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Cover Letter

Dear Editor,

We would like to submit to **Water Research** the following paper:

Polymer functionalized nanocomposites for metals removal from water and wastewater: an overview

Thisreview paper deals with **emerging nano-based technologies** for **metals**removal from wastewater as tertiary or quaternary treatment.

We reviewed and organised the existing information about polymer functionalized nanocomposites (PFNCs) about **metals/metalloids removal** evidencing the existing gaps into the knowledge about their composition, **effects related to pH, temperature, contact time with wastewater, adsorbent capacity compared to metals' concentration, and their regeneration and reuse.** Data were discussed evidencing how efficient the technology could be as well as the role of metal speciation, their toxicity as a whole and final consideration about PFNCs' design.

Pollution by metal and metalloid ions is one of the most widespread environmental concern. They are non-biodegradable, and, generally, present high water solubility facilitating their environmental mobilisation interacting with abiotic and biotic components such as adsorption onto natural colloids or even accumulation by living organisms, thus, threatening human health and ecosystems. Therefore, there is a high demand for effective removal treatments of heavy metals, making the application of adsorption materials such as PFNCs, increasingly attractive. PFNCs retain the inherent remarkable surface properties of nanoparticles, while the polymeric support materials provide high stability and processability. These nanoparticle-matrix materials are of great interest for metals and metalloids removal thanks to the functional groups of the polymeric matrixes that provide specific bindings to target pollutants. Despite the promises of these adsorbents, several issues related to their use still remain to be addressed:

- Safety for human health and the environment has not been fully assessed - further research is expected in the near future investigating the long term exposure and effects considering various biological targets;
- Greening the PFNCs production is expected in order to minimize the use of solvents and make their use more environmentally friendly;
- Removal efficiency and cost optimization per unit volume treated waiting for an economy of scale;
- Life cycle impact analysis according to the reuse, recovery and regeneration approaches and zero-waste perspective.

The authors state that there is no conflict of interest and agreed to the submission.

Highlights

- PFNCs incorporate NPs surface features and the polymers binding capacity
- The interest in PFNCs is increasing, but many gaps into the knowledge exist
- Interesting removal rates for metals/metalloids, but no data on toxicity effects

Polymer functionalized nanocomposites for metals removal from water and wastewater: an overview

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Abstract

Pollution by metal and metalloid ions is one of the most widespread environmental concern. They are non-biodegradable, and, generally, present high water solubility facilitating their environmental mobilisation interacting with abiotic and biotic components such as adsorption onto natural colloids or even accumulation by living organisms, thus, threatening human health and ecosystems. Therefore, there is a high demand for effective removal treatments of heavy metals, making the application of adsorption materials such as polymer-functionalized nanocomposites (PFNCs), increasingly attractive. PFNCs retain the inherent remarkable surface properties of nanoparticles, while the polymeric support materials provide high stability and processability. These nanoparticle-matrix materials are of great interest for metals and metalloids removal thanks to the functional groups of the polymeric matrixes that provide specific bindings to target pollutants. This review discuss PFNCs synthesis, characterization and performance in adsorption processes as well as the potential environmental risks and perspectives.

Keywords

Polymer functionalized nano-composites; metalloid; metal; nanoparticles; removal efficiency; toxicity

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1. Introduction

As a consequence of the growing pressure on water supply, the use of unconventional water sources such as treated wastewater will be a new norm, especially in historically water-stressed regions (Qu et al., 2013). This has resulted in several technological innovations within the field of wastewater treatment, including advanced oxidation processes, adsorption, and membrane separation (Grassi et al., 2012; Carotenuto et al., 2014). However, the application of these technologies has been restricted due to processing efficiencies, operational methods, energy requirements, and economic benefit. A promising technological breakthrough is expected from the nanotechnology field, which holds a great potential for advancing water and wastewater treatment with improved treatment efficiency and lower energy consumption, being considered one of the largest engineering innovations since the Industrial Revolution (Wang et al., 2013). Some applications utilize the smoothly scalable size-dependent properties of nanoparticles (NPs) related to their high specific surface area, such as fast dissolution, high reactivity, and strong sorption, whereas others take advantage of their discontinuous properties, such as superparamagnetism, localized surface plasmon resonance, and quantum confinement effects (Mahdavian and Mirrahimi, 2010; Qu et al., 2013). The nano-size of particles may be of concern about mass transport and excessive pressure drops when applied in fixed-bed or any other flow-through systems, as well as difficulties in separation and reuse, and even possible risk to human health and the ecosystems caused by their potential release into the environment (Zhao et al., 2011).

Polymer-functionalized nanocomposites (PFNCs) incorporate the remarkable features of both NPs and polymers: the unique physical and chemical properties resulting from the large surface area to volume ratios, the high interfacial reactivity of nanofillers, and outstanding mechanical properties and compatibility owing to their polymer matrix (Pan et al., 2009; Zhao et al., 2011), being also amenable to regeneration and reuse (Zhou et al., 2009; Nassar et al. 2010). These features made of a promising class of adsorbent materials for metals removal from water and wastewater (Ghorbani

and Eisazadeh, 2013). The overall objective of this review focuses on the PFNCs synthesis, characterization, toxicity, and adsorption performance, including a perspective of new research trends.

2. Synthesis and characterization of polymer functionalized nanocomposites

In the last decades, several PFNCs have been fabricated for the adsorptive removal of heavy metals from water and wastewater (DeMarco et al., 2003; Cumbal and Sengupta, 2005; Sylvester et al., 2007; Pan et al., 2010). According to the formation processes, PFNCs can be fabricated by i) grafting NPs into polymer structures, or ii) by anchoring polymers to NPs (Mahdavian and Mirrahimi, 2010). As shown in Figure 1, two methods can be used for their fabrication: i) direct compounding; and ii) *in situ* synthesis (Zhao et al., 2011). Depending on the host materials, they can be classified as synthetic (S-PFNCs) and biopolymer (B-PFNCs) functionalized nanocomposites. The synthesis processes of S-PFNCs and B-PFNCs as reported in literature are shown in Table 1 and Table 2, respectively.

2.1 S-PFNCs

Polymeric ion exchangers can be positively or negatively charged (Figure 2). In a polymeric cation exchanger, negatively charged sulfonic acid groups are covalently attached to the polymer chains, usually polystyrene. Conversely, a polymeric anion exchanger contains a high concentration of non-diffusible positively charged quaternary ammonium functional groups.

Among S-PFNCs, the polystyrene-sulfone, as a polymeric cation exchanger, represents the most common host material used to fabricate hybrid adsorbents by grafting NPs into polymers (DeMarco et al., 2003; Cumbal and Sengupta, 2005; Pan et al., 2006; Sylvester et al., 2007; Zhang et al., 2008; Sarkar et al., 2011).

The selective sorption of these hybrid polymers toward heavy metals can be explained on the basis of their specific structure including: i) the negatively charged host material, and ii) the highly dispersion of the NPs onto the inner surface of the polymers. Such sorption preference is mainly attributed to two mechanisms: i) Donnan's membrane effect caused by the negatively charged supporting material, and ii) specific affinity between NPs and heavy metals.

Several NPs are used to fabricate this kind of PFNCs, most cases by *in situ* synthesis (Table 1). Hydrated iron (III) oxide (HFO), which is innocuous, inexpensive, readily available, and chemically stable over a wide pH range 2 - 8, is the most common NPs used to fabricate S-PFNCs, as shown in Table 1.

Amino-functionalized materials are expected to be highly effective for the removal of heavy metals, since the elimination of anionic metal species can be achieved via electrostatic interaction, ion exchange or hydrogen bonding, whereas the removal of the cationic metal species can be performed via coordination with the amino groups (Zhao et al., 2010; Shen et al., 2012).

The main drawback of this kind of granular type adsorbents is related to their recovery once saturated and their potential inhomogeneous dispersion. A large variety of fibrous exchangers based on different polymers has been synthesized and tested in different processes to overcome these limitations (Vatutsina et al., 2007).

2.2 B-PFNCs

Several authors reported that magnetic NPs functionalized with biopolymers such as chitosan (Chang and Chen, 2005) (Tran et al., 2010) (Zhou et al., 2009), alginate (Bée et al., 2011); Lim et al., 2009), gum Arabic (Banerjee and Chen, 2007) and cellulose (Guo and Chen, 2005) Zhu et al., 2011) are highly efficient for the removal of toxic metals from aqueous solutions. The main advantages of using iron oxides as composite materials with host materials are the high porosity, magnetic properties, and, usually, good settling properties. Since surface functional group reactions are involved in the sorption processes, higher content of surface functional group sites in a sorbent

would lead to a higher sorption capacity for the removal of contaminants (Nah et al., 2006; Jin et al. 2007). Among biopolymers, chitosan represents a valuable alternative having great potential applications in the areas of biotechnology for wastewater treatment. Chang and Chen (2005) developed a novel B-PFNC by carboxy-methylated chitosan covalently bounded on the surface of Fe_3O_4 NPs (Ch-(Fe_2O_3)), via *in situ* synthesis. Chitosan functionalization can be achieved by using environmentally friendly reagents. Zhou et al. (2009) carried out the surface modification of chitosan-coated magnetic NPs (Ch - (γ-Fe_2O_3)) with α-ketoglutaric acid (α-KA), which is a natural, inexpensive, harmless and biological reagent containing active functional groups like carboxyl groups. Physical characterization confirmed that the chitosan coating process did not alter significantly the γ-Fe_2O_3 morphology and the superparamagnetic properties of the α-KA- Ch - (γ-Fe_2O_3) did not change markedly after coating. Bée et al. (2011) developed a B-PFNC by encapsulation of magnetic functionalized NPs in calcium-alginate beads (CA - (γ-Fe_2O_3)), one of the main components of brown seaweed. The authors reported that the use of nanosized magnetic material improves the adsorption capacity of the alginate beads because of their large surface area and the presence of surface binding groups due to the citrate coating. As shown in Table 2, most B-PFNCs were obtained by *in situ* synthesis, whereas the alginate based ones were produced via direct compounding. A novel B-PFNC was also developed by Banerjee and Chen (2007) treating Fe_3O_4 NPs with gum Arabic (GA-(Fe_3O_4)). The surface modification did not result in the phase change of Fe_3O_4 leading to the formation of secondary particles in the range of 13-67 nm. Spherical Fe_3O_4/bacterial cellulose (Ce-(Fe_3O_4)) B-PFNCs were biosynthesized from *Gluconacetobacter xylinum* by agitation fermentation (Zhu et al., 2011). The ability of cyclodextrins (CDs), cyclic oligosaccharides consisting of 6 (α), 7 (β), 8 (γ) glucopyranose units linked together via α (1–4) linkages, to complex various metals was found to be highly dependent on the modification of the CDs with suitable functional groups through esterification, oxidation reactions and cross-linking of hydroxyls outside the interior cavity (Norkus, 2009). Carboxymethyl-β-cyclodextrin (C – β – CD)

polymer modified (C- β-CD- (Fe_3O_4)) presented the lowest diameter (8 nm) compared to the other B-PFNCs (Badruddoza et al., 2011, 2012, 2013a).

2.3 Characterization

Various and complementary multiscale characterization techniques are required for the analysis of structural, morphological and functional properties of PFNCs. The polymer nanocomposite morphology is mainly investigated by a large variety of microscopy techniques, depending on the scale of interest, and ranging from optical to electron microscopy (SEM and TEM, with related diffraction techniques) and scanning probe microscopy (SPM). The development of nanocomposite science and technology and the optimization of the functional properties of PFNCs has been possible because of the unparalleled information gathered with the use of these techniques. The information about morphology and structure achieved at the different scales regards not only the structure and distribution of the filler itself, but also the filler-matrix adhesion, and how the presence of the filler impacts on the embedding polymer matrix properties (Michler et al., 2008).

Currently, there is a growing interest focused on the use of specialized microscopy techniques such as electron tomography and the low voltage approach due to their ability to provide quantitative information about the adhesion and dispersion of the filler in the embedding polymeric matrix (Khare and Burris 2010). When *in situ* investigations are applicable and possible, specific information can be obtained on the filler matrix interaction properties thus increasing the comprehension of the mechanisms behind the characteristics enhancement observed for nanocomposites. Other commonly and widely used characterization tools are: i) X-ray diffraction (XRD) for the structural analysis, ii) Fourier Transform Infrared (FTIR) and Raman spectroscopy, for the study of the modes of surface groups and the nature of chemical bonds, iii) thermal analysis for the determination of water uptake, and iv) ionic exchange capacity.

3 Removal of metals by PFNCs

The basic principle for the use of PFNCs for metals removal is adsorption. Overall, various effects contribute determining the whole efficacy of PFNCs action.

3.1 Adsorption isotherms

The investigation of the interactions between adsorbate and adsorbent showed that adsorption isotherms are the most significant. Adsorption isotherms are functional expressions that correlate the amount of solute adsorbed per unit weight of the adsorbent and the concentration of the adsorbate in the bulk solution at a given temperature under equilibrium conditions. The isotherms based on Langmuir (Langmuir, 1918) (Eq. 1) and Freundlich (Freundlich, 1906) (Eq. 2) approaches are the most widely used to describe the equilibrium sorption of metal ions:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \qquad \text{(Eq. 1)}$$

$$ln\, q_e = \left(\frac{1}{n}\right) ln\, C_e + ln\, K_L \; ln\, q_e = \left(\frac{1}{n}\right) ln\, C_e + ln\, K_L \qquad \text{(Eq. 2)}$$

In Eq. 1, q_e is the amount of adsorbate adsorbed per mass of adsorbent at equilibrium (mg g^{-1}), C_e is the equilibrium concentration of adsorbate in aqueous solution (mg L^{-1}), q_m is the monolayer adsorption capacity at equilibrium (mg g^{-1}) and K_L the Langmuir equilibrium constant. In Eq. 2, K_F is an index of adsorption capacity, and n is the Freundlich constant (index of adsorption intensity or surface heterogeneity). The Freundlich model assumes adsorption can occur in multiple layer, so that saturation cannot occur, whereas the Langmuir model assumes adsorption occurs in only one layer. Therefore the Langmuir constant represents the monolayer saturation at equilibrium.

To determine whether the adsorption is favourable, a dimensionless constant separation factor or equilibrium parameter R_L is defined based on Eq. 3 (Weber and Chakravorti, 1974):

$$R_L = \frac{1}{1 + K_L C_i} \qquad \text{(Eq. 3)}$$

where, C_i (mg L^{-1}) is the initial metal concentration, and R_L value indicates whether the type of the isotherm is favourable ($0 < R_L < 1$), unfavourable ($R_L > 1$), linear ($R_L = 1$), or irreversible ($R_L = 0$). Badruddoza et al. (2013) reported R_L values between 0 and 1 for the Langmuir isotherm, and Freundlich adsorption intensity variables (*n* values) > 2 supporting the favourable adsorption of metal ions by C- β-CD - (Fe_3O_4). R_L values also between 0 and 1 were determined for nano magnetic polymer adsorbents coupled with different diamino groups for any initial concentration of Cr(VI) (Zhao et al., 2010). For an initial concentration of Cr(VI) of 50 mg L^{-1}, the polymer nano-adsorbents R_L values were 0.11, 0.04, 0.21, and 0.14 for EDA-(Fe_3O_4), DETA-(Fe_3O_4), TETA-(Fe_3O_4) and TEPA-(Fe_3O_4), respectively. The adsorption isotherms followed the Langmuir rules. The isotherm parameters are summarised in Table 3 and Table 4 for S-PFNCs and B-PFNCs, respectively.

3.2 Effect of polymer matrix and NPs composition

Cumbal and Sengupta (2005) observed that, despite greater HFO content, the sorbents based on cation-exchanger were practically unable to remove As(V) compared to the anion-exchanger based sorbents. This phenomenon was explained by the Donnan exclusion effect, which is essentially an extension of the second law of thermodynamics, concerning in a specific way the completely ionized electrolytes in a heterogeneous system.

The magnetic properties of the composite materials and their possible result in higher adsorption capacities towards metals is currently under discussion (Bibak, 1994). Davis and Bhatnagar, (1995) have shown the ratio between the magnetic “core” and the “shell” plays an important role: i) a low ratio of the magnetic oxide (the “core”) may cease a magnetic response, while ii) a low ratio of polymer component (the “shell”) may lead to a decrease on the adsorption capacity.

The adsorption of Hg^{2+} by MP-(Fe_3O_4) seems to be highly related to the content of Fe_3O_4 magnetic core in the adsorbents (Pan et al., 2012). The maximum adsorption capacity increased from 129.9 mg g^{-1} to 256.4 mg g^{-1} with an increase from 0 to 1.0 g of Fe_3O_4 used for the MP-(Fe_3O_4)

preparation, whereas a decrease from 256.4 mg g^{-1} to 158.7 mg g^{-1} was obtained when increasing the Fe_3O_4 quantity from 1.0 g to 2.0 g. The optimized content of the magnetic core on the MP - (Fe_3O_4) was 5.88% of Fe_3O_4. Similarly, the amount of iron as oxyhydroxide was also a crucial factor for the arsenic adsorption capacity (Guo and Chen, 2005). Katsoyiannis and Zouboulis, (2002) observed that the adsorption capacity of CPDB - (HFO) increased with an increasing amount of coated iron oxide.

3.3 Effect of pH

The pH affects the functional groups deprotonation determining the strength of the complexation or adsorption of the metals and metalloids. A first approach to evaluate the adsorption capacity of adsorbents towards metals is the determination of the pH at the point of zero charge (PZC). The overall surface charge on a PFNC becomes positive when the pH of the solution is below the PZC inhibiting the approach of the positively charged metal ions (electrostatic repulsion) (Zhou et al., 2009). Guo and Chen (2005) studied the influence of pH in the range (4-11) on the adsorption of AsO_3^{3-} and AsO_4^{3-} (300 mg L^{-1}). In general, the removal rate of AsO_4^{3-} decreased with increasing pH. The percentage removal of AsO_4^{3-} by Ce-(HFO) decreased from 96.2% to 52.6% when changing the pH from 4 to 11. The percentage of AsO_3^{3-} removal by Ce-(HFO) was higher than that for AsO_4^{3-} (90% for pH values between 5-10) except when pH was 4 – 5. Optimal AsO_3^{3-} adsorption by Ce-(HFO) was found at pH 7 – 9 where the percentage removed was above 95% (Table 4).

The adsorption capacities of MP-(Fe_3O_4) for Hg^{2+} increased with increasing the pH, reaching a steady-state at pH between 4 - 6 (Pan et al., 2012). This could be explained by the PZC of MP-(Fe_3O_4) at pH 2.03 – 2.72, indicating that repulsion takes place when there is the presence of cations such as Hg^{2+}, $HgOH^+$ and $HgCl^+$, thus, resulting in low adsorption capacities at pH below 2.7.

3.4 Effect of temperature and contact time

Some studies (Chang and Chen, 2005; Badruddoza et al., 2011, 2012, 2013a) reported that the adsorption capacity of metal ions decreases with increasing temperature, indicating that adsorption is an exothermic process being the electrostatic interaction between metal ions and PFNCs lower at higher temperatures. Also the contact time between the adsorbent and adsorbate is an important parameter to design the adsorption processes.

The time at which the equilibrium is reached may drastically change depending on adsorption sites on the exterior of the adsorbents: 100 min for Cd^{2+}, Cu^{2+}, and Pb^{2+} adsorption by D001 - (HFO) (Pan et al., 2010), 240 min for Pb^{2+} adsorption by CA-(γ-Fe_2O_3) Bée et al. (2011), 2 min for Cu^{2+} adsorption rate by GA-(Fe_3O_4) (Banerjee and Chen 2007).

3.5 Effect of initial concentration of metal ions and adsorbent dose

Zhu et al., 2011 reported that when the concentrations of Mn^{2+} and Cr^{3+} were lower than 60 mg mL^{-1}, the adsorbed quantities on Ce-(Fe_3O_4) resulted proportional to their concentrations.

An optimum adsorbent dose is required to maximize the interactions between the metal ions and the available adsorption sites on the adsorbent. Zhou et al. (2009) observed that the increase of Ch - (γ-Fe_2O_3) from 0 to 7 g L^{-1} resulted in an increase of the Cu^{2+} removal efficiency (99%), whereas higher concentrations lead to an adsorption decrease (Table 4). Evidently, that this effect is dependent on external factors such as the stirring of the solution, in fact the increase of the PFNC concentration with no change of the agitation speed can result in aggregation of the PFNC lowering the availability of the functional groups for complexation of the metal ions. The solution ion concentration drops to a lower value at higher adsorbent dose, and the system reaches equilibrium at lower values of the concentration of adsorbed metal indicating that the adsorption sites remain unsaturated.

3.7 Effect of coexisting ions

Coexisting ions in solution can compete with metals for the adsorption sites affecting the removal process (Guo and Chen, 2005; Vatutsina et al., 2007; Pan et al., 2012). The major anionic antagonistic components are phosphate (PO_4^{2-}), silicate (SiO_4^{4-}), and sulphate (SO_4^{-}), which are usually present in groundwater streams. According to Katsoyiannis and Zouboulis (2002), phosphate concentrations < 50 mg L^{-1} do not show any significant inhibition on As removal by CPDB-(HFO), whereas for concentrations above 200 mg L^{-1} PO_4^{2-} strongly compete with As for the available adsorption sites even impeding its removal when attaining concentrations of 400 mg $L^{-1.}$. When the presence of SiO_4^{4-}, the removal rate of AsO_3^{3-} decreases by Ce-(HFO) decrease to 85%, but with less importance on the Ce-(HFO) adsorption when in presence of PO_4^{2-} (Guo and Chen, 2005).

The effect of Ca^{2+}, Mg^{2+}, and Na^{+} on the adsorption of Hg^{2+} seems not to be significant since these cations have less affinity to –SH groups than Hg^{2+} as predicted by HSAB theory (Pan et al., 2012).

3.8 Regeneration and reuse

Hybrid ion exchangers can offer advantages over other adsorbents due to their chemical stability, and durable physical structure and amenability to regeneration and reuse (Sarkar et al., 2011). Regeneration of adsorbents has two main objectives: i) to restore the adsorption capacity of exhausted adsorbents, and ii) to recover valuable metals present in the adsorbed phase. The first aim can be attained under acidic conditions; the H^{+} ions protonate the adsorbent surface, *i.e.*, the carboxyl groups (-COOH), resulting in desorption of the positively charged metal ions (*i.e.*, competition between the H^{+} and the M^{z+} for the $-COO^{-}$ groups).

The regeneration efficiency of Ch-(γ-Fe_2O_3) was tested (Zhou et al., 2009) by using four different eluents, Na_2EDTA, HCl, CH_3COOH and citric acid, at two different concentrations, 25 and 100 mmol L^{-1}. The obtained results showed that 100 mmol L^{-1} of Na_2EDTA have had the highest efficiency (91.5%), due to its larger complexation capacity towards the metal ions. Yu et al. (2011)

showed the highest efficiency of Na_2EDTA to desorb Pb^{2+} ions when added to C-β-CD-(Fe_3O_4). Also, Nassar et al. (2010) showed that HNO_3 and Na_2EDTA solutions have very high desorption efficiencies for Pb^{2+} from CDpoly-MNPs (96.0 and 94.2% recovery, respectively), whereas H_3PO_4 was found to be a better eluent for Cd^{2+} and Ni^{2+} desorption (with a recovery of 61.8 and 82.7%, respectively).

The desorption data of adsorbed Pb^{2+} ions from magnetic alginate beads by elution with 2 mol L^{-1} HNO_3 showed that 88.9% of the Pb^{2+} ions were released in the solution after 30 min (Bée et al., 2011). The adsorption capacity of the magsorbent was maintained at the same level even after 5 elution cycles, indicating that the magsorbent can be reused for the removal of heavy metals (Nassar et al 2010).

Zhu et al. (2011) also showed that spherical Fe_3O_4/bacterial cellulose nanocomposites (Fe_3O_4/BC) could be regenerated by using sodium citrate and reused for further adsorption of metals.

4. Discussion

4.1 Synthesis methods

The direct compounding process is more convenient for operation, it has a low cost and is suitable for massive production (Katsoyiannis and Zouboulis, 2002). However, some drawbacks are related to: i) the decision about the space distribution parameter of NPs on the polymer matrix, ii) the possibility of NPs to form larger agglomerates during blending, greatly decreasing the advantages of their nano-size dimensions, and iii) the polymer degradation upon melt compounding and phase separation between the nano-phase and the polymer, which is sometimes severe (Zhao et al., 2011).

In situ synthesis methods allow synthesizing nanocomposites with tailored physical properties, and with a direct and homogeneous dispersion of the NPs into the liquid monomers or precursors avoiding their agglomeration in the polymer matrix, and thus improving the interfacial interactions between both phases. However, use of solvents and/or catalysts can be necessary (Zhao et al., 2011).

4.2 Process efficiency

As shown in Table 3, batch studies have shown that polymeric cation exchangers functionalized with HFO NPs PS-(HFO) represent the most common option for arsenic removal due to the high affinity of HFO for these metal ions (Etzel et al., 1997; De Marco et al., 2003; Cumbal et al., 2005; Sylvester et al., 2007; Möller et al., 2008). However, by using ACP - $N(CH_3)_2$ - (HFO), removal of approximately 90% of both AsO33- and AsO43- was obtained in only 10 min (Vatutsina et al., 2007). Zouboulis et al. (2002) noted that the removal of arsenic was greatly affected by the $Fe(NO_3)_3$ concentration used for the creation and doping of the iron oxide alginate beads. The amounts of doped iron oxides were 2.8 and 1.4 mg of Fe/g of wet alginate bead, respectively. The breakthrough point was reached after the treatment of around 80 and 55 bed volumes after the first and second runs, respectively.

For the removal of Pb^{2+}, Hg^{2+} and Cd^{2+} the use of PA-(HFO) showed a very high adsorption potential, as shown in Table 3. PEI – NCs were also found highly efficient for Cr^{4+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} removals. The use of PEI - (Fe_3O_4) + SiO_2 also produced high removal efficiencies the order being: $Cr^{6+} > Cu^{2+} > Zn^{2+} > Cd^{2+}$ with a starting concentration of 100 mg L^{-1} (Pang et al., 2011a, 2011b).

As shown in Table 4, Ch - (γ-Fe_2O_3) are also highly efficient (99%) for $Cu2^{+}$ removal at pH > 2. The adsorption rate equilibrium was achieved after 1 min due to the absence of internal diffusion resistance.

4.3 Metals dynamic speciation

Metal complexation is often strongly pH dependent and a function of metal-binding affinity, ligand concentration, and ionic strength (Domingos et al. 2015). Therefore, when the PNFCs are added to an environmental compartment, either a wastewater treatment facility or a river, where metals are present, these colloidal materials will absorb them through covalent, electrostatic, or hydrophobic interactions. If these colloidal materials are not well stabilized, they in turn can undergo several processes that are under dynamic control such as conformational changes of the organic colloids or the electrical surface field on the inorganic colloids, which implies that there will be a kinetic dependence on the metal complexation. These transformations result in a wider distribution of complexation affinities for metals and metalloids, and, thus in a broader distribution of their complex dissociation kinetics. In this case, the formed complexes can have different liabilities (Herman et al., 2001): i) labile complexes - the kinetic flux is much larger than the diffusive one so that the free metal ion will be in equilibrium with its complex forms all along the diffusion layer, thus all metals present will contribute to the overall flux; and ii) non-labile complexes - the kinetic and diffusive fluxes are of the same order of magnitude, thus both the free metal ion and a small part of the bound metal will contribute to the overall flux. Evidently, this is of critical importance for the evaluation of the removal efficiencies if the equilibrium is not attained. When no steady state is achieved it is necessary to consider the distributions of both thermodynamic and kinetic properties on the rigorous flux computations. Moreover, it is of crucial importance considering the kinetic features of metal complexation when evaluating the toxicity through the organisms. Currently, bioavailability and toxicity models are based only on the contribution of the free species, however, due to the dynamic of these systems, consideration of the labile complex for the internalization flux could be of great importance.

399 4.4 Toxicity evaluation

400 Despite the growing interest in the development of PFNCs, safety for human health and the
401 environment have not been properly addressed yet. The strict combination of polymers and NPs
402 (Ging et al., 2014) does not ease this investigation. NPs could pose some intrinsic potential risks.
403 For example, the biocompatibility investigations of graphene and graphene oxide have been
404 unsatisfactory with some papers demonstrating severe dose-dependent toxicity (Hu et al., 2011;
405 Wang et al., 2011), while others indicated that graphene NPs might improve cell growth (Lee et al.,
406 2011; Ruiz et al., 2011). Furthermore, not only the environmental toxicity, but also the fate of NPs
407 remains poorly understood, even for the most toxic NPs like Ag. As for toxicity effects, the fate of
408 NPs shows NP-specific partitioning behavior. Kaegi et al. (2013) evidenced little discharge for Ag
409 NPs into surface waters from urban wastewater cycle, whereas Ferry et al. (2009) demonstrated
410 how Au nano-rods could partition after an exposure period of 12 days in an aquatic mesocosm
411 being detectable in biofilm, the water column, clams and other biota. Preferably, the use of PFNCs
412 should reduce the release and potential toxic effects of NPs while the adsorption of the target
413 contaminant(s) by the nanocomposites should be comparable (or higher) than that obtained from the
414 free NPs (Önnby et al., 2014).

415 Currently, most data are referred mainly to PFNCs constituents and in just few cases to PFNC as a
416 whole. Tests on whole materials and after weathering experiments (e.g., UV ray, humidity, and
417 chemical and biological factors) are needed considering both *in vitro* and *in vivo* (eco)toxicology
418 (Posgai et al., 2011; Ging et al., 2014). Current research on the environmental stability of PFNCs
419 focused mostly on short-term stability, while the investigation of the long-term stability are missing.
420 Ging et al. (2014) investigated plain multi-walled carbon nanotubes (MWCNTs) and amino-
421 MWCNTs epoxy nanocomposites (after UV weathering for 1560 h) on *Drosophila melanogaster*
422 embryos (survivorship and developmental rate) showing no significant increase in toxicity,
423 probably because carbon nanotubes (CNTs) collected in abraded samples were still encapsulated in
424 the matrix, thus limiting the exposure. Paul et al. (2015) produced silver/polymer nanocomposites

425 functionalized by amino groups after reacting with end acidic groups from PLA and its co-polymer
426 with PLGA. While silver/polymer nanocomposites are used in biomedical materials and sensors
427 showing a low-toxicity for humans, but they inhibit the growth of a wide range of microorganisms
428 (Chaloupka et al., 2008). PLA (Jamshidian et al., 2010) and PLGA (Makadia et al., 2010) are well
429 known as non-toxic biodegradable materials (Danhier et al., 2012). PFNCs like silver/PLA and
430 silver/PLGA nanocomposites showed strong bactericidal properties (*Escherichia coli*) with almost
431 non-harmful effects to humans (Paul et al., 2015). Other PFNCs were mainly investigated for
432 biomedical applications (for orthopedic and dental applications) like injectable nanocomposites
433 made of biodegradable poly(-propylene fumarate) (Shi et al., 2008) proving the absence of
434 cytotoxicity (fibroblast cell line *in vitro* test).
435 Papers developing PFNC materials for specific water and wastewater applications did not
436 investigate any potential (eco)toxicity effects (Katsoyiannis and Zouboulis, 2002; Chang et al.,
437 2005; Guo and Chen, 2005; Chang et al., 2006; Say et al., 2006; Banerjee et al., 2007; Lim et al.,
438 2009; Wang and Wang, 2009; Zhou et al., 2009; Tran et al., 2010; Badruddoza, et al. 2011; Bée et
439 al., 2011; Shirsath et al., 2011; Zhu et al., 2011; Badruddoza et al., 2012; Badruddoza, et al.
440 2013a,b; Musico et al., 2013). An exception was done by Önnby et al. (2014), where they
441 investigated nanocomposites of aluminium oxide nanoparticles (Al NPs) incorporated in a PA
442 cryogel matrix for AsO_4^{3-} removal efficiency in the perspective of creating a water filter, also
443 demonstrating the potential toxicity of the filtrate by using human epithelial cells (Caco-2). No cell
444 death in relation to the presence of NP was evident, but cell viability was slightly affected probably
445 due to the levels of a residual monomer. Authors suggested further investigations stressing the
446 PNFC system performance using higher flow speeds and composite volumes, under more
447 aggressive pH conditions, and with higher ionic strength (Önnby et al., 2014).
448 Despite the use of PFNCs mainly as adsorbent for metals removal from water and wastewater,
449 several issues related to their safety are still open: i) in general few data on PFNC as a whole, and
450 very limited data for the specific water-related application is available; ii) existing stressing and

451 weathering experiments are occasional and short-term based; and iii) scarce toxicity data are
452 available only for cell lines and/or microorganisms still on a short time exposure, while no whole
453 multicellular eukaryotic biological models have been considered.
454
455 4.5 Design considerations
456 Most studies concerning metal removal via PFNCs are related to laboratory-scale set-ups. This
457 raises questions about the possibilities of deploying this technique into *in situ* situations. Lab-scale
458 configurations studies evidence three main configurations, as summarized in Figure 3:
459 • NPs are mixed with contaminated water, being the main problem of this approach the separation
460 of NPs from the water. However, if magnetic NPs are used, this can be achieved via magnetic
461 fields to overcome the main limitation of this approach (Manju et al., 2002).
462 • NPs are immobilized on membrane sheets or fibers and the contaminated water passes over
463 them making the adsorption process possible. The advantage of this design is that the NPs can
464 be recovered, but a suitable system (*i.e.* sufficient capacity) might require a large surface area
465 for efficient contaminants adsorption (Vatutsina et al., 2007). Membrane fouling is a current
466 problem requiring to regular cleaning procedure or membrane replacement.
467 • NPs can be immobilized onto larger particles that are easily separated from water at or near the
468 outlet of the treatment installation. This leads to a fixed bed or fluidized bed system, where the
469 water flows through the pores among the particles (Katsoyiannis and Zouboulis, 2002, Cumbal
470 and Sengupta, 2011). Fouling could reduce the effectiveness of the adsorption process, but the
471 replacement of larger particles can be continuous.
472 • NPs are immobilized on membrane sheets or fibers and the contaminated water passes over
473 them making adsorption possible. The advantage of this design is that the NPs can be recovered,
474 but a suitable system (*i.e.*, membrane fouling is a current problem requiring a regular cleaning
475 procedure or membrane replacement).
476

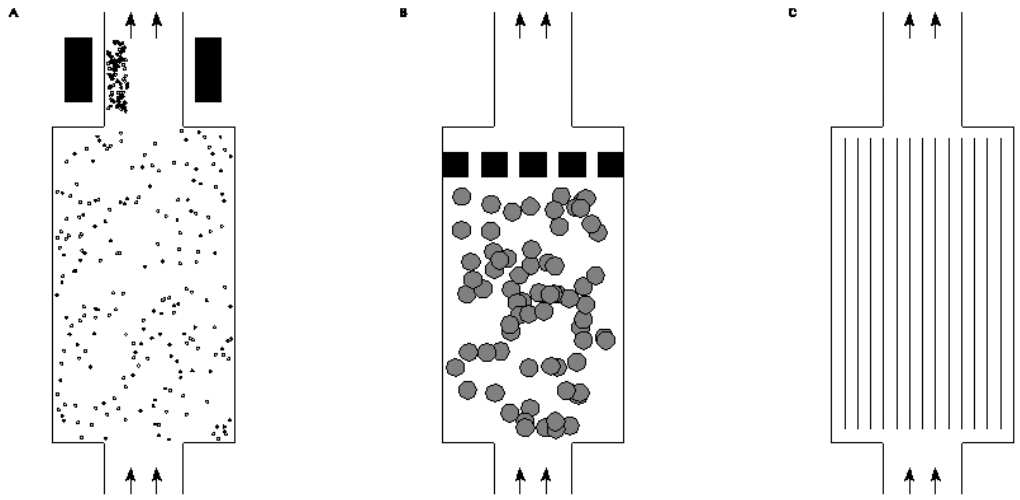

Figure 3 Rough sketch of various designs: A) Free NPs which are separated from the water via a magnetic field; B) NPs immobilized on macroscopic particles (fixed or fluidized bed); C) NPs immobilized on membranes.

Crucial parameters for the design are i) the total surface area available for adsorption processes determining the capacity, and ii) the achievable throughput causing the system footprint. To better elucidate the scale effect we can consider a case study where Cd contaminates water. Table 3 indicates an adsorption capacity of 21 mg Cd per g of PA-(HFO) (Manju et al., 2002), where the S-PFNCs are in suspension, so that the entire surface is available for adsorption. The total surface area per unit of volume ($m^2\ L^{-1}$) is provided by Eq. 4.

$$A = 4\pi R^2 N \qquad \text{(Eq. 4)}$$

where, R is the radius of the S-PFNCs (considering S-PFNCs as roughly spherical), and N is the number of NPs per unit of volume. This is related to the mass concentration C:

$$N = C / (\rho\ 4\pi/3\ R^3) \qquad \text{(Eq. 5)}$$

where, ρ is the density and the denominator is the mass per NP. Combining Eq. 4 and Eq. 5 leads to:

$$A = 3C/\rho R \qquad \text{(Eq. 6)}$$

According to Eq. 6 and using a density of 4000 kg/m^3 and a radius of 50 nm, removal of 1 g/m^3 of these NPs corresponds to 5 m^2 surface area per m^3 of suspension.

Since this concerns free-floating NPs, the full surface area is available. If the NPs are embedded in a polymer membrane, then roughly half of the surface will be available. Furthermore the NPs will be spread over the membrane and they may or may not be close together. Assuming that the S-PFNCs are indeed as close together as possible, then an estimate of the membrane area can be obtained, which will in fact be a lower limit. The adsorption of 21 mg Cd requires 1 g of HFO. From the above calculation the surface area of 1 g NPs is 5 m^2. Therefore at least 5 m^2 of membrane are required to adsorb that amount of Cd and probably more, since the NPs will be spread over the membrane rather than being very close together. This gives an idea of the dimensions of a device intended to adsorb metals from water via such membranes.

4.6 Cost evaluation

The cost of the materials is one of the key factors to evaluate the sustainability of PFNCs as adsorbents. The cost of producing PA - (HFO) is 7 US$ per 100 g which is approximately three times lower than the cost of some commercial resins such as Amberlite IRA-64, Amberlite IRP-88, Amberlite CG-50 and Duolite ES-468 (21-45 US$ per 100 g of resin) (Manju et al., 2002).

The cost of modification agents should also be estimated. For instance, α-KA is a harmless and environmental-friendly biologic reagent, while chemical modification reagents are general toxic to humans and animals, and also expensive. The cost of the α-KA- Ch - (γ-Fe_2O_3) is mainly related to the α-KA price, which is about 380 US$ per kg depending on the preparation procedure. However, the costs of the chitosan flakes cross-linked with glutaraldehyde and chitosan-coated polyvinyl chloride beads can reach up to 15,700 and 3,254 US$ per kg, respectively. The removal efficiency of α-KA- Ch - (γ-Fe_2O_3) reach 50% after 2 min, and its adsorption equilibrium can be attained after 60 min, whereas the equilibrium time for the chitosan flakes cross-linked with glutaraldehyde can be 16 times faster. The maximum uptake of the α-KA- Ch - (γ-Fe_2O_3) is 96.15 mg g^{-1}, while that of the chitosan flakes cross-linked with glutaraldehyde or chitosan-coated polyvinyl chloride beads is 85.5 or 87.9 mg g^{-1}, respectively. Therefore, the α-KA- Ch - (γ-Fe_2O_3) can be considered as a viable

522 economical alternative for the commercially available adsorbents for the removal of metals from
523 aqueous solutions (Zhou et al., 2009).
524

525 5. Conclusions

526 In the last decade, several studies have been devoted to the application of PFNCs for metals and
527 metalloids removal from water and wastewater. Despite the promises of these adsorbents, several
528 issues related to their use still remain to be addressed:

529 ▪ Safety for human health and the environment has not been fully assessed - further research
530 is expected in the near future investigating the long term exposure and effects considering
531 various biological targets;

532 ▪ Greening the PFNCs production is expected in order to minimize the use of solvents and
533 make their use more environmentally friendly;

534 ▪ Removal efficiency and cost optimization per unit volume treated waiting for an economy of
535 scale;

536 ▪ Support the life cycle impact analysis according to the reuse, recovery and regeneration
537 approaches and zero-waste perspective.

538

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542

Nomenclature

α-KA = α-ketoglutaric acid

CA – (γ-Fe_2O_3) = Calcium alginate coated iron oxide

(C – β – CD) = Carboxymethyl-β-cyclodextrin

ACP – $N(CH_3)_2$ – (HFO) = Acrylic polymer +N(CH3)2 supported Hydrated Iron (III) Oxide

C – β – CD – (Fe_3O_4) = Carboxymethyl – β – cyclodextrin modified (Fe_3O_4)

CA – (Fe_3O_4) = Calcium alginate encapsulated (Fe_3O_4)

CA – (HFO) = Calcium alginate coated hydrous iron oxide

CDs = Cyclodextrins

Ce – (Fe_3O_4) = (Fe_3O_4)/bacterial cellulose

Ce – (HFO) = Cellulose loaded with hydrous iron oxide

Ch – (γ-Fe_2O_3) = Chitosan coated iron oxide

Ch – (Cu^0) = Chitosan supported copper

Ch – (Fe_2O_3) = Chitosan supported iron oxide

CNTs = Carbon Nanotubes

CPDB – (HFO) = Polystirene + Divinilbenzene copolymer coated by Hydrated Iron (III) Oxide

D001 – (HFO) = Hydrated Fe(III) oxide (HFO) Nanoparticles within a cation-exchange resin D-001

DETA – (Fe_3O_4) = Diethylenetriamine supported Fe_3O_4magnetic

EDA – (Fe_3O_4) = Ethylenediamine supported Fe_3O_4magnetic

FT – IR = Fourier Trasform Infra-Red

GA – (Fe_3O_4) = Gum arabic supported (Fe_3O_4)

HFO = Hydrated Iron (III) Oxide

HSAB theory= Hard–Soft Acid–Base theory

MP – (Fe_3O_4) = Mercapto-functionalized core-shell nano-magnetic Fe_3O_4polymers

MWCNTs = Multi Walled Carbon Nanotubes

mPAA – (Fe_3O_4) = Magnetic polyacrylic acid sodium salt supported Fe_3O_4 magnetic

PA – (HFO) = Polyacrylamide grafted Hydrated Iron (III) Oxide

PA = Polyacrylamide

PA – (HFO) = Polyacrylamide-grafted hydrous iron(III) oxide

PEI – (Fe_3O_4) + SiO_2 = Polyethylenimine supported Fe_3O_4 magnetic

PEI – (Fe_3O_4) = Polyethylenimine supported Fe_3O_4 magnetic

PEI – C = Polyethylenimine supported nanocarbon

PEI – NC = Polyethylenimine nanocomposite

PLA = polyactide

PLCy – (γ-Fe_2O_3) = Poly-L-cysteine immobilized onto the surface of iron oxide

PLGA = polyglycolide

PnV – G = Poly (n- vinylcarbazole) blended with graphene oxide nanoparticles

PP = polypropylene

PS – (HFO) = Polystirene sulfone supported Hydrated Iron (III) Oxide

PS – (HMO) = Polystirene sulfone supported Hydrated Iron (III) Oxide

PS – ZrP = Polystirene sulfone supported Zirconium phosphate

PS – $Zr(HPO_3S)_2$ = Polystirene sulfone supported Zirconium hydrogen monothio phosphate

SEM = Scanning Electron Microscopy

SPM = Scanning Probe Microscopy

TEM = Transmition Electron Microscopy

TEPA – (Fe_3O_4) = Tetraethylenepenthamine supported Fe_3O_4 magnetic

TETA – (Fe_3O_4) = Triethylenetetramine supported Fe_3O_4 magnetic

XRD = X-Ray Diffraction

544

545

546 6. References

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Figures Captions

Figure 1 Fabrication methods of PFNCs

Figure 2 Schematic representations of the polymeric cation and anion exchangers used on the S-PFNCs HFO - Hydrated iron (III) oxide. (Modified from Cumbal and Sengupta, 2005

Figure 3 Rough sketch of various designs: A. Free NPs which are separated from the water via a magnetic field; B. NPs immobilized on macroscopic particles (fixed or fluidized bed); C. NPs immobilized on membran**es.**

Table Captions

Table 1 Synthesis of Synthetic polymer functionalized nanocomposites (S- PFNCs)

Table 2 Synthesis of Biopolymers functionalized nanocomposites (B- PFNCs)

Table 3 Behaviour of S- PFNCs for metal removal

Table 2 Behaviour of S B- PFNCs- adsorption

Table

Click here to download Table: Table 1 S_PFNCs synthesis and charcterization.docx

Table 1

Polymer matrix	**NPs**	**S-PFNCs**	**Preparation method**	**Ref.**
Polystirene sulfone	Hydrated iron oxide (HFO)	PS-(HFO)	In *situ* synthesis[1]	Etzel et al., 1997
	Hydrated iron oxide (HFO)	PS-(HFO)	In *situ* synthesis[1]	Cumbal and Sengupta., 2005
	Hydrated iron oxide (HFO)	PS-(HFO)	In *situ* synthesis[1]	DeMarco et al., 2002
	Hydrated iron oxide (HFO)	PS-(HFO)	In *situ* synthesis[1]	Sylvester et al., 2007
	Hydrated iron oxide (HFO)	PS-(HFO)	In *situ* synthesis[1]	Möller et al., 2008
	Hydrated iron oxide (HFO)	PS-(HFO)	In *situ* synthesis[1]	Pan et al., 2010
	Hydrous manganese oxide (HMO)	PS-(HMO)	In *situ* synthesis[1]	Pan et al., 2007
	Zirconium hydrogen monothio phosphate $Zr(HPO_3S)_2$	PS- $Zr(HPO_3S)_2$	In *situ* synthesis[1]	Zhang et al., 2008
	Zirconium phosphate	PS-ZrP	In *situ* synthesis[1]	Pan et al., 2006
Copolymer (Polystyrene+divi	Hydrated iron oxide	CPDB- (HFO)	Direct compounding	Katsoyiannis et al, 2002

nylbenzene)	(HFO)			
Acrylic polymer +$N(CH_3)_2$	Hydrated iron oxide (HFO)	ACP- $N(CH_3)_2$ - (HFO)	In *situ* synthesis[1]	Vatutsina et al., 2007
Polyacrylamide	Hydrated iron oxide (HFO)	PA-(HFO)	In *situ* synthesis[2]	Manju et al, 2002
Mercapto – functionalized polymer	Magnetite (Fe_3O_4)	MP- (Fe_3O_4)	In *situ* synthesis[1]	Pan et al, 2012
Polyethylenimine	Magnetite (Fe_3O_4)	PEI-(Fe_3O_4)	Direct compounding	Pang et al, 2011b
	Magnetite (Fe_3O_4) +SiO_2	PEI-(Fe_3O_4) +SiO_2	Direct compounding	Pang et al, 2011a
	C	PEI-C	In *situ* synthesis[1]	Khaydarov et al, 2010
m-PAA-Na	Magnetite (Fe_3O_4)	m-PAA – Na-(Fe_3O_4)	In *situ* synthesis[2]	Mahdavian et al, 2010
Ammino-functionalizedpolymer (TEPA)	Magnetite (Fe_3O_4)	TEPA- (Fe_3O_4)	In *situ* synthesis[2]	Zhao et al., 2010
	Magnetite (Fe_3O_4)	TEPA- (Fe_3O_4)	In *situ* synthesis[2]	Shen et al., 2012
Poly (n-vinylcarbazole)	Graphene oxide	PnV- G	Direct compounding	Musico et al., 2013

[1,2] These numbers are referred to the preparation methods shown in Figure 1

Table

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Table 2

Polymer matrix	NPs	B-PNCs	Preparation method	Ref.
Calcium alginate	Iron oxide (Fe_2O_3)	CA-(γ-Fe_2O_3)	In *situ* synthesis[2]	Bèe et al, 2011
	Hydrated iron oxide (HFO)	CA-(HFO)	Direct compounding	Zouboulis et al., 2002
	Magnetite (Fe_3O_4)	CA-(Fe_3O_4)	-	Lim et al., 2009
Carboxymethyl – β – cyclodextrin	Magnetite (Fe_3O_4)	C- β-CD- (Fe_3O_4)	In *situ* synthesis[2]	Badruddoza et al., 2011, 2012, 2013
		C- β-CD- (Fe_3O_4)	-	Yu et al. 2011
Cellulose	Hydrated iron oxide (HFO)	Ce - (HFO)	In *situ* synthesis[2]	Guoand Chen 2005
	Magnetite (Fe_3O_4)	Ce - (Fe_3O_4)	In *situ* synthesis[2]	Zhu et al., 2011
Chitosan	Iron oxide (Fe_2O_3)	Ch - (γ-Fe_2O_3)	In *situ* synthesis[2]	Zhou et al., 2009
	Magnetite (Fe_3O_4)	Ch-(Fe_3O_4)	In *situ* synthesis[2]	Tran et al., 2010
	Magnetite (Fe_3O_4)	Ch-(Fe_3O_4)	In *situ* synthesis[2]	Chang and Chen, 2005
	Magnetite (Fe_3O_4)	Ch-(Fe_3O_4)	In *situ* synthesis[2]	Chang et al, 2006
	Cu^0	Ch-(Cu^0)	In *situ*synthesis[2]	Wu et al, 2009
Gum arabic	Magnetite (Fe_3O_4)	GA-(Fe_3O_4)	In *situ*synthesis[2]	Banerjee and Chen, 2007
Poly-L-cysteine	Iron oxide (Fe_2O_3)	PLCy–(γ-Fe_2O_3)	In *situ*synthesis[2]	White et al., 2009

[2]Thenumberis referred to the preparation methods shown in Figure 1

Table

Click here to download Table: Table 3 S_PFNCs Adsorption processes_GL.docx

Table 3

Metals	S-PFNPs	pH	C_0 [mg L^{-1}]	Adsorption capacities	Removal (%)	Adsorption constants	References
As(III)	PS – (HFO)	7.2	0.100	< 10 ppb within 2000 BV	> 90		De Marco et al., 2002
	PS – (HFO)		100	< 10 ppb within 12 000 BV	> 90	-	Cumbal and Sengupta, 2005
	ACP – $N(CH_3)_2$ – (HFO)	9	60	< 10 ppb within 10000 BV	90	K_L = 1.52 L $mmol^{-1}$ K_F = 0.58 L $mmol^{-1}$	Vatutsina et al., 2007
As(V)	PS – (HFO)		100	< 0.5 ppm	> 95	-	Etzel et al., 1997
	PS – (HFO)	7.2	0.050	< 10 ppb within 4000 BV	> 80		De Marco et al., 2002
	PS – (HFO)		0.100	< 10 ppb within 10 000 BV,	> 90	-	Cumbal and Sengupta, 2005
	PS – (HFO)	8.16	0.023	< 0.5 ppb within 33196 BV	> 98		Sylvester et al., 2007
	PS – (HFO)		0.020 0.300	< 10 ppb within 17500 BV < 10 ppb within 3500 BV	> 50 > 96		Möller et al., 2008
	CPDB – (HFO)		0.100	< 10 ppb within 65 BV	90		Katsoyiannis and Zouboulis, 2002
	ACP – $N(CH_3)_2$ – (HFO)	5.64	60	< 10 ppb within 10000 BV	90	K_L = 3.23 L $mmol^{-1}$ K_F = 0.68 L $mmol^{-1}$	Vatutsina et al., 2007
Cd(II)	PA – (HFO)	5 - 6	25	21.03 mg g^{-1}	81	K_L = 0.0206L mg^{-1}	Manju et al, 2002

	PS – (HFO)		1	< 5 ppb within 7000 BV	> 99		Pan et al., 2007
	PS – HMO			sorption capacities increased by 50 – 300% compared to host exchangers		K_d increased by 20 – 800 times as compared to host exchangers	Pan et al., 2008
	PS – $Zr(HPO_3S)$		45	< 0.09 mg L^{-1} within 1600 BV	> 99	-	Zhang et al., 2008
	m-PAA – Na – (Fe_3O_4)	8	1.8	5.0 mg g^{-1}	-		Mahdavian et al, 2010
	PEI – C	6	3	< 0.005 ppm	99	-	Khaydarov et al, 2010
	PEI – (Fe_3O_4) + SiO_2	6.5	100	105.2 mg g^{-1}	78	K_L = 0.0290 L mg^{-1} $K_{F=}$ 11.545 Lg^{-1}	Pang et al, 2011a
Cr (VI)	PEI – (Fe_3O_4)	2 – 3		83.33 mg g^{-1}	95	K_L = 0.125 L mg^{-1} K_F = 20.85 L g^{-1}	Pang et al, 2011b
	TEPA – (Fe_3O_4)			370.37 mg g^{-1}		K_L = 0.1233 L mg^{-1}	Zhao et al., 2010
	TEPA – (Fe_3O_4)	2	50 500 1000		99 73 42		Shen et al., 2012
Cu (II)	PS – (HFO)		1	< 5 ppb within 7000 BV	> 99	-	Pan et al., 2007
	PEI – (Fe_3O_4) + SiO_2	6.5	100	157.8 mg g^{-1}	98	K_L = 0.0318 L mg^{-1} K_F = 42.561 L g^{-1}	Pang et al, 2011a
	PEI – C	6	10	< 0.005 ppm	99		Khaydarov et al, 2010
	m-PAA – Na – (Fe_3O_4)	8	18	27.0 mg g^{-1}	-	-	Mahdavian et al, 2010

	TEPA – (Fe_3O_4)	4	10 100 300	116.80 mg g^{-1}	99.85 78.51 17.66	K_L = 0.4009 L mg^{-1}	Shen et al., 2012
Hg(II)	PA – (HFO)	5	25	21.38 mg g-1	85	K_L = 0.0246 L mg-1	Manju et al, 2002
	MP – (Fe_3O_4)	2 - 6	-	256.4 mg g^{-1}	-	K_L = 0.0585 L mg^{-1} K_F = 50.54 L g^{-1}	Pan et al, 2012
Ni(II)	m-PAA – Na – (Fe_3O_4)		18	25.0 mg g^{-1}	-	-	Mahdavian et al, 2010
Pb(II)	PS – HMO			sorption capacities increased by 50 – 300% compared to host exchangers		K_d increased by 20 – 800 times as compared to host exchangers	Pan et al., 2008
	PA – (HFO)	6	25	23.79 mg g^{-1}	96	K_L = 0.0250 L mg^{-1}	Manju et al, 2002
	PS – $Zr(HPO_3S)$		80	< 0.01 mg L^{-1} within 1600 BV	> 99	-	Zhang et al., 2008
	PS – ZrP		0.5	< 0.05 ppm within 2000 BV	98		Pan et al., 2006
	PS – (HFO)		1	< 5 ppb within 7000 BV	> 99		Pan et al., 2010
	m-PAA – Na – (Fe_3O_4)	8	18	40.0 mg g^{-1}	-		Mahdavian et al, 2010
	PnV – G	7	5 – 300	982.86 mg g^{-1}	97	K_L = 0.0187 L mg^{-1}	Musico et al., 2013
Zn(II)	PS – HMO			sorption capacities increased by 50 – 300% compared to host exchangers		K_d increased by 20 – 800 times as compared to host exchangers	Pan et al., 2007
	PS – $Zr(HPO_3S)_2$		15	< 0.06 mg L^{-1} within	> 99		Zhang et al., 2008

				120 BV			
	PEI – C	6	5	< 0.010 ppm	99		Khaydarov et al, 2010
	PEI – (Fe_3O_4) + SiO_2	6.5	100	138.8 mg g^{-1}	80%	K_L = 0.0245 L mg^{-1} K_F = 33.986 L g^{-1}	Pang et al, 2011a
Se(IV)	PS – (HFO)		100	< 0.5 ppm	> 99	-	Etzel et al., 1997

Table
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Table 4

Metals	B-PFNCs	Optimum pH	C_o [mg L^{-1}]	Adsorption capacities	Removal (%)	Adsorption constants K_L [L mg^{-1}] K_F [L g^{-1}]	References
As(III)	CA- (HFO)	7	0.05	< 10 ppb within 45 BV	> 95	-	Zouboulis and Katsoyiannis, 2002
	Ce - (HFO)	7 – 9	7.5	99.6 mg g^{-1}	95	K_L = 0.120	Guo and Chen, 2005
	PLCy – (γ-Fe_2O_3)	7 (4 – 9)	1	25.6 mg g^{-1}	22	-	White et al., 2009
As(V)	CA- (HFO)	7	0.05	< 10 ppb within 230 BV	> 95	-	Zouboulis and Katsoyiannis, 2002
	Ce - (HFO)	7 (5 – 11)	7.5	33.2 mg g^{-1}	90	K_L = 2.29	Guo and Chen, 2005
Au (III)	Ch- (Fe_3O_4)	2 (2 – 10)	1039 (200 – 3000)	59.52 mg g^{-1}		K_L = 0.066 K_F = 13.14	Chang and Chen, 2006
Cu (II)	CA- (Fe_3O_4)	5 (2 – 6)	1 (1 – 6)	60 mg g^{-1}		K_L = 1.43	Lim et al., 2009
	C-β- CD- (Fe_3O_4)	6 (2 – 6)	(50 – 200)	47.2 mg g^{-1}		K_L = 0.0237 K_F = 7.064	Badruddoza et al., 2011
	Ch - (γ-Fe_2O_3)	6 (2 – 8)	200 (100 – 400)	96.15 mg g^{-1}	55 – 99	K_L = 0.0493 K_F = 16.406	Zhou et al., 2009
	Ch- (Fe_3O_4)	5 (2 – 5)	1150 (200 – 1150)	21.5 mg g^{-1}		K_L = 0.0165	Chang and Chen, 2005
	GA- (Fe_3O_4)	5.1	200	38.5 mg g^{-1}		K_L = 0.012	Banerjee and Chen, 2007
	PLCy – (γ-Fe_2O_3)	7 (4 – 9)	1	43.3 mg g^{-1}	60	-	White et al., 2009
Cd (II)	C-β- C - (Fe_3O_4)	5.5 – 6	300	27.7 mg g^{-1}	55.9	K_L = 0.214 K_F = 17.64	Badruddoza et al., 2013
	PLCy – (γ-Fe_2O_3)	7	1	43.3 mg g^{-1}	71	-	White et al., 2009

		(4 – 9)					
Cr(III)	Ce-(Fe_3O_4)	-	0 – 100 100 – 200	25 mg g^{-1}	35 25	-	Zhu et al., 2011
Cr (VI)	Ch- (Cu^0)	4.85	5 50	3.96 mg g^{-1} 47.8 mg g^{-1}		-	Wu et al, 2009
Mn(II)	Ce-(Fe_3O_4)	-	0 – 100 100 – 200	33 mg g^{-1}	46 33	-	Zhu et al., 2011
Ni(II)	C-β- CD - (Fe_3O_4)	5.5 – 6	300	13.2 mg g^{-1}	24.3	K_L = 0.043 K_F = 2.39	Badruddoza et al., 2013
	Ch- (Fe_3O_4)	6 (4 – 6)	70 (50-80)	52.55 mg g^{-1}	> 75	K_L = 1.3448	Tran et al., 2010
	PLCy – (γ-Fe_2O_3)	7 (4 – 9)	1	32.8 mg g^{-1}	89	-	White et al., 2009
Pb (II)	CA-(γ-Fe_2O_3)	4.7 (1 - 6)	51.8 – 4972.8 1502.2	97.4 mg g^{-1}		K_L = 0.076	Bèe et al, 2011
	Ce-(Fe_3O_4)		0 – 100 100 – 200	65 mg g^{-1} 52 mg g^{-1}	90 65	-	Zhu et al., 2011
	Ch- (Fe_3O_4)	6 (4 – 6)	70 (50 – 80)	63.33 mg g^{-1}	> 90	K_L = 0.1097	Tran et al., 2010
	C-β- CD - (Fe_3O_4)	5.5 – 6	200	52.20 mg g^{-1}		K_L = 0.208 K_F =16.43	Badruddoza et al., 2012
	C-β- CD - (Fe_3O_4)	5.5 – 6	300	64.5 mg g^{-1}	99.5	K_L = 0.417 K_F = 25.82	Badruddoza et al., 2013
	PLCy – (γ-Fe_2O_3)	7 (4 – 9)	1	14.7 mg g^{-1}	67	-	White et al., 2009
Zn	PLCy – (γ-Fe_2O_3)	7 (4 – 9)	1	24.1 mg g^{-1}	50	-	White et al., 2009

Figure

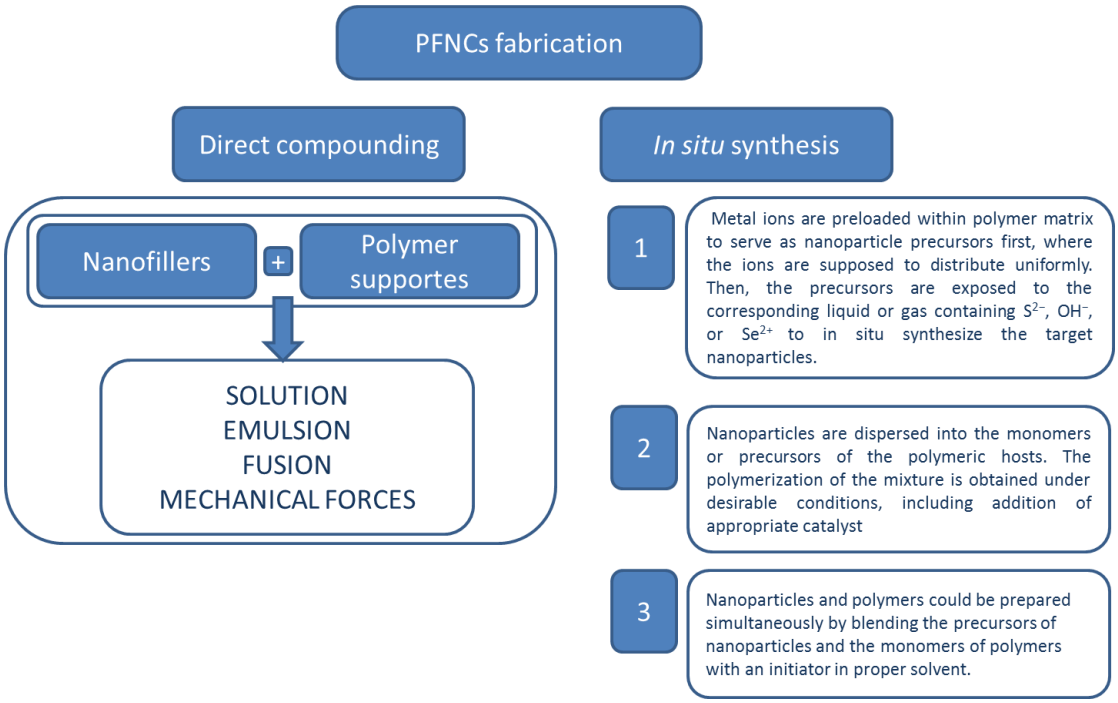

Figure 1 Fabrication methods of PFNCs

Figure 2 Schematic representations of thepolymeric cation and anion exchangers used on the S-PFNCs HFO - Hydrated iron (III) oxide. (Modified from Cumbal and Sengupta, 2005).