Polymer-supported organic-inorganic nanomaterials: fabrication, characterization and environmental application

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In the recent decades, polymer-based hybrid nanomaterials were widely fabricated and applied in heavy metal removal and other inorganic pollutants retention. The present review focused on the fabrication, sorption performance and mechanism towards heavy metal ions for water purification of the hybrid nanocomposites. Besides, the specific properties related surface chemistry of matrix and mechanical strength were also discussed.

Keywords: nanocomposites; heavy metal; nano-materials; adsorbents

1. Introduction

Water pollution by heavy metals still remains a serious environmental and public concern all over the world. Today, some of the toxic metals (e.g., lead and cadmium) even at trace levels are believed to pose adverse effects on human health [1, 2]. Thus, it is significant to develop efficient technologies for enhanced removal of heavy metal ions from contaminated waters. Up to now, various technologies have been proposed to trap heavy metals from waters, and adsorption, which has been widely studied and applied in treatment of metal contaminated waters[3, 4], serves as one of the most efficient and attractive approaches.

In the past few decades, more and more inorganic nanoparticles, such as atomic metals, metal oxides, and inorganic salts, were exploited as highly efficient materials for environmental remediation [5-8]. For instance, nanosized ZnO were extensively explored for abatement of heavy metals like Pb(II) and Cu(II) [9]; ferric oxide nanoparticles were found to exhibit preferable sorption toward toxic heavy metals and arsenic species [10-12]; nanosized zirconium phosphate, Zr(H2PO4)2, (ZrP), and its thiol derivative exhibited highly efficient removal of toxic metals through specific complex interactions [13, 14]. Such attractive performance of inorganic nanoparticles is greatly dependent upon their larger surface/volume ratio and more active sites than the bulky ones except for the potential-specific interactions with the targeted contaminants.

However, inorganic nanoparticles usually tend to aggregate and, thereafter, greatly weaken their efficiency for environmental application [15]. In addition, it is still a challenging task to separate economically and efficiently the ultrafine particles from aqueous or gaseous systems to overcome such technical bottlenecks [16], organic/inorganic nanocomposites have been emerging as a new class of environmental materials by dispersing inorganic nanoparticles into conventional porous hosts, such as diatomite [17-19], granular [20-22], cellulose [23, 24], and porous polymeric resins [25, 26]. The host materials of larger particle size greatly improve the permeability and separation of the resulting nanocomposites for facile operation. Also, they help us to inhibit the aggregation of the inorganic nanoparticles encapsulated therein due to the steric effect caused by their rigid matrices.

In recent years, more and more nanocomposites have been developed for efficient remediation of contaminated environment. Highly cross-linked porous polystyrene adsorbents have proved to be ideal support materials, and hybrid sorbents based on surface charged polymeric supports (e.g., cation or anion exchangers) were found to exhibit more favorable sorption toward trace target metals. This is because the immobilized charged groups on a polymeric matrix would greatly enhance metal permeation and preconcentration prior to effective sorption by inorganic particles; the phenomenon is the so-called “Donnan membrane effect” [10, 11, 27]. Here, here a review is provided on the recent progress in fabrication of these Polymer-based hybrid nanomaterials as well as their performance in environmental remediation. Besides, the specific sorption properties related surface chemistry of matrix was also briefly discussed.

2. Fabrication of the hybrid nanomaterials

2.1 Preparation procedures

Various methods have been developed and applied for preparation of hybrid nanomaterial. According to the formation processes of the nanocomposites, they could be generally divided into two categories. Those are ion-exchange in situ deposition technique and metal precursor diffusion deposition synthesis.

Ion-exchange deposition technique: The cation exchange resin incorporated with HFO particles, referred to as HFO-001, was fabricated according to Ion-exchange deposition technique[10] and the detailed procedures were shown.
in Fig. 1 In brief, the preparation procedure of HFO-001 consisted of the following four steps. First, 10.0 g D-001 beads were immersed into 100 mL aqueous solution containing 20 g FeCl₃. The mixture was stirred for 24 h to allow the Fe(III) to react with negative charged SO₃⁻ modified on the inner surface of D-001 through a typical cation-exchange process. Second, the Fe(III)-type D-001 beads were filtered, and transferred to a NaOH-NaCl solution, and then stirred for 24 h. Fe(III) preloaded on D-001 was then precipitated as Fe(III) hydroxides onto the inner surface of D-001. Third, the resulting particles were rinsed with the deionized water until the conductivity of the filtrate close to that of the deionized water, finally, the solid particles were thermally treated at 328 K for 6 h under N₂ atmosphere and then vacuum desiccated to yield HFO-001 spheres.

Precursor diffusion deposition synthesis: As for the host materials containing positive charged groups for nanocomposite fabrication. It might be impossible to undertake ion exchange reaction between metal cation and surface groups due to repulsion. So, the methods of precursor diffusion deposition might be the preferential choice. The synthesis of nano-sized zirconium phosphate (ZrP) loaded onto anion exchanger was depicted in Fig. 2[28, 29]. Briefly, the first step was to add 25.0 g of D-201 beads into ZrOCl₂-HCl solution (10.0 g ZrOCl₂.8H₂O was dissolved in 150 mL 10% HCl solution), and then the mixture was gradually evaporated off to ensure the diffusion of ZrOCl₂ within the nanopores of D-201 beads. Subsequently, the resulting particles immobilized with Zr(IV) were exposed to 350 mL H₃PO₄ solution (20% in mass) and stirred at 60 rpm for 12 h. The precipitation reaction of Zr(IV) and H₃PO₄ occurred in the nanopores of matrix and obtain the nano-materials ZrP-201. In this procedure, Zr(IV) salts enter into the inner surface of D201 by diffusion, rather than ion-exchange process.

3. Environmental application

Such hybrid materials could combine the nano-scale particles immobilization by the nanopore template within host matrix and better hydraulic conductivity due to large particle properties, as well as the specific affinities of inorganic nanoparticles towards heavy metals. Thus, it is feasible to utilize the inorganic adsorbent for the enhanced capture of target pollutants. In this section, trace heavy metals purification, including Pb(II), Cd(II), As(V) etc., using polymer-supported nanocomposites was discussed.

3.1 Polymer-based zirconium phosphate and derivative for heavy metal removal
Zirconium phosphate is an highly efficient ion-exchanger for trapping heavy metals including Pb^{2+}, Zn^{2+} and Cd^{2+} from solution [30], in recent study [28, 29], ZrP nanoparticles were dispersed onto a porous polymeric cation exchanger D-001 and obtained a new hybrid nano-materials ZrP-001. As indicated by the TEM image (Fig. 3) of ZrP-001, ZrP was dispersed into the inner surface of D-001 as nanoparticles of size less than 10 nm. Note that nanosized inorganic particles are expected to display larger accessible surface areas and stronger activity than bulk ones [31].

![Fig. 3 TEM image of ZrP-001](image)

**Fig. 3** TEM image of ZrP-001

A complete lead breakthrough curve onto ZrP-001 by comparison with D-001 and ZrP-CP for separate column runs under otherwise identical conditions.

![Fig. 4 A complete lead breakthrough curve onto ZrP-001 by comparison with D-001 and ZrP-CP for separate column runs under otherwise identical conditions.](image)

**Fig. 4** A complete lead breakthrough curve onto ZrP-001 by comparison with D-001 and ZrP-CP for separate column runs under otherwise identical conditions.

Fig. 4 illustrated an effluent history of a separate fixed-bed column packed with ZrP-001 for a feeding solution containing lead ion and competing cations (Na^+, Ca^{2+}, and Mg^{2+}), as compared to D-001. Lead broke through quickly onto D-001 due to its nonspecific selectivity toward lead. On the contrary, satisfactory breakthrough results were observed for ZrP-001 under otherwise identical conditions and ZrP-001 retention resulted in a dramatic lead decrease from 40 to less than 0.1 mg/L, such satisfactory performance mainly ascribed to the “Donnan membrane effects” i.e. the negatively charged polymeric matrix D-001 would greatly enhance lead permeation and preconcentration from solution to the active sorption sites, and lead concentrations around ZrP particles are much higher than in solution. Similar results were also reported by A.K. Sengupta [32, 33] and his co-workers for hydrated ferric oxides impregnated onto an anion exchanger for arsenic removal.
Fig. 5 Breakthrough curves of three heavy metals sorption from natural waters onto ZrPS-001 at 303 K. (the superficial liquid velocity (SLV) and the empty bed contact time are 3.0 m/h and 3.0 min)

Besides, thiol derivative (ZrPS) of ZrP also present preferable sorption towards heavy metals and the column adsorption results (Fig.5) for trapping trace heavy metals from drinking water also indicated ZrPS-001 can effectively reduce three toxic metals to below their corresponding drinking water standards [34].

3.2 Polymer-based hydrated manganese oxides (HMOs) for lead removal

Hydrated manganese oxides [35-37] can selectively bind heavy metals and anionic ligands (e.g., arsenate, phosphate) through inner–sphere complex formation. However, similar to ZrP, they cannot be directly used in columns or any other flow-through systems due to the fine or ultrafine particles. Polymer-supported hydrated manganese oxides were then developed to overcome the bottleneck [38-40].

(a)

(b)

(c)

Fig. 6 scanning electron micrographs of (a) D-001, (b) HMO-001, (c) TEM of HMO-001
As depicted in Fig. 6 the successful loading of HMO particles was demonstrated by comparing SEM images of D-001 and HMO-001. Moreover, TEM of HMO-001 indicates that HMO nanoparticles or nano-rods were loaded onto the inner surface of D-001.

Fig. 7 Breakthrough curves of lead adsorption from synthetic waters onto HMO-001 and D-001 at 298 K.

Fig. 7 illustrated a complete effluent history of a separate fixed-bed column packed with either HMO-001 or D-001 for a feeding solution containing lead ion and competing cations (Na⁺, Ca²⁺, and Mg²⁺). Lead broke through quickly on D-001 due to its poor selectivity towards lead. On the contrary, satisfactory breakthrough results were observed for HMO-001 even when the competing cations were about 200 times more than the lead ion in mass concentration. The lead concentration in the effluent decreased dramatically from 1.0 to less than 0.01 mg/L, which is the allowance of drinking water recommended by WHO. Additionally, the exhausted ZrP/ZrPS-001 beads can be efficiently regenerated by 2M HCl solution at 303K for repeated use without any significant capacity loss.

Similarly, other inorganic particles exhibiting specific affinity toward heavy metal ions, namely, hydrated zirconium oxides (HFOs) Ti(HPO₄)₂, hydrated ferric oxide (HFO), can also be anchored onto porous cation exchanger to obtain hybrid nano-materials [41, 42].

4. Specific properties of surface chemistry within the host matrix

4.1 Polymeric surface groups greatly affect nano-ZrP size and capacity

To evaluate the roles of surface groups of polymeric hosts in nano-ZrP dispersion, three macroporous polystyrene beads bound with different functional groups, i.e., -CH₂Cl, -SO₃⁻, and-CH₂N+(CH₃)₃, respectively were employed as the host materials. The fabricated nano-ZrP composite adsorbents were denoted as ZrP-C, ZrP-S, and ZrP-N, respectively. TEM images of the three nanocomposites (Fig. 8) showed that both ZrP-S and ZrP-N had ZrP nanoparticles with an average particle size of about 10-40 nm. Obvious particle agglomerates were observed within ZrP-C (20-140 nm). Considering the similar pore and frame structure of the three polymeric hosts, it is suggest that the different dispersions of nano-ZrP within the three nanocomposites are greatly attributed to the different surface chemistries of the polymeric supports. The presence of charged functional groups, whether negatively or positively, in the polymeric supports seems more favorable than the neutral chloromethyl group to lead to small ZrP nanoparticles. The specific role of the polymeric surface groups on nanoparticle size and dispersion could be interpreted by the DLVO theory [43, 44], i.e., nanoparticle dispersion or aggregation is greatly associated with both van der Waals attraction and electrostatic double -layer repulsion interaction between the particles. The repulsion interactions between adjacent nanoparticles generally dominate the extent of their aggregation and particle size distribution. Considering that the surrounding chemistry of the nanoparticles would greatly affect the repulsion interaction, zeta potentials of the three nanocomposites were determined to examine the repulsion interaction of adjacent nanoparticles. The values for ZrP–N, ZrP–S, and Zr–Cl were 38.5, -41.7, and -22.6 mV, respectively. It is generally known that larger zeta potentials suggest enhanced double layer repulsion as well as stability of nanoparticles [43, 45, 46]. ZrP–N and ZrP–S were of similar absolute values of zeta potential and were higher than that of ZrP–Cl, which is consistent with the improved ZrP dispersion of the two former nanocomposites.
Fig. 8 TEM images of three polymer-based nanocomposites. a ZrP–S, b ZrP–N, and c ZrP–C

Fig. 9 Sorption isotherms of Pb(II) ions onto three nanocomposite adsorbents in the presence of 1,000 mg/L Ca(II) ions at 298 K.

Speaking in general, inorganic nanoparticles usually exhibit larger accessible surface areas and higher reactivity than the bulky ones. In this study, lead sorption onto the three nanocomposites in the presence of calcium ions at high concentration levels was examined. Calcium ions were introduced into the test solution mainly to screen the nonspecific lead adsorption by the sulfonate groups of the polymeric host through Coulombic interaction. Note that -CH2Cl and –N+(CH3)3Cl display no direct attribution to lead adsorption because of their neutrally or positively charged nature. Preliminary tests demonstrated the negligible lead sorption by the host matrix under otherwise identical conditions as shown in Fig. 9 and the Results indicate that the capacities of the three nanocomposites were in the sequence of ZrP–S>ZrP–N>ZrP–Cl. Higher capacity of ZrP–S and ZrP–N than ZrP–Cl was reasonable because of their smaller ZrP nanoparticles than the latter one. As for the different performance of ZrP–S and ZrP–N, it may be explained by the potential Donnan membrane principle proposed by Sengupta et al [11, 12]. The immobilized negatively charged sulfonate groups are more favorable than the positively charged ammonium groups to enhance lead sorption by the immobilized nano-ZrP, particularly in the presence of co-ions at high concentration levels.

4.2 Nanoparticle immobilization improves the mechanical properties of the nano-materials

Till now, there are numerous nanocomposites developed for abatement of environmental pollutants the excellent mechanical properties of supports, such as activated carbon and polymers, further improved their feasibility for practical application. Nevertheless, little is known about the role of nanoparticle immobilization on the mechanical properties of...
the nanocomposites. In this section, cation exchanger D001 was selected as the host material and fabricated several composite adsorbents with different amounts of nano-ZrP. Then, the mechanical strength of the resulting composites was examined in terms of compressive strength and wear resistance, as compared with the host polymer.

![Image](image_url)

**Fig. 10** Maximum compressive strength of polymeric cation exchanger D001 loaded with varying amounts of nano-ZrP

The mechanical strength of several nanocomposites loaded with various amounts of nano-ZrP was examined, and the results are presented in Fig. 10. As compared with the host matrix, the maximum compressive strengths (MCS) of all the resulting nanocomposites were greatly improved. In addition, the optimum nano-ZrP loading of the composites was about 5 wt%. A further increase of ZrP loading would result in a slight decrease in MCS. Similar observations were also available, when nano-hydrated ferric oxides were preloaded on the granular activated carbon or polymeric adsorbents for decontamination of arsenic and heavy metals, and the nano-hydrated ferric oxides-encapsulated composites exhibited enhanced mechanical properties than the support materials. Consequently, it can be concluded that the immobilized nano-ZrP would help us to improve the mechanical properties of the resulting nanocomposites.
The wear-resistance performance of polymeric cation exchanger loaded with varying amounts of nano-ZrP. a Particle size distribution and b rolling sphericity.

Similar phenomenon was also detected in wear-resistance tests. Wear-resistance test of nano-ZrP preloaded D001 beads was performed by ball-milling methods, and their size distribution and rolling sphericity after the test are presented in Fig. 11a and b. From Fig. 11a, it is observed that about half of the host matrix was broken during the ball-milling, whereas almost all the nanocomposites retained same particle size before and after the test. Similar results were also available in terms of the rolling sphericity (Fig. 11b) with more than 95% of the nanocomposite beads appearing spherical regardless of nano-ZrP loadings, while about 50.5% of the host materials beads were broken during ball-milling. In conclusion, nano-ZrP immobilized within D-001 substantially reinforced the wear resistance of the nanocomposite materials. A slight decrease in sphericity of the nanocomposites was detected with the increase of nano-ZrP loadings, which is in agreement with the above results concerning MCS.

5. Conclusion

To date, the polymer-supported hybrid nano-materials are widely explored as highly efficient adsorbents for heavy metal removal from water/wastewater. They exhibit high capacity, simply operation, highly stabilities in chemical and thermal properties and selective sorption toward heavy metals in waters. Nevertheless, the practice application of nanocomposites is still in abatement and there still exist some technical bottlenecks to be solved. For instance, the poor diffusion kinetics resulting from the pore blocking in incorporation process, and in column operation, the relation of the excessive pressure drop and velocity of flow should be considered. Besides, almost all these hybrid nano-materials are still prepared in laboratory scale, and how to obtain the materials in large scale for application also remains a serious challenge and more works need to explore to promote the development of the nanocomposites.

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References


