

Facile preparation of multiphosponic acid functionalised multi-walled carbon nanotubes for enhanced adsorption properties for heavy metal ions from wastewaters

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This work presents facile preparation processes of multiphosponic acid functionalised multi-walled carbon nanotubes (HEDP-MWCNTs and ATMP-MWCNTs), which have been characterised by FT-IR, XPS, X-ray diffraction, TGA, and SEM, and have employed for heavy metal ions adsorption. The adsorption properties of MWCNTs, HEDP-MWCNTs, and ATMP-MWCNTs for gold ions, cadmium ions, copper ions, lead ions, nickel ions, cobalt ions, zinc ions, and chromium ions have been investigated, the experimental results reveal that the functionalised samples HEDP-MWCNTs and ATMP-MWCNTs have excellent adsorption properties for Pb(II) and Au(III), respectively. The investigation results on their adsorption selectivity represent that in the binary heavy metal ion systems, HEDP-MWCNTs/ATMP-MWCNTs has displayed a strong affinity for Pb(II)/Au(III) and even could exhibit 100% selectivity while coexisting with copper ions, nickel ions, cobalt ions, zinc ions, chromium ions, or cadmium ions. Furthermore, the adsorption kinetics of HEDP-MWCNTs for Pb(II) and ATMP-MWCNTs for Au(III) have also been studied at different solution temperatures. All these research work results show that two novel functionalised adsorbents HEDP-MWCNTs and ATMP-MWCNTs have shown excellent adsorption properties for heavy metal ions and they can be used in wastewater treatment, especially for lead/gold ions removal.

1. Introduction: Nowadays, there are many diseases in the world caused by water pollution, among which the heavy metal pollution is one of the most serious environmental impacts. Release of heavy metal to the environment as a result of industrial activities may pose a serious threat to the ecosystems [1–3]. Polluted water containing heavy metal ions is introduced into farmlands accidentally in the process of irrigation and/or fertilisation, which not only makes the soil be contaminated, but also infiltrates into rivers or groundwater. Excessive presence of heavy metal ions in the biological chain ultimately endangers human life through the circulation of natural water. Heavy metal ions cannot easily be discharged in the case they enter human bodies along with the food chains [4–6], and they pose a very severe threat to human health due to their non-biodegradability and high toxicity. Thus, it is very urgent to remove the heavy metal ions from the polluted water sources.

There are several ways to remove heavy metal ions from aquatic systems, such as adsorption, oxidation, precipitation, electrochemical method and so on. Among these methods, adsorption is one of the most used techniques to treat heavy metal ions contaminated wastewaters, it is superior to other conventional methods because of its high-level effectiveness in removing heavy metal ions from wastewaters, the ready availability of adsorbents, the simple and amenable process, and the excellent recyclability [7–10]. For the above-mentioned reason, there is a strong research interest in developing the adsorbents that have high efficiency and selectivity for heavy metal ions removal, efficient adsorbents have become the decisive factor in the removal process of heavy metal ions, and many different types of adsorbents have been developed and used for the removal of heavy metal ions to obtain good removal performances, including manganese oxides [11–13], functionalised silica gel [14–17], activated carbon [18, 19], zeolite [20–22], chitosan [23–25], granular biomass [26] etc. Among them, carbon nanotubes (CNTs) have emerged to be excellent heavy metal ions adsorbents because of their unique chemical and physical properties, such as high surface area, tunable surface chemistry, and non-corrosive property [27–31]. Especially while some types of functional groups are added to their surface, the chemical

functionalisation could remarkably improve their adsorption capacity, adsorption selectivity to heavy metal ions because the removal of metal ions by CNTs adsorption is usually dominated by the surface complexation [32]. For example, diphenylcarbazide has been grafted onto the surface of CNTs, it is found that this type of modified CNTs could selectively adsorb and remove Cd(II) ions, and the removal efficiency for cadmium ions could reach 97% [33].

In this study, the paper mainly explores the facile preparation of HEDP-MWCNTs and ATMP-MWCNTs and their applications in the adsorption and removal of heavy metal ions. The multiphosponic acid functional groups are introduced on the surface of HEDP-MWCNTs and ATMP-MWCNTs, which could chelate effectively with heavy metal ions and thereby efficiently promote their adsorption properties for those ions. The adsorption performance of HEDP-MWCNTs and ATMP-MWCNTs is evaluated using batch experiment and their physiochemical properties are studied by characterisation techniques. The adsorption properties of HEDP-MWCNTs and ATMP-MWCNTs for heavy metal ions in the single/binary metal ion systems have been investigated, and the experimental research results reveal that they have excellent adsorption capacity and selectivity for Pb(II) and Au(III), respectively. Moreover, the adsorption kinetics of HEDP-MWCNTs for Pb(II) and ATMP-MWCNTs for Au(III) have also been studied at different solution temperatures.

2. Experimental procedure

2.1. Preparation of the adsorbents HEDP-MWCNTs and ATMP-MWCNTs: In this experiment, 2.5 g of the hydroxylated MWCNTs are firstly washed with distilled water and sonicated for 10 min, then treated with sulfuric acid and nitric acid. After the refluxing process for 4 h, the mixture is filtered and washed until the filtrate pH is close to 6, and then dried at 60°C. 20 ml of 50% HEDP (hydroxyethylidenediphosphonic acid)/ATMP (aminotrimethylenephosphonic acid) has been mixed with 5.0 g of treated MWCNTs, and they react at a temperature of 120°C for 4 h, then the samples are washed with distilled water until pH ≈ 6 and dried at 60°C. The prepared products are labelled as HEDP-MWCNTs and ATMP-MWCNTs, respectively.

The hydroxylated MWCNTs are chemically pure grade which has been provided by the Chinese Academy of Sciences Chengdu Organic Chemistry Co., Ltd. Other reagents are purchased from Sinopharm Chemical Reagent Co., Ltd. and of analytical grade.

2.2. Characterisations: Fourier transform infrared (FT-IR) spectroscopy has been utilised for functional group analysis on a Nicolet MAGNA-IR 550 spectrophotometer. The X-ray photoelectron spectroscopy (XPS) measurement has been made on a Perkin-Elmer PHI 550-ESCA/SAM photoelectron spectrometer operated at 10 kV and 30 mA. High-resolution XPS spectra are generated with the analyser pass energy set at 10 and 50 eV, respectively. The X-ray diffraction (XRD) patterns from 5.0° to 70.0° have been recorded with a Rigaku Max-2500VPC diffractometer using Cu-K α_1 radiation. Thermogravimetric analysis (TGA) has been carried out on a Netzsch STA 409, the functionalised MWCNTs have been heated in an N₂ atmosphere with a flow rate of 30 ml/min. The concentrations of the studied heavy metal ions are detected on a flame atomic absorption GBC-932A spectrophotometer. The SEM and The EDXAS of the samples are performed on a HITACH SU8010 analytical instrument.

2.3. Heavy metal ion adsorption measurements: Static adsorption experiment has been used to get the adsorption capacities of the pristine and derivatised MWCTNs for different heavy metal ions. The static adsorption experiments are conducted by mixing the prepared adsorbents (20.0 mg) with the solutions that contain heavy metal ions (20.0 ml). The mixture is equilibrated at 25°C for 24 h with the shaking method. Then the solutions are separated from the adsorbents and the concentration of metal ions is quantified by atomic absorption spectrometer.

The following formula has been used to compute the corresponding adsorption amount of these adsorbents Q (mg/g):

$$Q = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 and C_e are the concentrations in the initial solution and the equilibrium solution of the respective heavy metal ions(mg/ml); V and W represent the volume of the solution (ml) and the weight of the adsorbents used in the adsorption studies (g), respectively. During the experimental procedure, these studied systems are mixed at the speed of 150 r/min through a rotary shaker. Each adsorption experiment has been conducted in triplicates and the average value is adopted.

2.4. Investigations on the emulative adsorption for Pb(II)/Au(III): The prepared HEDP-MWCTNs/ATMP-MWCTNs (20.0 mg) has been mixed with the binary ions solutions (20.0 ml) containing equal initial concentrations (2.0 mmol/l) of Pb(II)/Au(III) and other simultaneously existing metal ions, and then these systems oscillate 16 h. After that, these solutions are separated from the adsorbents and the concentrations of metal ions have been detected by atomic absorption spectrometer.

2.5. Adsorption kinetics investigations: The adsorption kinetics of Pb(II)/Au(III) ion by the prepared adsorbents have been studied by mixing the prepared adsorbents (20.0 mg) with the solutions that contain heavy metal ions (20.0 ml) in a series of flasks at 15, 25, or 35°C with the initial concentration of Pb(II)/Au(III) being 1.5 mmol/l. At a certain time interval, the adsorbents are filtrated and the concentrations of Pb(II)/Au(III) have been measured.

3. Results and discussion: MWCNTs consist of a group of graphene sheets wrapped around themselves to form cylinders nested together [7]. The surface of the hydroxylated MWCNTs contains a large number of hydroxyl functional groups that can react with multiphosphonic acid HEDP/ATMP under the

above-mentioned experimental conditions. The introduction of the organophosphonic acid functional groups onto MWCNTs has very strong coordinating properties and they can chelate with heavy metal ions, and thereby enhance greatly adsorption properties of the adsorbents. FT-IR spectra of MWCNTs, HEDP-MWCNTs and ATMP-MWCNTs are shown in Fig. 1, which could be used to identify the chemical grafting of multiphosphonic acids on MWCNTs [34–35]. In Fig. 1, three broad and intense peaks around 3430 cm⁻¹ can be attributed to the O–H stretching vibration of hydroxyl groups. Comparing with the FT-IR spectrum of MWCNTs, the stretching vibration peaks of PO–(C) located at 910 and 1064 cm⁻¹ and the adsorption peak of P=O at 1165 cm⁻¹ are detected in the spectrum of HEDP-MWCNTs. Similarly, the stretching vibration peaks of PO–(C) at 931 and 1079 cm⁻¹ and the adsorption peak of P=O at 1184 cm⁻¹ are also observed in the spectrum of ATMP-MWCNTs. These results indicate that the organophosphonic acid groups have been successfully grafted onto MWCNTs.

Further efforts are required to confirm the chemical modification of organophosphonic acids on the surface of MWCNTs; therefore, the X-ray photoelectron spectroscopy (XPS) has been performed on the two adsorbent samples. XPS spectra of HEDP-MWCNTs and ATMP-MWCNTs are displayed in Fig. 2. An overview investigation of the peaks in the XPS spectrum of HEDP-MWCNTs (Fig. 2a) indicates the presence of carbon, oxygen, and phosphorus. The main carbon peak at 283.24 eV can be attributed to the C–C bond from the CNT skeleton [34]. Further analysis of the individual phosphorus peaks by high-resolution XPS (Fig. 2a (inset)) shows that the P 2p peak at 132.22 eV [34, 36] constitutes 3.08% of atomic concentration, which can be assigned to phosphorus from P–(C, O) of the phosphonate groups on the HEDP-MWCNTs. XPS of ATMP-MWCNTs (Fig. 2b) is similar to that of HEDP-MWCNTs, but the amount of aminotrimethylenephosphonic acid functional groups are small, and phosphorus spectrum is weak and not labelled in its full survey scan spectrum. And its binding energies of P 2p at is 132.17 eV (Fig. 2b (inset)), and the atomic concentration of phosphorus is 0.44%, indicating aminotrimethylenephosphonic acid functional groups have been grafted successfully onto the surface of MWCNTs, which is in good agreement with the result of FT-IR analysis. Therefore, both FT-IR and XPS characterisation results have confirmed the presence of phosphonic acid functional groups in HEDP-MWCNTs and ATMP-MWCNTs, and the successful incorporation of the organophosphonate functional groups onto the MWCNTs.

Fig. 3 represents the XRD patterns of MWCNTs, HEDP-MWCNTs and ATMP-MWCNTs, the diffraction peaks observed for all these three samples at $2\theta=26.0^\circ$ are corresponded to carbon structure [37], and there is no new diffraction peak appeared after the facile preparation reaction processes. This indicates that the

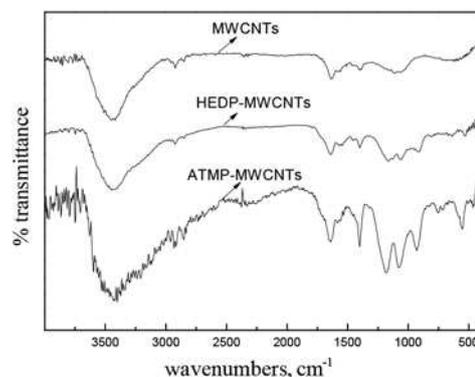
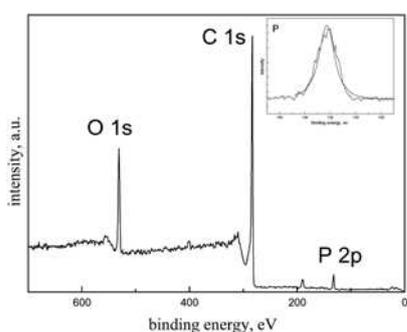
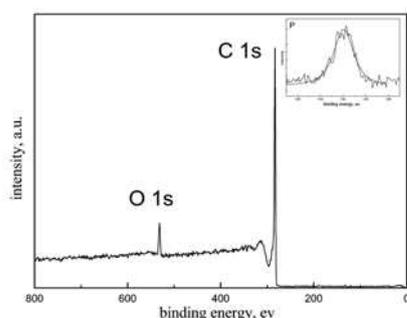


Fig. 1 FT-IR spectra of MWCNTs, HEDP-MWCNTs, and ATMP-MWCNTs



a



b

Fig. 2 XPS spectra of *a* HEDP-MWCNTs and *b* ATMP-MWCNTs including their own full survey scan spectrum and the high-resolution spectrum of P 2p (inset)

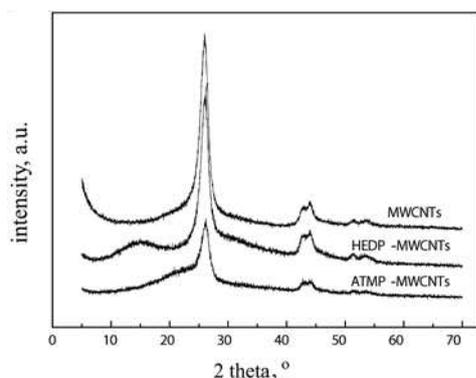


Fig. 3 XRD patterns of MWCNTs, HEDP-MWCNTs, and ATMP-MWCNTs

crystal structure of MWCNTs has not been affected by the addition of organophosphonic acid functional groups, and there are not any essential structure changes occurred after the chemical modification reaction of MWCNTs with HEDP/ATMP. Moreover, this figure implies that MWCNTs are stable enough to go through the chemical modification reactions, the organophosphonic acid chemical treatment does not change the structure of MWCNTs, and the organophosphonic acid functional groups might be present in amorphous forms in the prepared adsorbents. The TGA has been conducted on the functionalised MWCNTs samples in order to detect their thermal stability, and Fig. 4 displays the corresponding experimental results. It is clear that the thermogravimetric curves of both functionalised MWCNTs adsorbents represent a few decomposition stages between 25 and 800°C. The weight loss percentage data of 12.24 and 9.67% between 25 and 100°C are attributable to water absorbed physically in HEDP-MWCNTs and ATMP-MWCNTs, respectively. Further weight loss percentage above 100°C can be assigned to the organic component decomposition. It is obvious that there is just a little weight loss for both

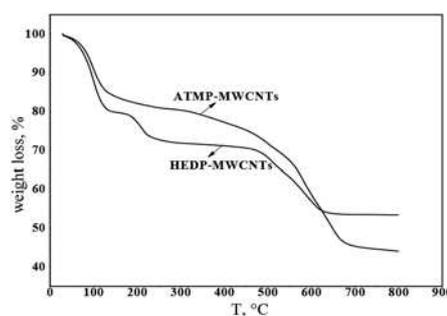
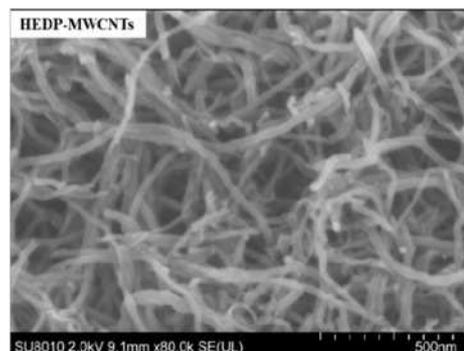
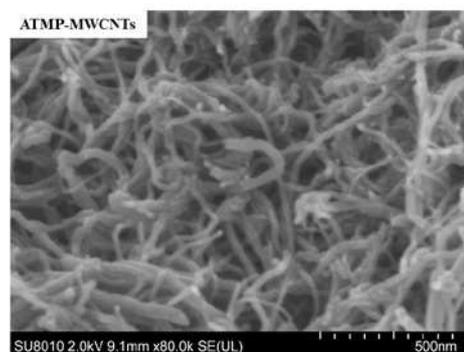


Fig. 4 Thermogravimetric curves of HEDP-MWCNTs and ATMP-MWCNTs



a



b

Fig. 5 SEM of *a* HEDP-MWCNTs and *b* ATMP-MWCNTs

HEDP-MWCNTs and ATMP-MWCNTs between 25 and 50°C. It is well known that the operating temperature of the adsorbents is usually <50°C. Hence, the prepared HEDP-MWCNTs and ATMP-MWCNTs can display their nice thermal stability in the application process. Moreover, Fig. 5 has been provided to show the SEM of HEDP-MWCNTs (a) and ATMP-MWCNTs (b), and it can be seen that after modification, both HEDP-MWCNTs and ATMP-MWCNTs have still kept the structures of nanotubes, and these nanotubes are aligned randomly, which would benefit to the heavy metal adsorption. It is expected that HEDP-MWCNTs and ATMP-MWCNTs can present excellent chemical and physical characteristics to adsorb metal ions due to the introduction of organophosphonic acid chelating functional groups.

Saturated adsorption capacities for heavy metal ions are essential parameters for evaluating the adsorption ability of the adsorbents. Fig. 6 shows the static adsorption capacities of MWCNTs, HEDP-MWCNTs, and ATMP-MWCNTs for gold ions, cadmium

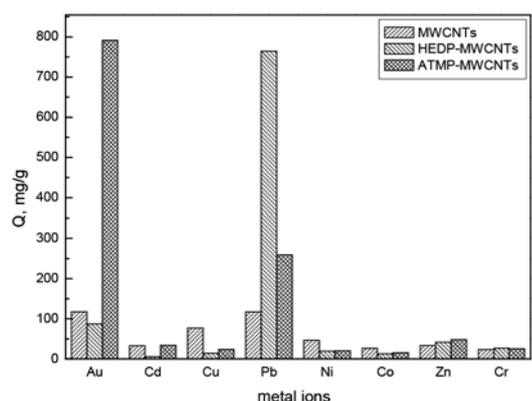


Fig. 6 Static adsorption capacities of MWCNTs, HEDP-MWCNTs, and ATMP-MWCNTs for heavy metal ions at 25°C

ions, copper ions, lead ions, nickel ions, cobalt ions, zinc ions, and chromium ions. It is noted that HEDP-MWCNTs/ATMP-MWCNTs display the outstanding adsorbability for lead ions/gold ions, respectively, compared to the unmodified MWCNTs (Fig. 6). They have shown a high affinity towards Pb(II) and Au(III), and their corresponding adsorption capacities are 764.42 and 791.22 mg/g, respectively. It indicates that the organomulti-phosphonic acid functional groups existing on the surface of MWCNTs have obvious influences on their adsorption properties and can strongly affect and improve their heavy metal ions adsorption capacities in the aqueous solutions. The surface modification can further provide binding sites and greatly promote the adsorption properties for some particular metal ions, especially for Pb(II)/Au(III). It is worth mentioning that the adsorption capacities of ATMP-MWCNTs for gold ions are much more than the ones in our previous work [38]. The lead/gold ions adsorption capacities of HEDP-MWCNTs/ATMP-MWCNTs are greatly enhanced after the functionalisation of organophosphonic acid, HEDP-MWCNTs/ATMP-MWCNTs has the highest adsorption capacities for Pb(II)/Au(III), respectively, and the multiorganophosphonic acid functional groups on the surface of MWCNTs might possess high affinity for lead/gold ions.

The adsorptive selectivity is also an indispensable factor for evaluating the properties of an adsorbent, by which the adsorbent can be used to adsorb some specific metal ions or to separate some specific metal ions from mixed metal ions solutions [37]. In this study, the adsorption selectivity of HEDP-MWCNTs/ATMP-MWCNTs to the target ion Pb(II)/Au(III) has been evaluated by the competitive adsorption with mercury ions/copper ions/nickel ions/cobalt ions/chromium ions/cadmium ions as the co-ions. The adsorption selectivity experiments by HEDP-MWCNTs/ATMP-MWCNTs have been carried out in several binary ions systems, and the obtained results for Pb(II)/Au(III) adsorption at 25°C are presented in Table 1. The selective coefficient α is the result of the adsorption capacity of Pb(II)/Au(III)

ion divided by one of the other metal ions in the binary ion systems. The experimental results display the prepared diphosphonic acid functionalised-MWCNTs/tri-phosphonic acid functionalised-MWCNTs show high selectivity towards Pb(II)/Au(III) in the binary ion systems, especially their selectivity efficiency of 100% can be obtained with coexisting of copper ions, nickel ions, cobalt ions, zinc ions, chromium ions, or cadmium ions, which reveals that they can maintain excellent removal performance for Pb(II)/Au(III) in these binary ion systems. These results reveal that a higher adsorption efficiency of HEDP-MWCNTs/ATMP-MWCNTs for Pb(II)/Au(III) over these other coexisting metal ions, HEDP-MWCNTs/ATMP-MWCNTs has a preferential affinity for lead/gold ions. HEDP-MWCNTs/ATMP-MWCNTs can maintain their excellent removal performance for lead/gold ions from binary ion systems, and they can be used in the extraction, separation and recovery of lead/gold ions from multi-ionic aqueous systems, respectively.

The study of adsorption kinetics includes careful monitoring of the experimental conditions that influence the adsorption speed in its race towards equilibrium. Fig. 7 shows the adsorption kinetics curves of HEDP-MWCNTs for Pb(II) (Fig. 7a) and ATMP-MWCNTs for Au(III) (Fig. 7b) at different solution temperatures, which are investigated at 15, 25, and 35°C to determine the adsorption equilibrium time. As shown in Fig. 7, the adsorption capacities of HEDP-MWCNTs for Pb(II) ATMP-MWCNTs for Au(III) increased with the extension of contact time; it is obvious that in the first 25/60 min of short contact time for HEDP-MWCNTs/ATMP-MWCNTs, the adsorption capacities rise rapidly, and then slow down gradually when approaching equilibrium. The kinetic curves are smooth and continuous, leading to the adsorption saturation, suggesting that the possibility of the formation of monolayer coverage of heavy metal ions onto the surface of the adsorbents [39]. The adsorption rate is fast at the initial stage of adsorption because the metal ions can easily enter the accessible pore sites and bind with the chelating ligands in initial fast adsorption step, and then it is slow for the metal ions might be hampered to diffusion into the deeper pores. It is also seen from Fig. 7 that the adsorption capacity increases with the increase of temperature. The equilibrium adsorption capacity of Pb(II) ions on the HEDP/MWCNTs surface increases significantly from 406.8 to 558.6 mg/g upon increasing the adsorption temperature from 15 to 35°C, and that is from 428.1 to 551.0 mg/g for Au(III) adsorption on ATMP/MWCNTs. The rise of the temperature has provided a greater driving force for the mass transfer and subsequent surface adsorption. Moreover, the results show that to reach their own adsorption equilibrium, the adsorption process of HEDP-MWCNTs for Pb(II) needs at least 6 h, and that of ATMP-MWCNTs for Au(III) requires at least 16 h to reach adsorption equilibrium. As significant practical importance, the rapid kinetics will facilitate smaller reactor volumes, ensuring efficiency and economy. It can be observed that these modified carbon MWCNTs with organo-phosphonic acid chelating ligands required 6/16 h to reach their own adsorption equilibriums. Furthermore, the EDXAS of

Table 1 Adsorption selectivity of HEDP-MWCNTs and ATMP-MWCNTs for lead ions/gold ions at 25°C, respectively

Binary ion systems	Selective coefficient α (HEDP-MWCNTs)	Binary ion systems	Selective coefficient α (ATMP-MWCNTs)
lead-mercury	36	gold-mercury	25
lead-gold	398	gold-lead	297
lead-copper	∞	gold-copper	∞
lead-nickel	∞	gold-nickel	∞
lead-cobalt	∞	gold-cobalt	∞
lead-zinc	∞	gold-zinc	∞
lead-chromium	∞	gold-chromium	∞
lead-cadmium	∞	gold-cadmium	∞

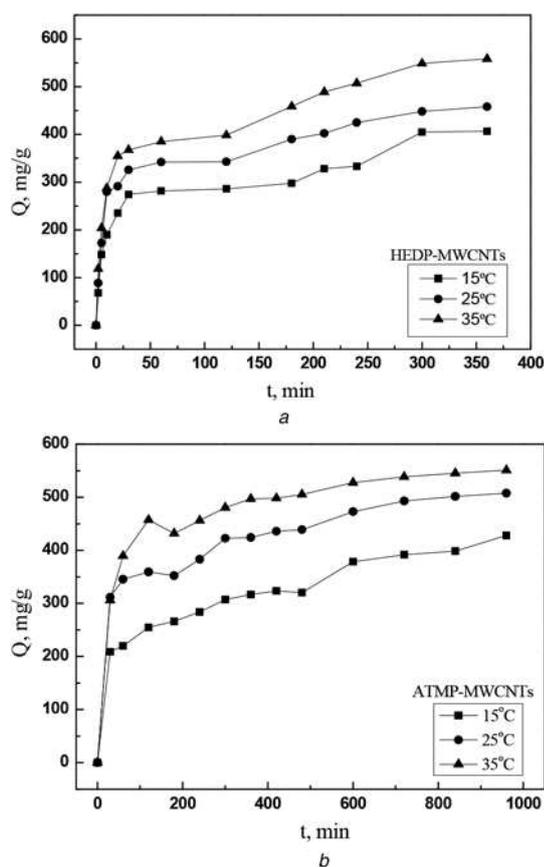


Fig. 7 Adsorption kinetics of Pb(II) and Au(III) onto a HEDP-MWCNTs and b ATMP-MWCNTs, respectively, at different solution temperatures

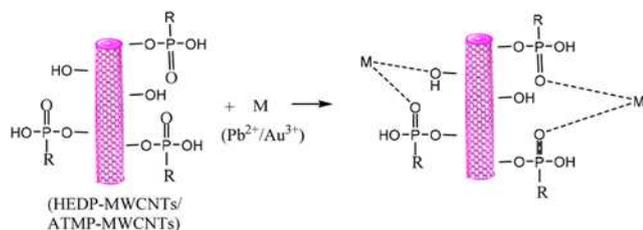


Fig. 8 Coordination interaction between lead/gold ions and HEDP/ATMP-MWCNTs

HEDP/ATMP-MWCNTs has been investigated after their adsorption for lead/gold ions, respectively, and the corresponding weight percentage of metal ions is 72.04%/39.01%. The high adsorption capacity of HEDP/ATMP-MWCNTs for lead/gold ions might be attributed to the coordination interaction between lead/gold ions and the functional phosphonic acid and hydroxyl groups on the MWCNTs surfaces (Fig. 8). Compared with the previously reported kinds of literature, HEDP/ATMP-MWCNTs have the advantages of simple preparation and high adsorption performance. For example, the adsorption capacity of HEDP-MWCNTs for lead ions is higher those (44.44 mg/g, 83.20 mg/g) reported in [40–41], and the adsorption capacity of ATMP-MWCNTs for gold ions is higher the data (298.5 mg/g) reported in [42]. The above-mentioned research results show that HEDP-MWCNTs/ATMP-MWCNTs is very favourable for the removal of lead/gold ions, and the excellent adsorption properties make them good promising candidate materials for the removal of Pb(II)/Au(III). In order to further promote the commercial viability of these

adsorbents, the functionalisation of low-cost industrial grade MWCNTs will be investigated in the future.

4. Conclusion: Heavy metal ions are of special environmental concern because they are non-degradable and therefore persistent. In this Letter, CNTs have modified by organomultiphosphonic acid group impregnation to enhance their affinity towards heavy metal ions, two novel adsorbents multiphosphonic acid-functionalised MWCNTs (HEDP-MWCNTs and ATMP-MWCNTs) with high efficiency and selectivity for Au(III)/Pb(II) removal have been synthesised and characterised, and the results show that the phosphonic acid functional groups have been grafted onto MWCNTs surface successfully. The adsorption batch experimental results for heavy metal gold ions, cadmium ions, copper ions, lead ions, nickel ions, cobalt ions, zinc ions, and chromium ions in the simulated wastewater solutions show that the prepared HEDP-MWCNTs/ATMP-MWCNTs display the outstanding adsorbability for lead ions/gold ions, respectively, compared to the unmodified MWCNTs. The adsorption selectivity investigation results show that the synthesised HEDP-MWCNTs/ATMP-MWCNTs displays a strong affinity for Pb(II)/Au(III), respectively, and their selectivity efficiency of 100% can be obtained with coexisting of copper ions, nickel ions, cobalt ions, zinc ions, chromium ions, or cadmium ions, which reveals that they can maintain excellent removal performance for Pb(II)/Au(III) in these binary ion systems. All of the fabulous features of HEDP-MWCNTs and ATMP-MWCNTs will ensure their applicability and feasibility on the industrial scale. In the field of practical application, high adsorption capacity and good selective adsorption ability can make these two adsorbents organophosphonic acid-modified MWCNTs have significant potential in heavy metal ions uptake in industrial wastewaters. Moreover, the functionalisation of low-cost industrial grade MWCNTs will be further carried out to promote the commercial viability of these types of adsorbents.

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6 References

- [1] Idris A., Ismail N.S.M., Hassan N., *ET AL.*: 'Synthesis of magnetic alginate beads based on maghemite nanoparticles for Pb(II) removal in aqueous solution', *J. Ind. Eng. Chem.*, 2012, **18**, pp. 1582–1589
- [2] Chen C., Wang J.: 'Removal of Pb²⁺, Ag⁺, Cs⁺ and Sr²⁺ from aqueous solution by Brewery's waste biomass', *J. Hazard. Mater.*, 2008, **151**, (1), pp. 65–70
- [3] Zhang Z., Zhu L., Zhang Z., *ET AL.*: 'Synthesis of polyethyleneimine modified polyurethane foam for removal of Pb(II) ion from aqueous solution', *Desal. Water Treat.*, 2019, **160**, pp. 288–296
- [4] Zhang P., Qin C., Hong X., *ET AL.*: 'Risk assessment and source of soil heavy metal pollution from lower reaches of Yellow River irrigation in China', *Sci. Total Environ.*, 2018, **633**, pp. 1136–1147
- [5] Li X., Li Z., Lin C., *ET AL.*: 'Health risks of heavy metal exposure through vegetable consumption near a large-scale Pb/Zn smelter in central China', *Ecotox. Environ. Safety*, 2018, **161**, pp. 99–110
- [6] Wang W., Lu Q., Ren X., *ET AL.*: 'Synthesis of novel ECH crosslinked chitosan Schiff base-sodium alginate for adsorption of Cd(II) ion from aqueous solution', *Desal. Water Treat.*, 2019, **145**, pp. 169–178
- [7] Fiyadh S.S., AlSaadi M.A., Jaafar W.Z., *ET AL.*: 'Review on heavy metal adsorption processes by carbon nanotubes', *J. Clean. Prod.*, 2019, **230**, pp. 783–793
- [8] Debnath S., Ghosh U.C.: 'Kinetics: isotherm and thermodynamics for Cr(III) and Cr(VI) adsorption from aqueous solutions by crystalline hydrous titanium oxide', *J. Chem. Thermodyn.*, 2008, **40**, pp. 67–77
- [9] Ding Y., Jing D., Gong H., *ET AL.*: 'Biosorption of aquatic cadmium(II) by unmodified rice straw', *Bioresour. Technol.*, 2012, **114**, pp. 20–25

- [10] Anirudhan T.S., Sreekumari S.S.: 'Adsorptive removal of heavy metal ions from industrial effluents using activated carbon derived from waste coconut buttons', *J. Environ. Sci.*, 2011, **23**, (12), pp. 1989–1998
- [11] Kim E.J., Lee C.S., Chang Y.Y., *ET AL.*: 'Hierarchically structured manganese oxide-coated magnetic nanocomposites for the efficient removal of heavy metal ions from aqueous systems', *ACS Appl. Mater. Interf.*, 2013, **5**, (19), pp. 9628–9634
- [12] Outram J.G., Couperthwaite S.J., Millar G.J.: 'Enhanced removal of high Mn(II) and minor heavy metals from acid mine drainage using tunnelled manganese oxides', *J. Environ. Chem. Eng.*, 2018, **6**, (2), pp. 3249–3261
- [13] Wen Z., Zhang Y., Guo S., *ET AL.*: 'facile template-free fabrication of iron manganese bimetal oxides nanospheres with excellent capability for heavy metals removal', *J. Colloid Interf. Sci.*, 2017, **486**, pp. 211–218
- [14] Lu J., Wu X., Li Y., *ET AL.*: 'Modified silica gel surface with chelating ligand for effective mercury ions adsorption', *Surface. Interf.*, 2018, **12**, pp. 108–115
- [15] Wang Z., Yin P., Wang Z., *ET AL.*: 'Chelating resins silica gel supported aminophosphonic acids prepared by heterogeneous synthesis method and homogeneous synthesis method and the removal properties for Hg(II) from aqueous solutions', *Ind. Eng. Chem. Res.*, 2012, **51**, (25), pp. 8598–8607
- [16] Yin P., Xu Q., Qu R., *ET AL.*: 'Adsorption of transition metal ions from aqueous solutions onto a novel silica gel matrix inorganic–organic composite material', *J. Hazard. Mater.*, 2010, **173**, (1–3), pp. 710–716
- [17] Yin P., Tian Y., Wang Z., *ET AL.*: 'Synthesis of functionalized silica gel with poly(diethylenetriamine bis(methylene phosphonic acid)) and its adsorption properties of transition metal ions', *Mater. Chem. Phys.*, 2011, **129**, (1–2), pp. 168–175
- [18] ShamsiJazeyi H., Kaghazchi T.: 'Investigation of nitric acid treatment of activated carbon for enhanced aqueous mercury removal', *J. Ind. Eng. Chem.*, 2010, **16**, pp. 852–858
- [19] Sounthararajah D., Loganathan P., Kandasamy J., *ET AL.*: 'Adsorptive removal of heavy metals from water using sodium titanate nanofibres loaded onto GAC in fixed-bed columns', *J. Hazard. Mater.*, 2015, **287**, pp. 306–316
- [20] Shirzadi H., Nezamzadeh-Ejehieh A.: 'An efficient modified zeolite for simultaneous removal of Pb(II) and Hg(II) from aqueous solution', *J. Mol. Liq.*, 2017, **230**, pp. 221–229
- [21] Zhao Y.: 'Review of the natural, modified, and synthetic zeolites for heavy metals removal from wastewater', *Environ. Eng. Sci.*, 2016, **33**, pp. 443–454
- [22] Chao H.P., Chen S.H.: 'Adsorption characteristics of both cationic and oxyanionic metal ions on hexadecyltrimethylammonium bromide-modified Nay zeolite', *Chem. Eng. J.*, 2012, **193–194**, pp. 283–289
- [23] Vakili M., Deng S., Cagnetta G., *ET AL.*: 'Regeneration of chitosan-based adsorbents used in heavy metal adsorption: a review', *Sep. Purif. Technol.*, 2019, **224**, pp. 373–387
- [24] Fujiwara K., Ramesh A., Maki T., *ET AL.*: 'Adsorption of platinum (IV), palladium (II) and gold (III) from aqueous solutions onto L-lysine modified crosslinked chitosan resin', *J. Hazard. Mater.*, 2007, **146**, pp. 39–50
- [25] Bhatt R., Padmaj P.: 'A chitosan-thiomer polymer for highly efficacious adsorption of mercury', *Carbohydr. Polym.*, 2019, **207**, pp. 663–674
- [26] Hawari A.H., Mulligan C.N.: 'Biosorption of lead (II), cadmium (II), copper (II) and nickel(II) by anaerobic granular biomass', *Bioresour. Technol.*, 2006, **97**, (4), pp. 692–700
- [27] Iijima S.: 'Helical microtubules of graphitic carbon', *Nature*, 1991, **354**, pp. 56–58
- [28] Stafiej A., Pyrzynska K.: 'Adsorption of heavy metal ions with carbon nanotubes', *Sep. Purif. Technol.*, 2007, **58**, (1), pp. 49–52
- [29] Wang H. J., Zhou A. L., Peng F., *ET AL.*: 'Adsorption characteristic of acidified carbon nanotubes for heavy metal Pb(II) in aqueous solution', *Mater. Sci. Eng. A*, 2007, **466**, (1–2), pp. 201–206
- [30] Ma X., Yang S., Tang H., *ET AL.*: 'Competitive adsorption of heavy metal ions on carbon nanotubes and the desorption in simulated biofluids', *J. Colloid Interf. Sci.*, 2015, **448**, pp. 347–355
- [31] Xu J., Cao Z., Zhang Y., *ET AL.*: 'A review of functionalized carbon nanotubes and graphene for heavy metal adsorption from water: preparation, application, and mechanism', *Chemosphere*, 2018, **195**, pp. 351–364
- [32] Mubarak N.M., Sahu J.N., Abdullah E.C., *ET AL.*: 'Removal of heavy metals from wastewater using carbon nanotubes', *Sep. Purif. Meth.*, 2014, **43**, pp. 311–338
- [33] Behbahani M., Bagheri A., Amini M.M., *ET AL.*: 'Application of multi-walled carbon nanotubes modified by diphenylcarbide for selective solid phase extraction of ultra-traces Cd(II) in water samples and food products', *Food Chem.*, 2013, **141**, (1), pp. 48–53
- [34] Mamba G., Mbianda X.Y., Govender P.P.: 'Phosphorylated multi-walled carbon nanotube-cyclodextrin polymer: synthesis, characterization and potential application in water purification', *Carbohydr. Polym.*, 2013, **98**, pp. 470–476
- [35] Tian Y., Yin P., Qu R., *ET AL.*: 'Removal of transition metal ions from aqueous solutions by adsorption using a novel hybrid material silica gel chemically modified by triethylenetetraminomethylene phosphonic acid', *Chem. Eng. J.*, 2010, **162**, (2), pp. 573–579
- [36] Li Y., Wang J., Huang H., *ET AL.*: 'Co-coating effect of GdPO₄ and carbon on LiFePO₄ cathode surface for lithium ion batteries', *Adv. Powder Technol.*, 2019, **30**, pp. 1442–1449
- [37] Fan L., Zhou A., Zhong L., *ET AL.*: 'Selective and effective adsorption of Hg(II) from solution over wide pH range by thiol functionalized magnetic carbon nanotubes', *Chemosphere*, 2019, **226**, pp. 405–412
- [38] Yin P., Wang Z., Qu R., *ET AL.*: 'Biosorption of heavy metal ions onto agricultural residues buckwheat hulls functionalized with 1-hydroxyethylidenediphosphonic acid', *J. Agric. Food Chem.*, 2012, **60**, pp. 11664–11674
- [39] Bandaru N.M., Reta N., Dalal H., *ET AL.*: 'Enhanced adsorption of mercury ions on thiol derivatized single wall carbon nanotubes', *J. Hazard. Mater.*, 2013, **261**, pp. 534–541
- [40] Kończyk J., Żarska S., Ciesielski W.: 'Adsorptive removal of Pb(II) ions from aqueous solutions by multi-walled carbon nanotubes functionalised by selenophosphoryl groups: kinetic, mechanism, and thermodynamic studies', *Colloid Surf. A*, 2019, **575**, pp. 271–282
- [41] Wang H., Shang H., Sun X., *ET AL.*: 'Preparation of thermo-sensitive surface ion-imprinted polymers based on multi-walled carbon nanotube composites for selective adsorption of lead(II) ion', *Colloid Surf. A*, 2020, **585**, p. 124139
- [42] Liu F., Peng G., Li T., *ET AL.*: 'Au(III) adsorption and reduction to gold particles on cost-effective tannin acid immobilized dialdehyde corn starch', *Chem. Eng. J.*, 2019, **370**, pp. 228–236