\text{mg}\cdot\text{L}^{-1}$  (c), Cr(VI) 1000  $\text{mg}\cdot\text{L}^{-1}$  (d), and TEPA-NMPs before adsorption (e) were recorded. Compared with the spectra of the TEPA-NMPs, before (Fig. 5 (e)) and after adsorption (Figs. 5, (a), (b), (c) and (d)), the characteristic bands at ~1575  $\text{cm}^{-1}$ , assigned to N-H groups, had been disappeared along with the appearance of the bands at ~1650  $\text{cm}^{-1}$ , which may be attributed to the formation of the N→Cr and N→Cu coordination bonds, subsequently weakened the N-H bonding and resulted in a large shift (~80  $\text{cm}^{-1}$ ).

This results furtherly supported our previous findings that the adsorption mechanism of adsorbents to Cr(VI) on TEPA-NMPs could be related with coordination interactions.

Besides, with the increase of initial concentration of Cr(VI), the characteristic bands at ~1150  $\text{cm}^{-1}$ , assigned to SO<sub>4</sub><sup>2-</sup> groups, had been disappeared gradually along with the appearance of the bands at ~940  $\text{cm}^{-1}$ , which may be attributed to HCrO<sub>4</sub><sup>-</sup> groups.

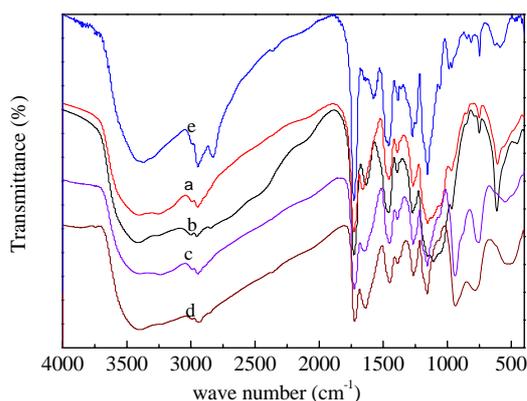


Fig. 5. The FTIR of TEPA-NMPs after adsorption to Cu(II) 500 mg·L<sup>-1</sup>(a), Cu(II) 500 mg·L<sup>-1</sup> and Cr(VI) 200 mg·L<sup>-1</sup>(b), Cu(II) 500 mg·L<sup>-1</sup> and Cr(VI) 800 mg·L<sup>-1</sup> (c), Cr(VI) 1000 mg·L<sup>-1</sup>(d), and TEPA-NMPs before adsorption (e)

This phenomenon could be explained that the SO<sub>4</sub><sup>2-</sup> groups adsorbed on TEPA-NMPs *via* electrostatic attraction were replaced by HCrO<sub>4</sub><sup>-</sup>, indicating the ion exchange happened in the adsorption of Cr(VI) [12].

#### IV. Conclusion

In this study, the effect of the coexisting cations, e. g., Cu(II), Ni(II) and Zn(II), on the adsorption Cr(VI) on the tetraethylenepentamine (TEPA) functionalized, nano magnetic polymer adsorbents (TEPA-NMPs) have been studied. The results showed that the adsorption of Cr(VI) on TEPA-NMPs could be suppressed by the coexisting cations in the order of Cu(II)>Ni(II)>Zn(II).

With the increasing of the initial Cu(II) concentration, the maximum adsorption capacities of Cr(VI) decreased from 370.4 mg·g<sup>-1</sup> to 294.1 mg·g<sup>-1</sup>, 263.2 mg·g<sup>-1</sup>, 243.9 mg·g<sup>-1</sup>, and 232.6 mg·g<sup>-1</sup>, when the coexisting Cu(II) concentration was 10 mg·L<sup>-1</sup>, 50 mg·L<sup>-1</sup>, 100 mg·L<sup>-1</sup>, 500 mg·L<sup>-1</sup>, respectively. The results furtherly supported that the adsorption mechanism of adsorbents to Cr(VI) on TEPA-NMPs could be related with electrostatic attraction, ion exchange and coordination interactions.

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#### Author's information

<sup>1</sup>Ningbo Institute of Technology, Zhejiang University. Ningbo, 315100, China.

<sup>2</sup>College of Science, Zhejiang University. Hangzhou, 310027, China. E-mail: [hyshen@nit.zju.edu.cn](mailto:hyshen@nit.zju.edu.cn)



**Prof. Shen** was born in China in Jan. 1971. Prof. SHEN gained her bachelor degree and master degree from Central China Normal University in 1993, and 1996, respectively. Then she gained her doctor degree in Nankai University in 1999. Prof. SHEN continued her post-doctorate research in Fudan University in 2001. Then she worked as a Research Fellow in Chemical Engineering and Process Center, and Institute of Chemical Engineering and Sciences, Singapore from 2002 to 2003. She is now a professor of Ningbo Institute of Technology, Zhejiang University. Her research interests are mainly focused on nano-magnetic material preparation and applications, green chemistry and environmental sciences. At present, she has published around one hundred papers in various journals for Chemical and Chemical Engineering field.

**Yun Zhang** is a master student. She earned her Bachelor degree in Qufu Normal University in 2010. And now she is studying in the Department of Chemistry, Zhejiang University. She majors the application of functionalized magnetic polymers for pollutants treatment in waste water.

**Qifeng Mao** was awarded a pharmaceutical engineering Bachelor degree at Ningbo Institute of Technology, Zhejiang University in 2010. And he is working for the research of drug synthesis.

**Yonggang Zhao** was awarded a Chemistry Master degree at the Zhejiang University in 2010. And now he is working in Ningbo municipal center for disease control & prevention. His research interest is on the preparation of materials and analytical chemistry.

**Shengdong Pan** was awarded a Chemistry Master degree at the Zhejiang University in 2012. And now he is working in Ningbo municipal center for disease control & prevention. He is interested in the preparation and application of nano-magnetic materials.