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Removal of Anionic Pollutants from Waters and Wastewaters and Materials Perspective for Their Selective Sorption

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Abstract The presence of some anionic species, such as nitrate, nitrite, chloride, sulfide, fluoride, and cyanide, in water supplies may represent a serious environmental problem. In this work, the main sources and harmful effects of their bioaccumulation on living organisms are reviewed, as well as the most adopted technologies for their uptake. The major advantages and disadvantages of each methodology are also listed. In general, ion-exchange has been elucidated as the most suitable removal process. In view of that the most promising materials used to remove anionic pollutants from aqueous solutions are highlighted in this review. In particular, the major efforts towards the development of low-cost and easily available effective sorbents for water decontamination are covered. For instance, natural waste solid materials and derivatives have emerged as promising low-cost exchangers for selective anions uptake. Besides, a number of structural modifications including the introduction of more suitable surface functional groups or compensation species into the sorbent matrix have been investigated in order to enhance sorbents selectivity and capacity for anionic pollutants. The influence of speciation and removal conditions is also focused.

Keywords Anion · Ion-exchange · Pollutants · Sorbent · Water treatment

Nomenclature

AC	Activated carbon
C	Concentration in solution
C_0	Initial concentration in solution
DWD	European Drinking Water Directive
Fe(III) LECCA	Fe(III)-loaded ligand exchange cotton cellulose adsorbent
GRM	Granular red mud
LDHs	Layered double hydroxides
MMO	Mixed metal oxide
t	Time
T	Temperature
TAC	Total anodic compartment
WHO	World Health Organization
X	Dimensionless concentration in solution
Y	Dimensionless concentration in the solid phase

1 Introduction

A number of anionic species, such as nitrate, nitrite, chloride, sulfide, fluoride, and cyanide, may be

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considered as pollutants when present in water supplies above certain levels. Moreover, their bioaccumulation becomes an environmental concern when their concentrations in the environment begin to affect human health and ecosystems. Many of these species occurs naturally in the atmosphere, water, and soils (Lv et al. 2006a). For instance, nitrate and nitrite are found in atmospheric precipitation and mineral deposits, while fluorine is released into subsoil water sources by natural degradation of fluorine-containing rocks (Daifullah et al. 2007; Wajima et al. 2009; Biswas et al. 2010). Moreover, cyanide is present in several organic and inorganic compounds including plants and animals (Dash et al. 2009).

Besides their natural occurrence in the ecosystem, their extensive application in several industrial and agricultural sectors, in addition to the improper treatment of industrial and urban wastewaters, gives inevitably rise to their release and dispersion into the environment. Contamination of drinking water by these toxic contaminants may represent a public health problem given their harmful effects on living organisms. Accordingly, many countries and environmental protection agencies have been forced to implement limiting standards for drinking water and discharges of industrial wastewaters (Dabrowski et al. 2004). As a result, removal of such compounds from wastewaters becomes crucial toward the preservation of human's health and environment.

In order to accomplish the maximum permitted levels, many research works have been dedicated to the development and application of effective techniques to remove these compounds from aqueous solutions. Advanced treatments such as chemical and catalytic reduction, adsorption and ion-exchange, and membrane processes are some examples of the commonly preferred removal techniques. However, most of these methods experience important disadvantages such as complex and expensive operation, low selectivity, low capacity, difficulties in regeneration, and generation of secondary wastes (Islam and Patel 2010; Yang and Cheng 2007; Guo et al. 2008). Still, the ion-exchange technology has been considered particularly suitable to remove ionic contaminants from aqueous solutions given its simplicity, effectiveness, selectivity, recovery, and relatively low operating cost.

In this work, the most applied methodologies to remove nitrate, nitrite, chloride, sulfide, fluoride, and cyanide anions from aqueous solutions are reviewed and discussed. It is intended to complement a previous publication devoted specifically to the separation of the most common metallic cations from solution (Lopes et al. 2012). After a general introduction on the topic, the discussion is divided into each individual anionic pollutant. Special attention is focused on adsorption and ion-exchange technologies given their special practical interest.

2 Removal of Nitrate and Nitrite

Nitrates and nitrites are extremely toxic and harmful compounds and thus their presence in the environment is a serious problem in many regions of the world (Bogoczek et al. 2006). In recent years, the concentration of these nitrogenous compounds in surface and groundwater has been significantly rising largely owing to the extensive use of chemical fertilizers in addition to the improper treatment of industrial and urban wastewaters (Gao et al. 2004; Islam and Patel 2010; Samatya et al. 2006; Lin and Wu 1996; Öztürk and Köse 2008; Guo et al. 2008; Pintar and Batista 2006; Pintar et al. 2001). As a result, high nitrogen concentrations in drinking water have been found in regions of intensive agricultural activities, where fertilizers and farm animal wastes permeate through the soil into groundwater and water supplies, given their high solubility in water (Yang and Cheng 2007). Additional industrial sources of nitrate and nitrite include chemical manufacturing of explosives, production of dyes, synthesis of nitrogen-containing organic derivatives, and operations using nitrogen-containing products as corrosion inhibitors, cleaners, and metalworking fluids. Besides, atmospheric precipitation, local mineral deposits such as potassium nitrate, decomposition of biomass, and activities of nitrogen-fixing bacteria could also contribute to drinking water contamination, even in less extent than human activities contribution does (Yang and Cheng 2007; Samatya et al. 2006; Bogoczek et al. 2006). Furthermore, the concentration of nitrate and nitrite could also be increased in drinking water treatment and water-supply systems as a result of microorganism and bacteria activity.

Contamination of drinking water by nitrate and nitrite represents indeed a public health problem (Yang and Cheng 2007; Hradil et al. 1997; de Heredia et al. 2006; Öztürk and Köse 2008). Nitrite in the blood can combine with hemoglobin giving rise to methemoglobin (blue-baby syndrome), especially in newborn infants, which reduces the capability of the blood to hold oxygen. Besides, nitrite in the body can react with the amino groups of albumens being converted into carcinogenic nitrosamine, resulting in cancer and hypertension (Yang and Cheng 2007; Guo et al. 2008; Bogoczek et al. 2006; Samatya et al. 2006; Gao et al. 2004; Hradil et al. 1997). In turn, high nitrate levels in drinking water can stimulate eutrophication, which causes water pollution by heavy algal growth (Islam and Patel 2010; Chabani et al. 2006). Nitrate-contaminated water has been associated as well with human diseases. For instance, nitrate can cause abdominal pains, diarrhea, vomiting, hypertension, increased infant mortality, central nervous system birth defects, diabetes, spontaneous abortions, respiratory tract infections, and changes to the immune system (Yang and Cheng 2007). Besides, the toxicity of nitrates is further related with their reduction to the reactive nitrite ion in the stomach and in the saliva (Samatya et al. 2006; Rivas and del Carmen Aguirre 2007; Yang and Cheng 2007; Deganello et al. 2000).

In view of the abovementioned motivations, the removal of nitrogenous compounds from wastewaters becomes crucial toward the preservation of human's health and the environment. Accordingly, the European Drinking Water Directive has established the maximum permitted nitrate and nitrite concentrations in drinking water to 50 and 0.5 $\mathrm{mg\,L^{-1}}$, respectively. In order to achieve such rigorous levels, efforts have been dedicated to develop effective techniques to remove these compounds from aqueous solutions. For instance, advanced treatments including chemical and catalytic reduction, ion-exchange, reverse osmosis, electrodialysis, and biological denitrification have be applied (Yang and Cheng 2007; Samatya et al. 2006; de Heredia et al. 2006; Islam and Patel 2010). However, most of these methods suffer from technical and economical drawbacks such as complex and costly operation, low removal efficiencies, generation of secondary brine wastes, and involve frequent media regeneration (Islam and Patel 2010; Yang and Cheng 2007; Guo et al. 2008).

Ozonation has been gaining considerable interest for nitrite removal owing to its high efficiency found during the conversion of nitrite to nitrate, which is less toxic to aquatic and human health and has lower drinking water regulatory standards (Yang and Cheng 2007; Bogoczek et al. 2006). This methodology has been considered an economic and robust solution to control the nitrite levels in drinking water. Notwithstanding, nitrate formed by these techniques is an undesirable component in the wastewater and, consequently, must be further removed. As a result, water treatment technologies capable to completely remove all nitrogenous compounds are definitely preferable (Krüner and Rosenthal 1983; Lin and Wu 1996; Honn and Chavin 1976).

Metal-catalyzed reduction of nitrates and nitrites is an alternative technique to remove them from contaminated surface and groundwater (Samatya et al. 2006; Deganello et al. 2000). This process holds important benefits including its simple and fast operation, the specificity of catalytic hydrogenation which reduces interference with other compounds present in solution, and the absence of any additive avoiding secondary contamination. However, the capital cost associated to this process is relatively high (Samatya et al. 2006). Recently, liquid-phase catalytic reduction using hydrogen over a solid catalyst has been proved to be a potential decontamination methodology for nitrite elimination. In this process, nitrite is selectively converted into nitrogen in a three-phase reactor system under mild reaction conditions (Gao et al. 2004; Strukul et al. 1996; Guo et al. 2008; Deganello et al. 2000). Nonetheless, dissolution of ammonia formed from the reaction with gaseous nitrogen may occur during the catalytic hydrogenation. Several researchers have reported the possibility of using metallic iron to reduce nitrate (Cheng et al. 1997; Hu et al. 2001). Previous studies have confirmed its capability to completely reduce nitrate under both anoxic and aerobic conditions, being ammonium and nitrogen gas the major resulting products.

Biological denitrification is one of the most widely used techniques to remove nitrate from water solutions (Samatya et al. 2006; Pintar et al. 2001; Chabani et al. 2006). This method provides a highly selective nitrate reduction to nitrogen by degradation by microorganisms (Samatya et al. 2006). However, maintaining biological processes at their optimum conditions is not an easy task, and the contamination of drinking water by bacteria, organic matter, and hazardous byproducts must be avoided (Chabani et al. 2006; Samatya et al. 2006; Lehman et al. 2008). Accordingly, a purification step of the drinking water by, for instance, filtration and germicidal treatment is obligatory (Lüdtke et al. 1998), which in turn merely displace nitrate into concentrated waste brine, creating an additional disposal problem (Samatya et al. 2006).

Ion-exchange is one of the most effective and commonly used treatments for removal of ionic contaminants from aqueous solutions. Moreover, by ion-exchange ionic species can be either removed or separated, allowing the complete deionization or the selective removal of ionic pollutants or valuable metals (Dabrowski et al. 2004). Concerning nitrate decontamination, many researchers have considered ion-exchange the most appropriate technology given its simplicity, effectiveness, selectivity, relatively low capital and operating costs, and long effective lifetime of specific exchangers (Samatya et al. 2006; Pintar et al. 2001; Kim and Benjamin 2004). A number of materials can be used as exchangers, being zeolites, weak and strong anionic and cationic resins, chelating resins, and microbial and plant biomass the mostly commonly applied (Tchobanoglous et al. 2003). Table 1 compiles the most frequently used materials for the removal of nitrate and nitrite anions together with the corresponding experimental conditions (namely pH, temperature, and initial solution concentration) and major results found in literature.

Further developments on novel types of ion exchangers are in progress and their range of applicability have been remarkably extended. Several nitrate selective resins have been recently developed for water decontamination. Among them, strong base resins on styrene (divinylbenzene matrix with tetraalkylammonium groups) have been assumed as particularly suitable for selective removal of nitrates from natural waters (Soldatov et al. 2007). However, the economics of the process are highly related with the presence of competing ions in solution. For example, when present at substantial concentrations, sulfate may link to most of the binding sites on such resins which may reduce significantly their capacity (Kim and Benjamin 2004). As a result, nitrate-selective anion-exchange resins for systems containing NO_3^-, Cl^-, and SO_4^{2-} anions are highly desirable for effective denitrification of drinking water (Samatya et al. 2006).

For instance, Hradil et al. (1997) evaluated the effect of the structure of quaternary ammonium groups in anion exchangers with methacrylate matrix on their selectivity for NO_3^- in the presence of Cl^- and SO_4^{2-} anions. The authors synthesized a series of quaternary ammonium methacrylate anion-exchange resins by reaction of macroporous 2,3-epoxypropyl methacrylate-ethylene dimethacrylate copolymer with the appropriate tertiary amine-hydrochloride, or by the two-step reaction with dialkylamines followed by *N*-alkylation, and found a higher tributylammonium group selectivity for the nitrate. More precisely, the obtained results demonstrated that in the case of trimethylammonium, nitrate ion was firstly eluted in comparison with sulfate ion, while with longer alkyl derivatives nitrate was eluted simultaneously or even after sulfate. Furthermore, the trimethylammonium derivative resins were found to uniquely sorb nitrate anions together with sulfate anions, which makes them poor candidates for selective denitrification. Concerning tri(*n*-butyl)ammonium and di(*n*-hexyl-)(*n*-butyl)ammonium exchangers, the affinity of nitrate over sulfate was observed to increase with the length of branched chains, being the difference between both materials associated with sulfate-nitrate interchange.

Biçak and Filiz Şenkal (1998) proposed for the first time a nitrate-specific polymeric sorbent. The studied polymer was obtained by suspension polycondensation of ethylenediamine with epichlorohydrin and it was found to practically contain only secondary amino groups. Results revealed the hydrochloride form of the resin as extremely efficient and highly selective for nitrite ions in aqueous solution, even in very low concentrations. Besides, the nitrite-loaded resin was demonstrated to be successfully regenerated by concentrated acid solutions, without losing its activity. More recently, Samatya et al. (2006) evaluated the efficiency of the nitrate selective anion-exchange resin Purolite A 520E for the removal of nitrate from solutions containing chloride and sulfate anions. Although the presence of chloride and sulfate ions were demonstrated to influence the breakthrough capacity of the resin for nitrate, Purolite A 520E were able to generate ground water containing lower nitrate concentration than the permissible level for drinking water.

Many researchers consider the strong base resins of poly(styrene-*co*-divinylbenzene) with tetraalkylammonium groups the most suitable ones for that purpose. Soldatov et al. (2007) studied the binary exchange equilibria between Cl^- and NO_3^-, Cl^- and SO_4^{2-}, and NO_3^- and SO_4^{2-} on fibrous strong base anion exchangers based on poly(styrene-*co*-divinylbenzene) grafted into polypropylene fibers containing groups of benzyl

Table 1 Materials most frequently used for the removal of anionic species together with the corresponding experimental and major results found in literature

Anion	Material	Experimental conditions			Results						
		pH	T (°C)	C_0 (mg L^{-1})	Batch	Column	Kinetics	Equilibrium	Regeneration	Others	Ref.
NO_3^-	Quaternary ammonium methacrylate anion-exchange resins	N.A.	R.T.	16.1		x	x		x	Distribution coefficient, competitive ions, and separation factor	Hradil et al. (1997)
NO_2^-	Epoxy-amine resin	N.A.	R.T.	0.2 M	x		x		x	Capacity and efficiency	Biçak and Filiz Şenkal (1998)
NO_3^-	Purolite A 520E	N.A.	30	5 to 200	x	x	x	x		Competitive ions and breakthrough capacity	Samatya et al. (2006)
NO_3^-	Fibrous anion exchangers	N.A.	N.A.	0.1 eq L^{-1}	x	x	x			Capacity, binary equilibrium, and separation factor	Soldatov et al. (2007)
NO_3^-	Zn/Al chloride layered double hydroxide	6 to 12	R.T.	10, 50, and 100	x		x	x	x	Percentage removal, competitive ions, and thermodynamic study	Islam and Patel (2010)
NO_3^-	Quaternary amino anion exchanger	N.A.	20	100	x					Percentage removal	Gao et al. (2009)
NO_3^-	Lignocellulosic anion exchangers	N.A.	30	1 to 30	x			x		Capacity	Orlando et al. (2002)
NO_3^-	Waste natural materials	N.A.	30	1 to 30	x			x		Capacity	Orlando et al. (2003)
NO_3^-	Amberlite IRA 400	6.8	25 and 70	1 to 18	x		x	x		Capacity, percentage removal, distribution content, and fractional attainment of equilibrium	Chabani et al. (2006)
NO_3^-	Amberlite IRN-78	N.A.	20	47 to 747	x		x	x		Capacity and competitive ions	de Heredia et al. (2006)
NO_3^-	Activated carbon	6 to 6.4	R.T.	5 to 200	x		x	x		Capacity, effect of initial concentration, pH, and temperature	Bhatnagar et al. (2008)
NO_3^-	Clays	N.A.	N.A.	40,000	x					Characterization and BET measurements	Mena-Duran et al. (2007)
NO_3^-	Natural zeolite coated with chitosan	5	4 and 20	10 to 620 and 10 to 3,100	x			x		Capacity and selectivity	Arora et al. (2010)
NO_3^-	Chitosan	3 to 8	20 to 50	100 to 1,000	x		x	x	x	Capacity, isotherm, thermodynamic study, and effect of pH	Chatterjee and Woo (2009)
Cl^-	ZnAl–NO_3-layered double hydroxides	4 to 9	25 to 60	100	x		x	x		Capacity, percentage removal, and thermodynamic study	Lv et al. (2009)
Cl^-	Amberlite IRA-420	2.85 to 3.79	20 to 40	252 to 7,575	x		x	x		Competitive ions	Carmona et (al. 2008)
S^{2-}	Resins Reillex™ HPQ and Dowex-l-X8	7 to 13	25	10, 15, and 20 mM	x		x	x		Capacity, speciation, and fractional attainment of equilibrium	Chabani and Bensmaili (2005)
S^{2-}	Denitrification reactor	7.3 to 7.4	30	110						Conversion of sulfide	Vaiopoulou et al. (2005)
S^{2-}	Microbial fuel cells	6.5 to 8	R.T.	N.A.						Percentage removal and energy recovery	Rabaey et al. (2006)

Table 1 (continued)

Anion	Material	Experimental conditions			Results						Ref.
		pH	*T* (°C)	C_0 (mg L^{-1})	Batch	Column	Kinetics	Equilibrium	Regeneration	Others	
F^-	Titanium hydroxide-derived adsorbent	1 to 10	25	1.9 to 800	x		x	x	x	Percentage removal, capacity, and competitive ions	Wajima et al. (2009)
F^-	Zr(IV)-imobilized resin	1.5 to 12.5	30	2.5 to 80	x	x		x		Capacity and competitive ions	Samatya et al. (2010)
F^-	Hydroxyapatite, fluorspar, calcite, quartz, and quartz activated by ferric ions	6	R.T.	2.5×10^{-5} to 6.34×10^{-2}	x		x	x		Capacity and percentage removal	Fan et al. (2003)
F^-	Magnesia-amended silicon dioxide granules	3 to 12	R.T.	5, 10, and 20	x		x	x		Capacity, removal efficiency, and competitive ions	Zhu et al. (2009)
F^-	$KMnO_4^-$-modified activated carbon	2 to 11	25 to 55	5 to 20	x		x	x		Percentage removal, competitive ions, and thermodynamic study	Daifullah et al. (2007)
F^-	Ion-exchange fiber	2 to 12	25	2 to 10	x	x	x	x	x	Percentage removal	Ruixia et al. (2002)
F^-	Modified Amberlite XAD-4 resin	1 to 10	25	16	x	x	x	x	x	Capacity and competitive ions	Solangi et al. (2010)
F^-	Alumina/chitosan composite	3 to 11	30, 40, and 50	9 to 15	x		x	x		Capacity, competitive ions, and thermodynamic study	Viswanathan and Meenakshi (2010)
F^-	Fe(III)-loaded ligand exchange cotton cellulose adsorbent	1 to 9	25, 35, and 45	20	x	x	x	x	x	Capacity, percentage removal, and competitive ions	Zhao et al. (2008)
F^-	Iron(III)–aluminum(III)–chromium(III) ternary-mixed oxide	3 to 10	10, 30, and 45	10 to 50	x		x	x	x	Capacity and thermodynamic study	Biswas et al. (2010)
F^-	Activated and MnO_2-coated tamarind fruit shell	6 to 8	30	2 to 5	x	x	x			Capacity and competitive ions	Sivasankar et al. (2010)
F^-	Hydrated cement	3 to 12	30	5 to 40	x		x	x		Capacity, percentage removal, and competitive ions	Kagne et al. (2008)
F^-	Chelating resin (Indion FR 10) and anion-exchange resin (Ceralite IRA 400)	3 to 11	30, 40, and 50	2 to 10	x		x	x		Capacity, competitive ions, and thermodynamic study	Meenakshi and Viswanathan (2007)
F^-	Al-impregnated chitosan biopolymer	2 to 12	10 to 50	1 to 10	x		x	x	x	Percentage removal, competitive ions, and thermodynamic study	Swain et al. (2009)
F^-	Granular red mud	2.5 to 7.3	25	5 to 150	x	x	x	x	x	Percentage removal and capacity	Tor et al. (2009)
F^-	Anion-exchange resin Reillex HPQ and Dowex	7.5 to 13	25	5 to 20 mmol L^{-1}	x		x	x		Capacity and fractional attainment of equilibrium	Chanda and Rempel (1995)
F^-	Zn/Al hydrotalcite-like compound	4 to 10	30	2 to 60	x		x	x	x	Percentage removal and Competitive ionsthermodynamic study	Das et al. (2003)
F^-	Cellulose-supported layered double hydroxides	N.A.	25	10 to 100	x	x	x	x		Capacity	Mandal and Mayadevi (2008)
F^-	Trivalent-cation-exchanged zeolite F-9	4 to 9	20 to 40	10 to 80	x			x		Capacity	Onyango et al. (2004)

Table 1 (continued)

Anion	Material	Experimental conditions			Results						Ref.
		pH	*T* (°C)	C_0 (mg L^{-1})	Batch	Column	Kinetics	Equilibrium	Regeneration	Others	
F^-	Al^{3+} pretreated low–silica synthetic zeolites	2 to 11	25	5 to 80	x		x	x	x	Capacity	Onyango et al. (2006)
F^-	Stilbite zeolite modified with Fe(III)	3 to 11	R.T.	5 to 40	x		x	x	x	Competitive ions and percentage removal	Sun et al. (2011)
F^-	Natural zeolite loaded with Al^{3+}, La^{3+}, and ZrO^{2+}	6.5 to 7	30	1 to 20	x			x		Percentage removal;	Samatya et al. (2007)
F^-	Bauxite	2 to 10	30 to 60	4 to 12	x		x	x		Capacity, competitive ions, percentage removal, and thermodynamic study	Sujana and Anand (2011)
CN^-	Activated carbon	10	25	102 to 532	x		x	x		Capacity	Behnamfard and Salarirad (2009)
CN^-	Amberlite IRA-402	10 and 12	N.A.	200		x	x			Capacity, competitive ions, and speciation	Osathaphan et al. (2008)
CN^-	Activated carbon	10.5 to 11	N.A.	10 to 200	x		x	x		Capacity, percentage removal, and speciation	Deveci et al. (2006)

C_0 initial concentration of anion in solution, *N.A.* not available, *R.T.* room temperature

trimethyl-, triethyl-, and tributyl-ammonium, in order to evaluate their capacity to remove nitrate from aqueous media containing chlorides and sulfates. The synthesized resins were shown to have a high selectivity to nitrates, which increases with the size of alkyl radicals in their functional groups and with increasing percentage of divinylbenzene in the resins.

Notwithstanding the high performance generally achieved by synthetic resins, their higher costs still prevent their practical application (Orlando et al. 2003). Hydrotalcite compounds are inorganic materials with important properties for the removal of anionic pollutants from water. These materials are layered double hydroxides (LDHs) where some divalent cations are replaced by trivalent cations (such as Al^{3+}, Fe^{3+}, and Cr^{3+}) creating a layer charge which is counter balanced by anions such as carbonate, nitrate, sulfate, or chloride in the interlayer spaces (Islam and Patel 2010). As a result, hydrotalcite-like compounds have been considered promising anion exchangers for nitrate decontamination. Accordingly, Islam and Patel (2010) investigated the ability of Zn–Al–Cl LDH to remove nitrate from a synthetic nitrate solution. The Zn–Al–Cl LDH studied, synthesized by co-precipitation method, was demonstrated to efficiently remove 85.5 % of nitrate under neutral conditions, using 0.3 g of LDH in 100 mL of nitrate solution with initial concentration of 10 mgL^{-1}. The presence of competitive anions were found to influence nitrate removal, reducing it in the order carbonate>phosphate>chloride>sulfate. The authors also performed a regeneration study which revealed that Zn–Al–Cl hydrotalcite cannot be easily regenerated and reused (the percentage regeneration obtained was less than 2 %).

Waste natural materials were recently recognized as economically viable options to be used as anion exchangers (Orlando et al. 2002, 2003; Gao et al. 2009). For instance, lignocellulosic agriculture waste materials including rice hull, sugarcane bagasse, sawdust, coconut husk, tealeaf, and wheat straw are worldwide produced in large quantities in agro-industries. These agriculture waste materials fulfill the essential low-cost, availability, and environmental compatibility requirements. Besides, their exploitation reduces considerably the disposal problems associated with their massive production (Orlando et al. 2002; Gao et al. 2009). For instance, Orlando et al. (2002) used two lignocellulosic agriculture waste materials, namely sugarcane bagasse and rice hull, to obtain weak-base anion exchangers for nitrate removal and compared their performance with those obtained from pure cellulose and pure alkaline lignin. The anion exchangers were prepared by reaction with epichlorohydrin and dimethylamine using pyridine as catalyst and *N*,*N*-dimethylformamide as solvent. The material obtained from pure alkaline lignin showed the highest maximum exchange capacity for nitrate anions (1.8 mmol g^{-1}), followed by sugarcane bagasse (1.4 $mmol g^{-1}$), pure cellulose (1.34 $mmol g^{-1}$), and finally rice hull (1.32 $mmol g^{-1}$). The obtained results demonstrate the potential of both sugarcane bagasse and rice hull waste materials to purify nitrate-containing water. Later, Orlando et al. (2003) converted different waste natural materials with diverse chemical compositions into anion exchangers by consecutive chemical reactions with thionylchloride, dimethylamine, *N*,*N*-dimethylformamide as solvent, and formaldehyde as cross-linking agent. The authors verified that the materials containing small amounts of extractives and high content of holocellulose and lignin (*Moringa oleifera* hull, lauan sawdust, coconut husk, and rice hull) showed superior nitrate sorption capacity in comparison with those materials containing higher quantities of extractives (persimmon tealeaf, pine bark, and Chinese tealeaf). Nevertheless, all natural materials were considered potential raw materials for conversion into anion exchangers.

Wheat residue, one of the major agriculture residues in China, was used by Gao et al. (2009) to obtain a quaternary amino anion exchanger, after reaction with epichlorohydrin and triethylamine in the presence of *N*,*N*-dimethylformamide and catalyst. The nitrate removal was reported to be significantly higher than that generally obtained with wheat residue tertiary amino anion exchanger (89.1 versus 6–10 %). The high efficiency achieved by the synthesized material was coupled with its amount of cellulose, hemicellulose, and lignin which hold a large quantity of easily available hydroxyl groups suitable for preparation of various functional polymers.

Adsorption process is generally considered better in water treatment because of convenience, ease of operation, and simplicity of design. Furthermore, this process can remove/minimize different types of organic and inorganic pollutants from the water or wastewater and thus it has a wider applicability in water pollution control (Namasivayam and Sangeetha 2005; Guan et al. 2010). On the other hand, adsorption requires the disposal of the spent adsorbent and is highly dependable on pH and temperature. Several adsorbents like clay and carbon-based adsorbents, LDHs and hydrotalcite-like compounds, zeolites, and agricultural and industrial wastes have been used to remove nitrates from water and wastewater, some of which have already been discussed earlier under the scope of ion-exchange.

Among carbon-based absorbents, activated carbon is a well-know and well-established absorbent used for the removal of numerous water pollutants, mainly organic pollutants. However, it presents lower adsorption towards anionic pollutants. Powdered activated carbon and carbon nanotubes were used in the removal of NO_3^- from aqueous solutions by Khani and Mirzaei (2008) having shown a capacity of 10 and 25 mmol $NO_3^- g^{-1}$ of adsorbent, respectively.

Nitrate removal with commercial granular-activated carbon chemically activated with $ZnCl_2$ was also studied (Bhatnagar et al. 2008). Experiments evidenced that maximum removal from water was achieved with a chemical weight ratio of 200 % and an activation temperature of 500 °C. Lower adsorption was verified at 400 °C since the low temperature was not sufficient for the development of volatile matters necessary for pore creation, and 600 °C, due to a sintering effect followed by shrinkage of the char and rearrangement of the carbon structure which lead to reduced pore volumes.

Clays are hydrous aluminosilicate broadly defined as those minerals that make up the colloid fraction of soils, sediments, rocks, and water and may be composed of mixtures of fine-grained clay minerals and clay-sized crystals of other minerals such as quartz, carbonate, and metal oxides. Clays play an important role in the environment by acting as a natural scavenger of pollutants by taking up cations and anions either through ion-exchange or adsorption or both. Mena-Duran et al. (2007) studied the removal of nitrate with clays modified by acid thermoactivation with HCl and H_2SO_4 obtained from calcium bentonite. Calcium montmorrillonite showed better removal capacity. The BET analysis found that there was no relation between the surface area and nitrate removal capacity.

Zeolites are commonly used as adsorbents in purification and environmental cleaning processes. Surface-modified zeolites were utilized by Arora et al. (2010) to remove NO_3^- from water. This team coated a natural zeolite with a chitosan layer that was subsequently protonated with either sulfuric or hydrochloric acid. The zeolite ability to capture NO_3^- was tested at both 4 and 20 °C, and it was found that the protonation with hydrochloric acid allowed for a higher adsorption in comparison to protonation with sulfuric acid.

Chitin and chitosan-derivatives have gained wide attention as effective biosorbents due to low-cost and high contents of amino and hydroxyl functional groups which show significant adsorption potential for the removal of various aquatic pollutants. Chatterjee and Woo (2009) tested the adsorption of NO_3^- using chitosan hydrobeads that ultimately showed a capacity of 92.1 mg/g at 30 °C and pH 5. The nitrate adsorption increased by decreasing the pH of solution since lower pH means easy protonation of the chitosan. A decrease in adsorption capacity was verified when the temperature was 50 °C what can be explained either by equilibrium thermodynamics or the damage of the active binding sites.

3 Removal of Chloride

Chloride-containing wastewater is often released to the environment from landfills (Kameda et al. 2000, 2003a, b) and several industries such as tanning, pickling, and seafood (Panswad and Anan 1999; Saremi and Mahallati 2002). As a result, a high level of salt on wastewaters could originate problems in their treatment, particularly in biological units, and can give rise to chloride-induced corrosion of waste pipes, scaling, or crop damage (Lv et al. 2006b; Kameda et al. 2000; Saremi and Mahallati 2002).

The most frequently employed methods to remove chloride ions from aqueous solution include ion-exchange, adsorption, liquid extraction, and membrane technologies (Carmona et al. 2008; Gärtner et al. 2005; Lv et al. 2006a). In particular, membrane technology found relevant application for purification of domestic water (Sarkar and SenGupta 2008). For instance, electrodialysis has been used for wastewater desalination although it comprises some concerns related, for instance, with the existence of K^+ in the resulting salt (Lv et al. 2006b). Besides, reverse osmosis technique has been used worldwide for desalination of sea water (Spiegler and El-Sayed 2001; Ettouney et al. 2002). However, the high-energy consumption of this process together with the lack of durability of the membranes and its fouling susceptibility make reverse osmosis not as cost-effective as required (Sarkar and SenGupta 2008). Notwithstanding, some effort has been devoted to the improvement of membrane materials toward higher robustness and production. More recently, alternative membrane-based processes such as forward osmosis and membrane distillation have received increasing interest. However, the efficiency of all those processes is dependent on their energy efficiency.

Ion-exchange seems to be the most suitable process to remove chloride ions from solution given its simplicity, effectiveness, selectivity, recovery, and relatively low operating cost (Carmona et al. 2008; Chabani and Bensmaili 2005; Gärtner and Witkamp 2005). In Table 1, some of the more adopted materials for removal of chloride ions are listed, as well as the experimental conditions used and major results achieved. The use of ion-exchange resins has been reported as particularly advantageous. For instance, Carmona et al. (2008) demonstrated the efficiency of the strongly basic ion exchanger Amberlite IRA-420 for chloride removal from polyethylenimine (PEI) aqueous solution. In their study, the ion-exchange equilibrium and kinetics between chloride-polyethylenimine solution and OH^- form of Amberlite IRA-420 were investigated in order to assess the possibility of applying an ion-exchange process to convert the polyethylenimine flocculant solution (Cl^--form) into an adhesive product for printing applications. The obtained dimensionless form of equilibrium isotherms of chloride ions in PEI solution on Amberlite IRA-420 are given in Fig. 1 together with the isotherms of HCl and NaCl solutions. As

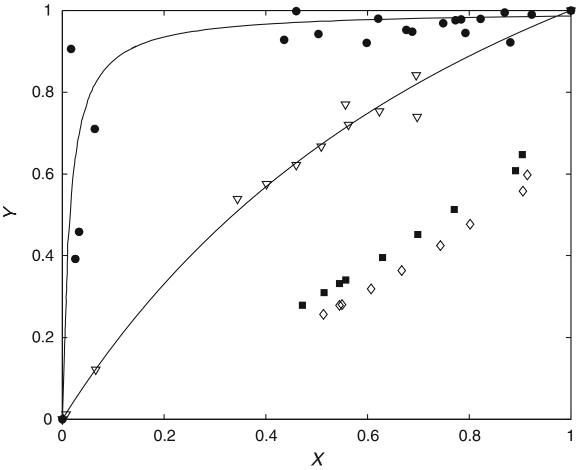

Fig. 1 Dimensionless isotherm of chloride ions on Amberlite 420 with different co-ions. Symbols: *filled circles* HCl, 303 K; *empty inverted triangles* NaCl, 303 K; *filled squares* PEI, 313 K; and *filled diamonds* PEI, 293 K. *Lines* Langmuir isotherm. Data from Carmona et al. (2008)

can be observed, a competition was established between the protonated amine groups of PEI and the quaternary groups of the resin for the chloride ions, which gave rise to a slightly nonfavorable equilibrium. The equilibrium between OH^--form resin and chloride anions may be simply represented by a conventional ion-exchange equation:

$$\overline{R-OH}+Cl^- \leftrightarrow \overline{R-Cl}+OH^- \tag{1}$$

while for HCl, the reaction between OH^- leaving the resins and H^+ in solution originates a typical irreversible isotherm:

$$\overline{R-OH}+Cl^- + H^+ \leftrightarrow \overline{R-Cl}+H_2O \tag{2}$$

In the case of PEI solution, the equilibrium isotherm would be expected to be similar to that for NaCl (aq), which was definitely not the case. Such result confirms the competition between the ammonium groups of the resin and the protonated PEI ($HPEI^+$), according to:

$$\overline{R-OH}+HPEI^+Cl^- \leftrightarrow \overline{R-Cl}+PEI+H_2O \tag{3}$$

In Eqs. (1) to (3), the top bars identify resin phase and R denotes the resin polymeric matrix.

Notwithstanding, the ion-exchange properties of most resins may be enhanced toward selectivity improvement by fixation of polyelectrolyte on the resin surface leading to a modification of hydrophilic and hydrophobic balance and changing of electronegativity of functional groups (Berbar et al. 2008), as well as by incorporating specific inorganic nanoparticles within the polymeric ion exchanger (DeMarco et al. 2003; Sarkar and SenGupta 2008; Cumbal et al. 2003).

The LDHs have been recently argued to contain a high anion-exchange capacity for a number of anions (Lv et al. 2009). Their ability of permanent interlayer anion-exchange, relatively large surface areas and high capacities make them promising decontaminants for toxic anionic species from aqueous systems. In view of that, Lv et al. (2009) used ZnAl–NO_3 LDHs as anion exchanger to remove chloride ion from aqueous solution. The NO_3^- LDHs with Zn/Al molar ratio of 2 showed a notable ability to remove chloride ions, with much higher capacity than that of MgAl–NO_3 LDHs. Besides, the solution pH was found to be poorly significant in the studied range (i.e., 5.0 to 8.0).

4 Removal of Sulfide

Sulfide is present in a wide range of industrial wastewaters including those from tannery and paper mills (Dutta et al. 2010), as well as in effluents from waste gas treatment industries, textile industry, treated plating, and petroleum refinery (Chanda and Rempel 1995). Sulfide is a toxic, corrosive, and odorous compound and, hence, must be eliminated from wastewaters before discharge to the environment (Dutta et al. 2010). Moreover, sulfide discharges could be problematic even to sewers, given its corrosive character and associated health risks in downstream wastewater treatment plants (Dutta et al. 2010; Zhang et al. 2008).

A number of chemical and biological treatments are available to eliminate sulfides from wastewater. The most frequently reported techniques include adsorption, chemical oxidation, biological oxidation, anaerobic digestion, and precipitation (Chanda and Rempel 1995). Concerning ion-exchange, only a few works have been reported dealing with sulfide removal. For instance, Chanda and Rempel (1995) compared the performance of a macroporous anion-exchange resin Reillex™ HPQ, containing about 70 % of the pyridine rings quaternized by the addition of methyl groups, with the common anion-exchange resin Dowex-l-X8, both in chloride form, for sulfide sorption from alkaline aqueous solutions. Their capacities for sulfide were 4.8 and 2.5 $mmol g^{-1}$ (dry), respectively, while the corresponding total exchange capacities are 4.6 and 5.6 $mEq g^{-1}$ (dry). The obtained results pointed out the predominant sorption of sulfide as HS^- on HPQ(Cl^-) and as S^{2-} on Dowex-l(Cl^-). The higher sulfide sorption by Cl^--form HPQ resin in comparison with that on the same resin but in OH^- form was ascribed to the presence of nearly 30 % of the pyridine sites in the protonated form that contribute to an acidic environment inside the resin, favoring the sorption of sulfide as univalent HS^-, which requires fewer sites than the bivalent S^{2-}. Concerning Dowex-1 resin, the similar capacities achieved by both Cl^- and OH^- forms corroborate the majority sorption of S^{2-}. Accordingly, the HPQ resin in Cl^--form was demonstrated to have nearly twice the sulfide sorption capacity than Dowex-1. Figure 2 illustrates the equilibrium speciation of H_2S in aqueous solutions. As may be observed, at pH below 5, H_2S is the predominant species while at pH of >9 HS^- and S^{2-} prevail. In Fig. 3, the equilibrium sorption of aqueous sulfide on

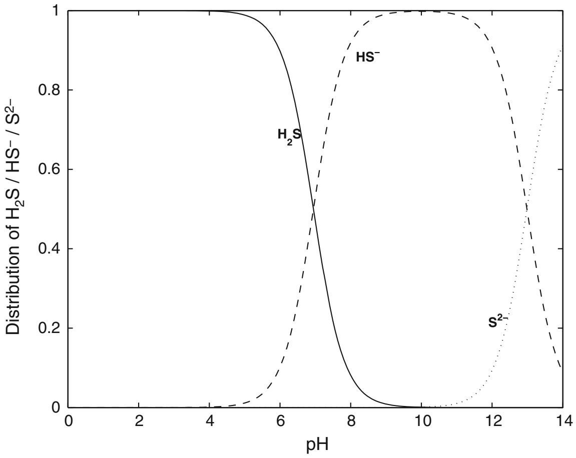

Fig. 2 Speciation for H_2S–HS^-–S^{2-} equilibrium

HPQ(Cl^-) and Dowex-1(Cl^-) are plotted against solution pH. Results clearly evidenced a continuous decrease of the sorption capacities of both exchangers with decreasing pH, which can be attributed to the predominance of HS^- in the pH range 9–11 and to the rapidly increase of H_2S concentration for pH below 9.

The electrochemical approach has been recently reported as a cost effective and selective separation method (Rajeshwar et al. 1994; Chen 2004) where sulfide can be directly oxidized at an anode (Rabaey et al. 2006), being the elemental sulfur the key oxidation product when carbon/graphite materials are used as the electrode material (Ateya et al. 2003). However, resulting precipitated sulfur could induce anode passivation during electrochemical sulfide removal (Ateya et al. 2003; Reimers et al. 2006; Dutta et al. 2008). In order to make this process more attractive, some strategies have been proposed to prevent electrode passivation and to regenerate electrodes. For instance, the use of organic solvents for sulfur extraction and subsequent solvent evaporation as well as the controlled sulfur precipitation in bulk solution with alkali addition at elevated temperature are some of the approaches proposed. However, the use of toxic organic compounds and the energy demands associated with these methodologies make them not as sustainable as required (Dutta et al. 2010). In view of that, Dutta et al. (2008) reported an electrochemical method consisting in a lab-scale fuel cell that simultaneously removes sulfide and produces energy. The apparatus was able to continuously remove aqueous sulfide for 2 months at a rate of 0.28 $kg m^{-3} day^{-1}$ of total anodic compartment (TAC), while generating a maximum power of 5 $W m^{-3}$ TAC. The presence of organic compounds (e.g., acetate) did not affect sulfide oxidation. Moreover, acetate concentration remained unchanged during the process, which may be particularly important for selective sulfide removal from wastewater where organics are essential for downstream nutrient removal. However, the elemental sulfur resulting from sulfide electrochemical oxidation remained deposited on the anode surface, which appeared to limit the operation of the fuel cell after 3 months. More recently, Dutta et al. (2010) investigated the electrochemical sulfide removal from an effluent of an anaerobic treatment plant of a paper mill. The experiments were carried out in a continuous lab scale electrochemical reactor, and the sulfide concentration was reduced from 44 to 8 $mg L^{-1}$, at a removal rate of 0.845 $kg m^{-3}$; 75 % of sulfide was recovered as pure concentrated alkaline sulfide/polysulfide solution, from which solid sulfur was obtained. Besides, the electrochemical sulfide removal was reported to be not affected by different soluble constituents present in the wastewater, even though sulfide removal was decreased due to biological sulfur reduction by the organics existent in solution. As a result, a periodic anode and cathode switching was developed. Despite the effective sulfide removal, biofilm formation had to be avoided as the pH of the cathode solution increased to inhibitory levels. During this process, pure solid elemental sulfur was completely recovered.

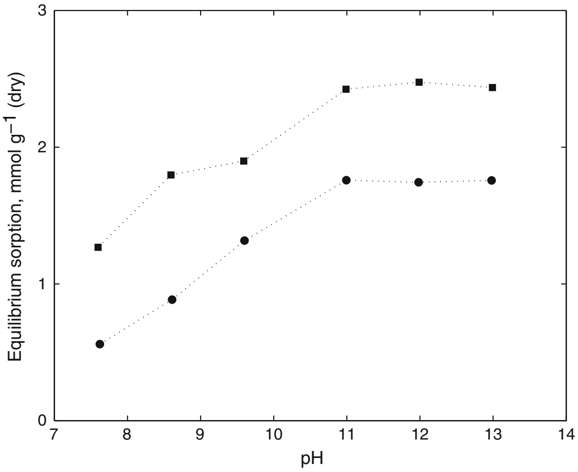

Fig. 3 Effect of pH on sulfide equilibrium on HPQ and Dowex-1 resins both in Cl^--form. Experimental conditions: resin loading at 4.0 g (wet) L^{-1} and initial concentration of Na_2S at 5.0 $mmol L^{-1}$ at 25 °C. Symbols: *filled squares* HPQ (Cl^-) and *filled circles* Dowex-1 (Cl^-). Data from Chanda and Rempel (1995)

More recently, Pikaar et al. (2011a) have compared the performance of five different mixed metal oxide (MMO)-coated titanium electrode materials (i.e., Ta/Ir, Ru/Ir, Pt/Ir, SnO_2, and PbO_2) for the electrochemical removal of sulfide from domestic wastewater. All electrode materials were found to perform similarly, with sulfide removals of 78, 77, 85, 84, and 83 %, respectively, at a current density of 10 $mA\,cm^{-2}$, for sulfide concentrations of approximately 10 $mg\,L^{-1}$. Moreover, sulfide removal was observed to take place by chemical oxidation with in situ generated oxygen, for all the materials used. Notwithstanding, Ta/Ir and Pt/Ir were considered specially promising given their low overpotential for oxygen evolution and stability even at low chloride concentrations. Besides, both materials have been already applied in full-scale applications. The same authors (Pikaar et al. 2011b) investigated in more detail the electrochemical oxidation of sulfide at Ir/Ta MMO-coated titanium electrodes to remove sulfide from both synthetic and real wastewaters at high rates. The authors obtained a maximum sulfide removal rate of 11.8 $g\,m^{-2}$ anode surface using domestic wastewater at sulfide concentrations of 30 $mg\,L^{-1}$ or higher. The indirect oxidation with in situ oxygen production was believed to be the main reaction mechanism occurred at the electrodes, being its final products sulfate, thiosulfate, and elemental sulfur. Besides, concentrations of both chloride and acetate were observed to remain constant during sulfide removal, which have revealed the potential of Ir/Ta MMO-coated titanium electrodes for indirect oxidation of sulfide with in situ generated oxygen.

Vaiopoulou et al. (2005) investigated the removal of hydrogen sulfide from oil-refining wastewater by autotrophic denitrification in a multistage treatment plant. Conducting anoxic sulfide to sulfate oxidation, the team was able to totally convert to SO_4^{2-} feed concentrations of 110 mg $S^{2-}L^{-1}$. After total denitrification, the concentration of S^{2-} in the reactor effluent was less than 0.1 $mg\,L^{-1}$. When applied to the refinery, this method, in conjunction with the current process of CO_2 stripping, allowed the reduction of 70 % in stripping costs.

Rabaey et al. (2006) used a microbial fuel cell with a hexacyanoferrate cathodic electrolyte to convert sulfide to elemental sulfur, generating electricity in the process. It was possible to achieve removals of sulfide of 98 % by coupling the microbial fuel cell with an anaerobic upflow anaerobic sludge blanket reactor.

5 Removal of Fluoride

Fluorine occurs naturally in the atmosphere, water, and soils (Lv et al. 2006a), being released into subsoil water sources by the slow natural degradation of fluorine-containing rocks (Daifullah et al. 2007; Wajima et al. 2009; Biswas et al. 2010). Besides, fluorine and its compounds are extensively used in industry and their effluent discharges have contributed significantly to water pollution (Daifullah et al. 2007; Wajima et al. 2009b). For instance, fluoride ions can be found in wastewaters from glass industry, chemical industry, metal industry, semiconductors and electronic devices industries, and aluminum smelters (Daifullah et al. 2007; Wajima et al. 2009; Zhang et al. 2009).

Fluoride is the most electronegative and reactive element present in the Periodic Table (Daifullah et al. 2007), and accordingly, it is easily attached giving rise to positively charged calcium in teeth and bones (Wajima et al. 2009). As a result, the presence of fluoride in drinking water is recognized to be beneficial to human diet, being at low concentrations an essential constituent for both humans and animals, especially to prevent skeletal and dental problems (Daifullah et al. 2007; Swain et al. 2009; Fan et al. 2003; Oh and Chikushi 2010; Tang et al. 2009; Kagne et al. 2008; Tor et al. 2009; Biswas et al. 2010). However, at higher concentration, fluoride is known to have serious adverse effects on human and animal health. In particular for human beings, excessive F^- intake may cause mottling of teeth, dental or skeletal fluorosis, as well as severe neurological damages (Swain et al. 2009; Fan et al. 2003; Daifullah et al. 2007; Oh and Chikushi 2010; Tang et al. 2009; Hichour et al. 2000; Kagne et al. 2008; Tor et al. 2009; Gao et al. 2004; Zhang et al. 2009; Biswas et al. 2010; Wajima et al. 2009; Sivasankar et al. 2010; Meenakshi and Viswanathan 2007).

According to the World Health Organization (WHO), the maximum acceptable concentration of fluoride in drinking water should not exceed 1.5 mg L^{-1} (Oh and Chikushi 2010; Daifullah et al. 2007; Tang et al. 2009; Lv et al. 2006a; Biswas et al. 2010), while the optimum fluoride level in drinking water for general good health is considered to be between 0.5 and 1.0 $mg\,L^{-1}$ (Sivasankar et al. 2010). However, many regions of the world have been reported to have excess of fluoride in groundwater, owing to either its natural presence in the earth's crust and its discharge by agricultural and industrial activities (Zhang et al. 2009; Fan et al. 2003; Tang et al. 2009; Wajima et al. 2009; Zhao et al. 2008). As a result, millions of people are affected by fluorosis in Africa, America, Europe, and Asia (Lv et al. 2006a; Tang et al. 2009; Wajima et al. 2009). More specifically, following an UNICEF report, fluorosis is endemic in at least 25 countries across the globe (Kagne et al. 2008; Zhao et al. 2008; Biswas et al. 2010). For instance, the groundwater fluoride concentration in some regions of North Africa may reach 20 $\mathrm{mg L^{-1}}$ (Fan et al. 2003). In India alone, excess of F^{-} in drinking water is prevalent in 150 districts of 17 states of the country. Besides, high fluoride concentrations have been reported also in some parts of China (Lv et al. 2006a). In view of that, it is essential to remove the excessive fluoride from drinking water until safe levels.

Treatment of wastewater containing fluoride ions requires a robust and effective removal process (Wajima et al. 2009). A number of defluoridation techniques have been suggested for that, including adsorption and biosorption, ion-exchange, chemical precipitation, and membrane processes such as reverse osmosis, Donnan dialysis, nano-filtration, and electrodialysis. Most of these methods have important drawbacks, including high initial cost, low selectivity, low capacity, and difficulties in operation or regeneration (Swain et al. 2009; Tang et al. 2009; Lv et al. 2006a; Sivasankar et al. 2010; Afkhami et al. 2007; Hichour et al. 2000; Kagne et al. 2008; Daifullah et al. 2007; Meenakshi and Viswanathan 2007; Tor et al. 2009; Biswas et al. 2010; Wajima et al. 2009). Moreover, although quite effective, ion-exchange, electrodialysis, and membrane processes are generally expensive and require frequent regeneration and cleaning of exchanger beads and membranes (Fan et al. 2003; Kagne et al. 2008; Biswas et al. 2010).

Precipitation of fluoride from industrial wastewater using calcium oxide to form insoluble CaF_2 is one of the most commonly applied techniques to remove F^{-} because of its high concentration in the industrial effluent (Wajima et al. 2009; Sivasankar et al. 2010; Fan et al. 2003). Lime is generally used as calcium source. In this process, after a first fluoride reduction, the calcium ions released from the lime interact with fluoride and form CaF_2 precipitate, while aluminum salts are subsequently used to further reduce the fluoride level to about 2 $\mathrm{mg L^{-1}}$. However, the precipitation process carries several disadvantages, mainly associated with the solubility of precipitated fluorite, calcium and aluminum salts, which limit the final fluoride concentration in the water (Wajima et al. 2009; Fan et al. 2003). Besides, the large volumes of CaF_2 produced during precipitation have to be treated before discharge, which requires a secondary treatment and additional operating costs.

Adsorption and ion-exchange are two of the most extensively applied technologies to uptake fluoride ions from wastewater due to their relatively simple and economical operation (Lv et al. 2006a; Sivasankar et al. 2010; Wajima et al. 2009; Daifullah et al. 2007; Biswas et al. 2010; Kagne et al. 2008). Even as a secondary separation method, for instance after precipitation, adsorptive methods have been argued as one of the most suitable techniques (Wajima et al. 2009). However, the viability of these methods is highly dependent on the development of effective materials. Table 1 displays the main results, found in literature, for several adsorbents and ion exchangers used to remove fluoride under different operating conditions. The most common sorbents for fluoride removal are activated carbon and activated alumina (Fan et al. 2003; Daifullah et al. 2007). Activated carbon is by far one of the most effective sorbents in removing pollutant compounds from aqueous solution (Daifullah et al. 2007). Besides, structural modifications, such as changing their inherent surface functional groups, could be carried out in order to improve its affinity for certain contaminants. Alumina is an adsorbent material with excellent physical and textural properties (Zhang and Pinnavaia 2002; Viswanathan and Meenakshi 2010; Kim et al. 2004). Among alumina and alumina-coated materials, activated alumina is particularly powerful for fluoride removal from drinking water owing to its high fluoride affinity, low-cost and abundance, and easy regeneration (Viswanathan and Meenakshi 2010; Tang et al. 2009). Nonetheless, the applicability of these sorbents has some limitations associated with its low capacity and uptake rate, and capacity decrease after regeneration (Zhao et al. 2008; Bulusu and Nawlakhe 1988).

The abovementioned restrictions associated with activated carbon and alumina compounds have prompted the research on new materials. Some examples of cost-effective sorbents are spent bleaching, clay, bentonite and activated bentonite, kaolinitic clay, calcite, agricultural by-products, fly ash, carbon slurry, biogas residual slurry, natural zeolites, bone char, and flax shive (Sivasankar et al. 2010; Daifullah et al. 2007; Fan et al. 2003; Biswas et al. 2010; Tor et al. 2009; Sun et al. 2011; Samatya et al. 2007) Furthermore, rare earth and Zr(IV) elements have been recently found to exhibit specific affinity for fluoride, which encouraged the development of various rare earth compounds and Zr(IV)-loaded polymers sorbents (Wajima et al. 2009). Samatya et al. (2010) have added polystyrene as a porogen to a Zr(IV)-immobilized resin resulting in a high adsorption capacity for fluoride removal from aqueous solutions. The higher adsorption capacities when adding polystyrene are explained by the increase in surface area caused by the porogen. However, in certain cases, the sorption rate of these materials is still slow and the equilibrium is often attained within several hours, which results in operational and control difficulties.

Fan et al. (2003) have foccused on the investigation of low-cost and effective materials for removal of low concentrations of fluoride, using hydroxyapatite, fluorspar, calcite, quartz, and quartz activated by ferric ions to remove radioisotope ^{18}F at natural pH. The obtained results (replicated in Fig. 4) demonstrated that the sorption capacities followed the order: hydroxyapatite > fluorspar > activated quartz > calcite > quartz. Fluoride uptake was revealed to be extremely fast on quartz, calcite and fluorspar, reaching equilibrium within 2 min. In turn, fluoride uptake on hydroxyapatite was shown to take as much as 150 min to attain equilibrium. Nonetheless, hydroxyapatite showed the highest fluoride capacity. The fluoride was believed to be exchanged with OH^- groups inside hydroxyapatite, which gives rise to a superior sorption capacity. In contrast, the fundamental process by the remaining materials was established to be only surface adsorption.

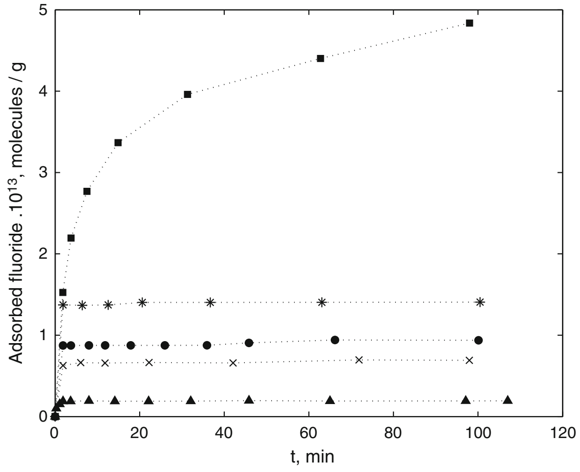

Fig. 4 Fluoride molecules sorbed on different materials at pH 6.0 and initial concentration 3×10^{-5} mgL^{-1}. Symbols: *filled squares* apatite; *asterisk* fluorspan; *filled circles* quartz + Fe; *crosses* calcite; *filled triangle* quartz. Data from Fan et al. (2003)

Portland cement, an abundant low-cost fine-powdered building material, consisting mainly in a mixture of tricalcium silicate, dicalcium silicate, tricalcium aluminate, and a tetracalcium aluminoferrite, could be also used as fluoride adsorbent. Portland cement could be mixed with water in order to get hydrated cement. Such material can be used to remove fluoride from aqueous solution without sludge production (Kagne et al. 2008). Kagne et al.(2008) investigated the defluoridation capability of hydrated cement prepared with Portland cement. The prepared material evidenced a quite significant F^- removal over a wide pH range. However, fluoride removal was found to be affected by the presence of carbonate and bicarbonate ions in solution, which compete for sorption sites.

The low-cost, high availability, and easy regeneration of LDH-like materials have suggested their application for defluoridation of water (Mohapatra et al. 2009). In view of that, Das et al. (2003) evaluated the physicochemical and sorption properties of calcined Zn/Al hydrotalcite-like material towards fluoride removal from aqueous solution. The authors established the pH range of 4–6 for optimum fluoride removal and confirmed their ability to be regenerated by dilute alkali solution.

A novel bead sorbent, Fe(III)-loaded ligand exchange cotton cellulose adsorbent (Fe(III)LECCA), was investigated by Zhao et al. (2008) for the removal of fluoride anions from drinking water. Fe(III)LECCA evidenced a good performance with saturation capacity of 18.6 mgg^{-1}. Furthermore, fluoride removal was shown to be not affected by the presence of coexisting anions demonstrating the high selectivity of Fe (III)LECCA towards fluoride. These results suggested Fe(III)LECC as a cost-effective and selective sorbent for drinking water treatment. More recently, Mandal and Mayadevi (2008) studied the application of cellulose-supported uncalcined LDHs, with different LDH loadings on cellulose, for defluoridation, and obtained a removal capacity two to four times higher than that of unsupported LDH. Besides, the removal features obtained with these prepared materials were higher than those generally reported for other sorbents, including activated alumina and carbon nanotubes.

Tor et al. (2009) investigated the potential of granular red mud (GRM), a widely available fine-grained mixture of oxides and hydroxides capable of removing several contaminants, to remove fluoride. Their work elucidated the high efficiency of GRM under low fluoride concentrations, their suitable capacity in both batch and column operating modes, as well as their ability to be rapidly regenerated. Besides no toxic sludge is produced during the process, red mud particles are generally too fine to be used in columns and their application has been confined to batch operation.

Hydrous titanium dioxide has been found to be a potential selective sorbent for fluoride ions, as well as coexisting arsenic compounds (Wajima et al. 2009; Tsuji and Abe 1986, 1991; Tokunaga et al. 1995). Wajima et al. (2009) investigated the capacity of a titanium hydroxide-derived material for fluoride removal in both aqueous sodium fluoride solutions and real wastewater containing fluoride ions. Results revealed that fluoride ions were sorbed even at low concentration and were selectively sorbed in solutions containing a high concentration of chloride, nitrate and sulfate ions, which demonstrate its effectiveness to remove fluoride down below permitted level from real wastewaters.

Concerning ion-exchange technology, resins are by far the most applied materials for removal of toxic metals from aqueous solution. However, fluoride removal by anion-exchange resins has been reported as a difficult process because of selectivity issues (Meenakshi and Viswanathan 2007). As a result, cation/chelating resins have been employed for fluoride sorption. For instance, Meenakshi and Viswanathan (2007) evaluated and compared the performance of anionic and chelating-type resins (namely Indion FR 10 and Ceralite IRA 400, respectively) under diverse equilibrating conditions and reported the last one as the most fluoride-selective material. The authors established that fluoride anions cannot be effectively exchanged using anion-exchange resins since its concentration is lower than the other anions present in water, and accordingly suggested the use of cation exchange/chelating type resins for an effective fluoride removal.

Recently, impregnated resins have been investigated for anions sorption using, for example, macroporous polymer beads of Amberlite XADs as support material (Solangi et al. 2010; Warshawsky 1974; Parrish 1977; Suzuki et al. 1991; Camel 2003). The use of Amberlite XADs may be especially suitable owing to their high surface area and good mechanical stability; in particular, Amberlite XAD-4™ has been considered quite attractive because of its low-cost and possibility of easy modification for searching more efficient exchanger resins. Solangi et al. (2010) reported an appropriate method to modify the Amberlite XQD-4™ resin, by introducing thiourea binding sites onto the aromatic rings. The modified resin was shown to be effective for the removal of fluoride from aqueous solution over wide pH range, exhibiting a fluoride sorption capacity of 3.286 $\mathrm{mmol\,g^{-1}}$.

Research work has revealed the excellent kinetic properties of fibrous sorbents provided by their physical–chemical structure. Ruixia et al. (2002) studied a new type of ion exchanger fiber for the removal of fluoride, phosphate, and arsenate ions. The new material was obtained by the cross-linking reaction of polyacrylonitrile fiber with hydrazine hydrate, and the functionalized reaction of the hydrazine-modified fiber in a mixture of sulfur powder and ethylenediamine. The uptake of all studied anions was pH dependent, being the maximum fluoride removal equal to 90.4 % at pH 3.0.

The use of zeolites to remove fluoride as well as other contaminant anions from aqueous solution has been explored during several years given their well known sorption, selectivity, and stability properties. However, a charge-reversion process must be carried out in order to confer zeolites the necessary anion-exchange capacity. For instance, Onyango et al. (2004) have prepared charge-reversed zeolites by exchanging sodium ions by trivalent ions (Al^{3+} or La^{3+}) in a commercial Na^+-loaded zeolite. While both unmodified and La^{3+}-loaded zeolites were demonstrated to be negatively charged over all pH range, the evaluation of the pH of the point of zero charge, determined from zeta potential measurements, revealed that Al^{3+}-modified zeolite carried a positive surface charge, which is counter balanced by negative ions. After this work, the authors studied the capacity of a Al^{3+} pretreated low-silica synthetic zeolites and demonstrated its effectiveness to defluoridate water to below WHO's maximum allowable concentration of 1.5 $\mathrm{mg\,L^{-1}}$ (Onyango et al. 2006; Onyango et al. 2005).

Following the work of Long's group (Li et al. 2000; Cheng et al. 2005) who studied the structure, modification, adsorption, and the catalytic nature of the stilbite zeolite, Sun et al. (2011) have modified a natural stilbite zeolite with Fe(III) ions to remove fluoride from drinking water. The zeolites were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy. Batch adsorption, regeneration, and kinetic studies were carried out to determine the effect of contact time, adsorbent dose, initial concentration, pH, and coexisting ions. The mechanism underlying the fluoride sorption is believed to be controlled by diffusion combined with chemisorption. The modified zeolites showed good capacity for the removal of fluoride until a concentration of 1 $\mathrm{mg L^{-1}}$, and this capacity is retained after regeneration with HCl.

Metal ions (Al^{3+}, La^{2+}, and ZrO^{2+}) have also been loaded in clinoptilolite (natural zeolite) with the purpose of removing fluoride from water (Samatya et al. 2007). Zeolites were prepared with each of the metal ions and sorption studies were conducted using the batch method. The metal ion loaded zeolite was found to be able to remove fluoride from aqueous solutions and tap water, where an increasing amount of metal ion increases the removal of fluoride.

Bauxite, an abundant and low-cost mineral, has been investigated for its ability to remove anionic pollutants (Erdem et al. 2004; Bhakat et al. 2007), and thermally activated titania-rich bauxite has been applied to fluoride removal (Das et al. 2005). More recently, untreated bauxite has been used to effectively remove fluoride from synthetic and ground water samples (Sujana and Anand 2011). Adsorption experiments were carried out and showed that the pH, temperature, initial concentration, as well as the presence of sulfate, nitrate, and phosphate competing ions have significant effects in the removal. The bauxite was characterized before and after adsorption using XRD, FTIR, and SEM-EDX. The adsorption rate followed first order kinetics and was controlled by intraparticle diffusion.

The removal of fluoride from water and wastewater can also be achieved through membrane processes like reverse osmosis, nanofiltration, dialysis, and electrodialysis. Ndiayea et al. (2005) used reverse osmosis to remove fluoride from effluents and observed that its retention was usually above 98 % if the membrane used was fully regenerated after each experiment. Since nanofiltration membranes possess larger pores, the pressures employed are lower and thus the energy requirements are less, fluxes are higher, and the removal of solute is less extensive. Using a nanofiltration pilot plant with two modules, Tahaikt et al. (2007, 2008) proceeded to remove fluoride from underground water and studied the effect of several operational parameters like the initial concentration of fluoride, pressure and reduction volume factor. Following on this work, the performance of several commercial membranes were compared under different configurations (simple pass, double pass with the same type of membranes and with two types. In dialysis, the membrane pores are less restrictive and the solute can permeate by either the Donnan effect or due to an applied electric field. Durmaz et al. (2005) carried out the removal of fluoride from a diluted solution using Neosepta AHA anion-exchange membrane by Donnan dialysis and studied the effects of concentration, pH, and accompanying anion on feed phase and receiving phase composition. The results were compared with two other membranes of which Neosepta AFN presented higher transport efficiency. Kabay et al. (2008) studied the fluoride removal by electrodialysis and verified that the performance increased either when the initial concentration of fluoride in the feed was increased or when the applied potential increased, but found no alteration when the feed flow rate was changed. An economical analysis on the use of electro-dialysis for fluoride removal has been done by Lahnid et al. (2008).

6 Removal of Cyanide

Cyanide is a toxic carbon–nitrogen radical produced by several bacteria, fungi, and algae, found in a wide variety of organic and inorganic compounds (Dash et al. 2009). For instance, cyanide is present in plants and foods, including beans, almonds and cashew nuts, as well as in animals such as centipedes, beetles and few species of butterflies, etc. (Dubey and Holmes 1995; Dash et al. 2009).

Besides its small concentration in living organisms, the extensive use of cyanides in industrial activities, mainly in metal finishing and mining industries, has been responsible for its release in the environment (Dash et al. 2009). In general, effluents from these industries contain total cyanide concentrations ranging between 0.01 and 10 $\mathrm{mg L^{-1}}$ (Ganczarczyk et al. 1985; Wild et al. 1994). However, cyanide levels as high as 100 $\mathrm{mg L^{-1}}$ have been found in effluents of electroplating and metal finishing plants after stored for periods of years (Dash et al. 2009; Kenfield et al. 1988;

Wild et al. 1994). In the presence of metals and organic compounds, cyanide easily forms simple and complex salts, some of which being particularly strong and fast acting toxins. For instance, neurological effects are consequence of immediate cyanide exposure while continuing contact may cause weight loss, thyroid effects, nerve damage and even death (Dash et al. 2009). As a result, cyanide-containing effluents must be previously treated before discharging into the environment. Accordingly, limiting standards for discharge of cyanide wastewaters have been implemented by many countries and environmental protection agencies. As an example, the US Environmental Protection Agency has proposed a total cyanide limit for drinking water of 200 ppb (Dash et al. 2009), whereas the WHO and the European Union have even inferior limits of 70 and 50 $\mu g L^{-1}$, respectively (Ma and Dasgupta 2010). Hence, cyanide levels must be reduced prior to discharge in order to meet regulatory limits (Dash et al. 2009; Deveci et al. 2006).

A wide variety of processes have been developed to reduce cyanide levels in wastewater, mainly those based on chemical and biological oxidation, natural degradation, and recovery/recycling techniques, each one owning their particular benefits and constraints (Behnamfard and Salarirad 2009). Chemical oxidation methods, using for instance chlorine, hydrogen peroxide, SO_2/air mixture, and Caro's acid, have been the most adopted ones for treatment of contaminated effluents. In this case, cyanide generally reacts directly with an oxidant, which makes oxidation approaches less cost efficient in the treatment of low cyanide concentrations. Besides, the presence of metals such as zinc, copper, or iron increases the oxidant demand as well as the process cost (Osathaphan et al. 2008). In the particular case of chlorination, oxidation could be not as effective as required when cyanide species are complexed with some metals, e.g., nickel or silver, given the slow reaction rates observed. Furthermore, the production of undesired sludge that must be previously disposed, the high quantity of chlorine required together with the production of several chlorinated organic compounds are additional disadvantages (Behnamfard and Salarirad 2009; Dash et al. 2009). As an alternative, biological degradation of cyanide has been assumed as economically viable and environmentally friendly for its removal. This method generally consists in the acclimation and enhancement of indigenous microorganisms, which can effectively convert cyanide into less toxic products: like bicarbonate and ammonia. These microorganisms can be a mixture of bacteria and fungus in either attached or suspended growth process in rotating biological contactors, packed beds, biological filters, sequencing batch reactors, facultative lagoons, and activated sludge systems. The most important process variables for the biological treatment of cyanides are the temperature, oxygen level, pH, and nutrient availability. There are four main paths for the biodegradation of cyanides: hydrolytic, oxidative, reductive, and substitution or transfer reactions. Hydrolytic reactions are catalyzed by enzymes like cyanide hydratase, and cyanidase that degrade the cyanide compounds. In oxidative reactions, cyanide monoxygenase converts cyanide to cyanate which in turn is transformed into ammonia and carbon dioxide. Through reductive reactions cyanide is converted in methane and ammonia, though these reactions are less common as the necessary enzymes are more difficult to find. At last, cyanide can also undergo substitution or transfer reactions to be converted into β-cyanoalanine which is then hydrolyzed to produce ammonia and an acid.

In addition to those methods where cyanide is degraded in solution, a number of effective techniques based on its recovery and recycling have been developed. Between them, acidification, volatilization, and reneutralization and ion-exchange processes have the advantage of recovering cyanide which balances the cost of the reagent used. In particular, ion-exchange resins can be successfully applied over wide ranges of concentrations (Osathaphan et al. 2008; Deveci et al. 2006). As an example, Osathaphan et al. (2008) investigated the removal efficiencies of cyanide and a zinc-cyanide complex using a strong basic anion-exchange resin, Amberlite IRA-402 Cl, based on crosslinked polystyrene with quaternary ammonium functional groups, and found pH-independent capacities around 1.2 and 0.9 $meq\,mL^{-1}$ for cyanide and zinc-cyanide complex solutions, respectively.

Besides ion-exchange processes, cyanide compounds can be removed from wastewaters by adsorption on a variety of organic and inorganic adsorbents (Deveci et al. 2006). For instance, activated carbon has been extensively used to adsorb gold, silver, copper, zinc, nickel, and mercury cyanides from contaminated leach liquors. The excellent adsorption properties of activated carbons rely mainly upon their high surface area; furthermore, their high degree of surface reactivity provides them additional catalyst properties for the oxidation of cyanide (Behnamfard and Salarirad 2009). As a result, Deveci et al. (2006) evaluated the effect of copper and silver impregnation, aeration, and concentrations of adsorbent and cyanide on the efficiency of free cyanide removal by activated carbon (AC). Their results pointed out a significant enhancement of the cyanide removal capacity of activated carbon after metal impregnation (up to 6.3-fold). Furthermore, silver-impregnated activated carbon (AC-Ag) was found to be more effective in reducing the cyanide level in solution; silver can be readily loaded onto activated carbon which results in a higher metal content after impregnation (i.e., 5.07 versus 0.43 % for silver and copper, respectively). The authors assigned the enhanced capacity of metal-impregnated activated carbons to the formation and adsorption of metal cyanide complexes on activated carbon, which was confirmed by speciation calculations of copper and silver cyanide complexes.

Aeration was also found to enhance remarkably the cyanide removal with increases up to 49.1 % in the capacity of plain and metal-impregnated activated carbons. In Fig. 5a, b, a comparison was established between cyanide removal by both AC and AC-Ag, respectively, with and without aeration for adsorbent dosages of 0.2 and 0.45 gL^{-1} (results for copper-impregnated activated carbon were not represented given their similarity with those of AC-Ag). As may be observed, the enhancement of the AC capacity was similar at 0.2 and 4.5 gL^{-1}, in contrast to what happened with AC-Ag, where the contribution of aeration tended to attenuate with increasing adsorbent dosage. However, this behaviour was attributed to the limited availability of cyanide in solution for sorption onto AC-Ag rather than to the reduction of the aeration contribution. The observed enhancement was ascribed to the formation of positively charged active sites on the activated carbon, originated by oxidation of chromene-type functional groups in the presence of molecular oxygen. As a result, the formation of positively charged active sites increases the sorption capacity of activated carbon for negatively charged ions. However, free cyanide was only weakly sorbed on AC and therefore a portion of cyanide was reported to be possibly removed also by catalytic oxidation.

More recently, Dai and Breuer (2009) proposed a simple process based on activated carbon adsorption to recover cyanide and copper cyanides following the leaching and recovery of gold from copper-containing gold ores. This process involves conversion of free cyanide to copper cyanide by dissolution of metallic copper and simultaneous decrease of the overall cyanide-to-copper ratio by converting $Cu(CN)_4^{3-}$ and the majority of $Cu(CN)_3^{2-}$ to $Cu(CN)_2^{-}$ complex, recovery of copper cyanides by activated carbon adsorption and desorption, and subsequent low pH copper electrowinning from the eluate stream and cyanide recycling. Table 1 displays the main results of several researchers on the removal of cyanide ions by adsorption and ion-exchange under different operating conditions.

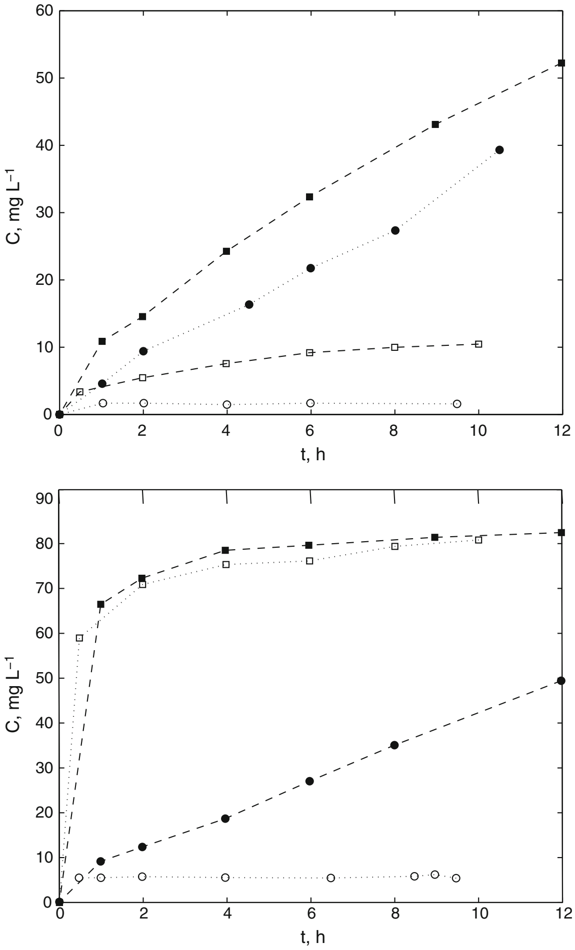

Fig. 5 Effect of aeration on the cyanide removal performance of **a** activated carbon and **b** silver-impregnated activated carbon. Experimental conditions: 0.27 $Lmin^{-1}$ of aeration, initial concentration of 100 mgL^{-1}, and pH 10.5–11. Symbols: *filled squares* 0.45 gL^{-1} with aeration; *filled circles* 0.2 gL^{-1} with aeration; *empty squares* 0.45 gL^{-1} without aeration; *empty circles* 0.2 gL^{-1} without aeration. Data from Deveci et al. (2006)

7 Conclusions

This paper presents an overview on mostly applied methodologies to remove nitrate, nitrite, chloride, sulfide, fluoride, and cyanide anions from aqueous solutions. In general, ion-exchange has been considered the most appropriate technology to remove these anionic species from aqueous solution. Hence, the most applied exchanger materials together with the main results obtained in literature and most recent developments in this area have been presented and discussed. Moreover, the importance of synthesis and operating conditions, particularly solution pH, on the removal efficiency has been emphasized here.

From the present review, it is possible to highlight the efforts made by researchers towards the development of low-cost and easily available effective sorbents, from which agriculture waste materials and derivatives are important examples of promising exchangers. Moreover, special attention has been devoted in an attempt to find out the most appropriate synthesis and operation conditions for drinking water purification. For instance, structural modifications by introducing more suitable surface functional groups or compensation species in the solid matrix have been some of the methodologies adopted to enhance their affinity for certain contaminants as well as to improve their capacity to reduce the pollutants level below the corresponding imposed limits. Besides, a number of operation strategies, including determination of the optimum solution pH or aeration, have been confirmed to significantly enhance materials performance.

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References

Afkhami, A., Madrakian, T., & Karimi, Z. (2007). The effect of acid treatment of carbon cloth on the adsorption of nitrite and nitrate ions. *Journal of Hazardous Materials, 144*(1–2), 427–431.

Arora, M., Eddy, N. K., Mumford, K. A., Baba, Y., Perera, J. M., & Stevens, G. W. (2010). Surface modification of natural zeolite by chitosan and its use for nitrate removal in cold regions. *Cold Regions Science and Technology, 62* (2–3), 92–97.

Ateya, B. G., AlKharafi, F. M., & Al-Azab, A. S. (2003). Electrodeposition of sulfur from sulfide contaminated brines. *Electrochemical and Solid-State Letters, 6*(9), C137–C140.

Behnamfard, A., & Salarirad, M. M. (2009). Equilibrium and kinetic studies on free cyanide adsorption from aqueous solution by activated carbon. *Journal of Hazardous Materials, 170*, 127–133.

Berbar, Y., Amara, M., & Kerdjoudj, H. (2008). Anion exchange resin applied to a separation between nitrate and chloride ions in the presence of aqueous soluble polyelectrolyte. *Desalination, 223*, 238–242.

Bhakat, P. B., Gupta, A. K., & Ayoob, S. (2007). Feasibility analysis of As(III) removal in a continuous flow fixed bed system by modified calcined bauxite (MCB). *Journal of Hazardous Materials, 139*(2), 286–292.

Bhatnagar, A., Ji, M., Choi, Y. H., Jung, W., Lee, S. H., Kim, S. J., et al. (2008). Removal of nitrate from water by adsorption onto zinc chloride treated activated carbon. *Separation Science and Technology, 43*(4), 886–907.

Biçak, N., & Filiz Şenkal, B. (1998). Removal of nitrite ions from aqueous solutions by cross-linked polymer of ethylenediamine with epichlorohydrin. *Reactive and Functional Polymers, 36*(1), 71–77.

Biswas, K., Gupta, K., Goswami, A., & Ghosh, U. C. (2010). Fluoride removal efficiency from aqueous solution by synthetic iron(III)-aluminum (III)-chromium(III) ternary mixed oxide. *Desalination, 255*, 44–51.

Bogoczek, R., Kociolek-Balawejder, E., & Stanislawska, E. (2006). A macromolecular oxidant, the *N,N*-dichlorosulfonamide for removal of residual nitrites from aqueous media. *Reactive and Functional Polymers, 66*(6), 609–617.

Bulusu, K. R., & Nawlakhe, W. G. (1988). Defluoridation of water with activated alumina: batch operations. *Indian Journal of Environmental Health, 30*(3), 262–299.

Camel, V. (2003). Solid phase extraction of trace elements. *Spectrochimica Acta: Part B Atomic Spectroscopy, 58*(7), 1177–1233.

Carmona, M., Perez, A., de Lucas, A., Rodriguez, L., & Rodriguez, J. F. (2008). Removal of chloride ions from an industrial polyethylenimine flocculant shifting it into an adhesive promoter using the anion exchange resin Amberlite IRA-420. *Reactive and Functional Polymers, 68*, 1218–1224.

Chabani, M., & Bensmaili, A. (2005). Kinetic modelling of the retention of nitrates by Amberlite IRA 410. *Desalination, 185*(1–3), 509–515.

Chabani, M., Amrane, A., & Bensmaili, A. (2006). Kinetic modelling of the adsorption of nitrates by ion exchange resin. *Chemical Engineering Journal, 125*, 111–117.

Chanda, M., & Rempel, G. L. (1995). Sorption of sulfide on a macroporous, quaternized poly(4-vinyl pyridine) in alkaline medium. *Reactive Polymers, 24*, 203–212.

Chatterjee, S., & Woo, S. H. (2009). The removal of nitrate from aqueous solutions by chitosan hydrogel beads. *Journal of Hazardous Materials, 164*(2–3), 1012–1018.

Chen, G. (2004). Electrochemical technologies in wastewater treatment. *Separation and Purification Technology, 38*(1), 11–41.

Cheng, I. F., Muftikian, R., Fernando, Q., & Korte, N. (1997). Reduction of nitrate to ammonia by zero-valent iron. *Chemosphere, 35*(11), 2689–2695.

Cheng, X. W., Zhong, Y., Wang, J., Guo, J., Huang, Q., & Long, Y. C. (2005). Studies on modification and structural ultra-stabilization of natural STI zeolite. *Microporous and Mesoporous Materials, 83*(1–3), 233–243.

Cumbal, L., Greenleaf, J., Leun, D., & SenGupta, A. K. (2003). Polymer supported inorganic nanoparticles: characterization and environmental applications. *Reactive and Functional Polymers, 54*(1–3), 167–180.

Dabrowski, A., Hubicki, Z., Podkoscielny, P., & Robens, E. (2004). Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method. *Chemosphere, 56*(2), 91–106.

Dai, X., & Breuer, P. L. (2009). Cyanide and copper cyanide recovery by activated carbon. *Minerals Engineering, 22*, 469–476.

Daifullah, A. A. M., Yakout, S. M., & Elreefy, S. A. (2007). Adsorption of fluoride in aqueous solutions using $KMnO_4$-modified activated carbon derived from steam pyrolysis of rice straw. *Journal of Hazardous Materials, 147*, 633–643.

Das, D. P., Das, J., & Parida, K. (2003). Physicochemical characterization and adsorption behavior of calcined Zn/Al hydrotalcite-like compound (HTlc) towards removal of fluoride from aqueous solution. *Journal of Colloid and Interface Science, 261*(2), 213–220.

Das, N., Pattanaik, P., & Das, R. (2005). Defluoridation of drinking water using activated titanium rich bauxite. *Journal of Colloid and Interface Science, 292*(1), 1–10.

Dash, R. R., Gaur, A., & Balomajumder, C. (2009). Review cyanide in industrial wastewaters and its removal: a review on biotreatment. *Journal of Hazardous Materials, 163*, 1–11.

de Heredia, J. B., Dominguez, J. R., Cano, Y., & Jimenez, I. (2006). Nitrate removal from groundwater using Amberlite IRN-78: Modelling the system. *Applied Surface Science, 252*, 6031–6035.

Deganello, F., Liotta, L. F., Macaluso, A., Venezia, A. M., & Deganello, G. (2000). Catalytic reduction of nitrates and nitrites in water solution on pumice-supported Pd–Cu catalysts. *Applied Catalysis B: Environmental, 24*(3–4), 265–273.

DeMarco, M. J., SenGupta, A. K., & Greenleaf, J. E. (2003). Arsenic removal using a polymeric/inorganic hybrid sorbent. *Water Research, 37*(1), 164–176.

Deveci, H., Yazıcı, E. Y., Alp, I., & Uslu, T. (2006). Removal of cyanide from aqueous solutions by plain and metal-impregnated granular activated carbons. *International Journal of Mineral Processing, 79*, 198–208.

Dubey, S. K., & Holmes, D. S. (1995). Biological cyanide destruction mediated by microorganisms. *World Journal of Microbiology and Biotechnology, 11*(3), 257–265.

Durmaz, F., Kara, H., Cengeloglu, Y., & Ersoz, M. (2005). Fluoride removal by Donnan dialysis with anion exchange membranes. *Desalination, 177*(1–3), 51–57.

Dutta, P. K., Rabaey, K., Yuan, Z., & Keller, J. (2008). Spontaneous electrochemical removal of aqueous sulfide. *Water Research, 42*(20), 4965–4975.

Dutta, P. K., Rabaey, K., Yuan, Z., Rozendal, R. A., & Keller, J. (2010). Electrochemical sulfide removal and recovery from paper mill anaerobic treatment effluent. *Water Research, 44*, 2563–2571.

Erdem, M., Altundogan, H. S., & Tumen, F. (2004). Removal of hexavalent chromium by using heat-activated bauxite. *Minerals Engineering, 17*(9–10), 1045–1052.

Ettouney, H. M., El-Dessouky, H. T., Faibish, R. S., & Gowin, P. J. (2002). Evaluating the economics of desalination. *Chemical Engineering Progress, 98*(12), 32–39.

Fan, X., Parker, D. J., & Smith, M. D. (2003). Adsorption kinetics of fluoride on low cost materials. *Water Research, 37*, 4929–4937.

Ganczarczyk, J. J., Takoaka, P. T., & Ohashi, D. A. (1985). Application of polysulfide for pretreatment of spent cyanide liquors. *Journal of the Water Pollution Control Federation, 57*(11), 1089–1093.

Gao, W., Chen, J., Guan, X., Jin, R., Zhang, F., & Guan, N. (2004). Catalytic reduction of nitrite ions in drinking water over Pd–Cu/TiO_2 bimetallic catalyst. *Catalysis Today, 93–95*, 333–339.

Gao, B.-Y., Xu, X., Wang, Y., Yue, Q.-Y., & Xu, X.-M. (2009). Preparation and characteristics of quaternary amino anion exchanger from wheat residue. *Journal of Hazardous Materials, 165*(1–3), 461–468.

Gärtner, R. S., & Witkamp, G. J. (2005). Regeneration of mixed solvent by ion exchange resin: selective removal of chloride and sulfate. *Separation Science and Technology, 40* (12), 2391–2410.

Gärtner, R. S., Wilhelm, F. G., Witkamp, G. J., & Wessling, M. (2005). Regeneration of mixed solvent by electrodialysis: selective removal of chloride and sulfate. *Journal of Membrane Science, 250*, 113–133.

Guan, H. D., Bestland, E., Zhu, C. Y., Zhu, H. L., Albertsdottir, D., Hutson, J., et al. (2010). Variation in performance of surfactant loading and resulting nitrate removal among four selected natural zeolites. *Journal of Hazardous Materials, 183*(1–3), 616–621.

Guo, Z., Zheng, Z., Gu, C., & Zheng, Y. (2008). Gamma irradiation-induced removal of low-concentration nitrite in aqueous solution. *Radiation Physics and Chemistry, 77* (6), 702–707.

Hichour, M., Persin, F., Sandeaux, J., & Gavach, C. (2000). Fluoride removal from waters by Donnan dialysis. *Separation and Purification Technology, 18*, 1–11.

Honn, K. V., & Chavin, W. (1976). Utility of ozone treatment in the maintenance of water quality in a closed marine system. *Marine Biology, 34*(3), 201–209.

Hradil, J., Králová, E., & Benes, M. J. (1997). Methacrylate anion exchangers with enhanced affinity for nitrates. *Reactive and Functional Polymers, 33*, 263–273.

Hu, H.-Y., Goto, N., & Fujie, K. (2001). Effect of ph on the reduction of nitrite in water by metallic iron. *Water Research, 35*(11), 2789–2793.

Islam, M., & Patel, R. (2010). Synthesis and physicochemical characterization of Zn/Al chloride layered double hydroxide and evaluation of its nitrate removal efficiency. *Desalination, 256*, 120–128.

Kabay, N., Arar, O., Samatya, S., Yuksel, U., & Yuksel, M. (2008). Separation of fluoride from aqueous solution by electrodialysis: effect of process parameters and other ionic species. *Journal of Hazardous Materials, 153*(1–2), 107–113.

Kagne, S., Jagtap, S., Dhawade, P., Kamble, S. P., Devotta, S., & Rayalu, S. S. (2008). Hydrated cement: a promising adsorbent for the removal of fluoride from aqueous solution. *Journal of Hazardous Materials, 154*, 88–95.

Kameda, T., Miyano, Y., Yoshioka, T., Uchida, M., & Okuwaki, A. (2000). New treatment methods for waste water containing chloride ion using magnesium-aluminum oxide. *Chemistry Letters, 10*, 1136–1137.

Kameda, T., Yabuuchi, F., Yoshioka, T., Uchida, M., & Okuwaki, A. (2003a). New method of treating dilute mineral acids using magnesium-aluminum oxide. *Water Research, 37*(7), 1545–1550.

Kameda, T., Yoshioka, T., Mitsuhashi, T., Uchida, M., & Okuwaki, A. (2003b). The simultaneous removal of calcium and chloride ions from calcium chloride solution using magnesium–aluminum oxide. *Water Research, 37*, 4045–4050.

Kenfield, C. F., Qin, R., Semmens, M. J., & Cussler, E. L. (1988). Cyanide recovery across hollow fiber gas membranes. *Environmental Science and Technology, 22*(10), 1151–1155.

Khani, A., & Mirzaei, M. (2008). Comparative study of nitrate removal from aquous solution using powder activated carbon and carbon nanotubes. Paper presented at the 2nd International IUPAC Conference in Green Chemistry.

Kim, J., & Benjamin, M. M. (2004). Modeling a novel ion exchange process for arsenic and nitrate removal. *Water Research, 38*, 2053–2062.

Kim, Y., Kim, C., Choi, I., Rengaraj, S., & Yi, J. (2004). Arsenic removal using mesoporous alumina prepared via a templating method. *Environmental Science and Technology, 38*(3), 924–931.

Krüner, G., & Rosenthal, H. (1983). Efficiency of nitrification in trickling filters using different substrates. *Aquacultural Engineering, 2*(1), 49–67.

Lahnid, S., Tahaikt, M., Elaroui, K., Idrissi, I., Hafsi, M., Laaziz, I., et al. (2008). Economic evaluation of fluoride removal by electrodialysis. *Desalination, 230*(1–3), 213–219.

Lehman, S. G., Badruzzaman, M., Adham, S., Roberts, D., & Clifford, D. A. (2008). Perchlorate and nitrate treatment by ion exchange integrated with biological brine treatment. *Water Research, 42*, 969–976.

Li, J., Qiu, J., Sun, Y. J., & Long, Y. C. (2000). Studies on natural STI zeolite: modification, structure, adsorption and catalysis. *Microporous and Mesoporous Materials, 37*(3), 365–378.

Lin, S. H., & Wu, C. L. (1996). Removal of nitrogenous compounds from aqueous solution by ozonation and ion exchange. *Water Research, 30*(8), 1851–1857.

Lopes, C. B., Lito, P. F., Cardoso, S. P., Pereira, E., Duarte, A. C., & Silva, C. M. (2012). Metal recovery, separation and/or concentration. In S. Inamuddin & M. Luqman (Eds.), *Ion-exchange technology: theory, materials and applications*. Berlin: Springer.

Lüdtke, K., Peinemann, K. V., Kasche, V., & Behling, R. D. (1998). Nitrate removal of drinking water by means of catalytically active membranes. *Journal of Membrane Science, 151*(1), 3–11.

Lv, L., He, J., Wei, M., Evans, D. G., & Duan, X. (2006a). Factors influencing the removal of fluoride from aqueous solution by calcined Mg–Al–CO_3 layered double hydroxides. *Journal of Hazardous Materials B, 133*, 119–128.

Lv, L., He, J., Wei, M., Evans, D. G., & Duan, X. (2006b). Uptake of chloride ion from aqueous solution by calcined layered double hydroxides: equilibrium and kinetic studies. *Water Research, 40*, 735–743.

Lv, L., Sun, P., Gu, Z., Du, H., Pang, X., Tao, X., et al. (2009). Removal of chloride ion from aqueous solution by ZnAl–NO_3 layered double hydroxides as anion-exchanger. *Journal of Hazardous Materials, 161*, 1444–1449.

Ma, J., & Dasgupta, P. K. (2010). Recent developments in cyanide detection: a review. *Analytica Chimica Acta, 673*, 117–125.

Mandal, S., & Mayadevi, S. (2008). Cellulose supported layered double hydroxides for the adsorption of fluoride from aqueous solution. *Chemosphere, 72*(6), 995–998.

Meenakshi, S., & Viswanathan, N. (2007). Identification of selective ion-exchange resin for fluoride sorption. *Journal of Colloid and Interface Science, 308*, 438–450.

Mena-Duran, C. J., Kou, M. R. S., Lopez, T., Azamar-Barrios, J. A., Aguilar, D. H., Dominguez, M. I., et al. (2007). Nitrate removal using natural clays modified by acid thermoactivation. *Applied Surface Science, 253*(13), 5762–5766.

Mohapatra, M., Anand, S., Mishra, B. K., Giles, D. E., & Singh, P. (2009). Review of fluoride removal from drinking water. *Journal of Environmental Management, 91*(1), 67–77.

Namasivayam, C., & Sangeetha, D. (2005). Removal and recovery of nitrate from water by $ZnCl_2$ activated carbon from coconut coir pith, an agricultural solid waste. *Indian Journal of Chemical Technology, 12*(5), 513–521.

Ndiayea, P. I., Moulin, P., Dominguez, L., Millet, J. C., & Charbit, F. (2005). Removal of fluoride from electronic industrial effluent by RO membrane separation. *Desalination, 173*(1), 25–32.

Oh, T.-K., & Chikushi, J. (2010). Fluoride adsorption on water treatment sludge processed by polyaluminium chloride. *Journal of Food, Agriculture & Environment, 8*(1), 358–362.

Onyango, M. S., Kojima, Y., Aoyi, O., Bernardo, E. C., & Matsuda, H. (2004). Adsorption equilibrium modeling and solution chemistry dependence of fluoride removal from water by trivalent-cation-exchanged zeolite F-9. *Journal of Colloid and Interface Science, 279*(2), 341–350.

Onyango, M. S., Kojima, Y., Kuchar, D., Osembo, S. O., & Matsuda, H. (2005). Diffusion kinetic modeling of fluoride removal from aqueous solution by charge-reversed zeolite particles. *Journal of Chemical Engineering of Japan, 38* (9), 701–710.

Onyango, M. S., Kojima, Y., Kumar, A., Kuchar, D., Kubota, M., & Matsuda, H. (2006). Uptake of fluoride by Al_3^+ pretreated low–silica synthetic zeolites: adsorption equilibrium and rate studies. *Separation Science and Technology, 41*(4), 683–704.

Orlando, U. S., Baes, A. U., Nishijima, W., & Okada, M. (2002). A new procedure to produce lignocellulosic anion exchangers from agricultural waste materials. *Bioresource Technology, 83*, 195–198.

Orlando, U. S., Okuda, T., Baes, A. U., Nishijima, W., & Okada, M. (2003). Chemical properties of anion-exchangers prepared from waste natural materials. *Reactive and Functional Polymers, 55*(3), 311–318.

Osathaphan, K., Boonpitak, T., Laopirojana, T., & Sharma, V. K. (2008). Removal of cyanide and zinc-cyanide complex by an ion-exchange process. *Water, Air, and Soil Pollution, 194*, 179–183.

Öztürk, N., & Köse, T. E. (2008). A kinetic study of nitrite adsorption onto sepiolite and powdered activated carbon. *Desalination, 223*, 174–179.

Panswad, T., & Anan, C. (1999). Impact of high chloride wastewater on an anaerobic/anoxic/aerobic process with and without inoculation of chloride acclimated seeds. *Water Research, 33*(5), 1165–1172.

Parrish, J. R. (1977). Macroporous resins as supports for a chelating liquid ion-exchanger in extraction chromatography. *Analytical Chemistry, 49*(8), 1189–1192.

Pikaar, I., Rozendal, R. A., Yuan, Z., Keller, J., & Rabaey, K. (2011a). Electrochemical sulfide oxidation from domestic wastewater using mixed metal-coated titanium electrodes. *Water Research, 45*(45), 5381–5388.

Pikaar, I., Rozendal, R. A., Yuan, Z., Keller, J., & Rabaey, K. (2011b). Electrochemical sulfide removal from synthetic and real domestic wastewater at high current densities. *Water Research, 45*, 2281–2289.

Pintar, A., & Batista, J. (2006). Improvement of an integrated ion-exchange/catalytic process for nitrate removal by introducing a two-stage denitrification step. *Applied Catalysis B: Environmental, 63*(1–2), 150–159.

Pintar, A., Batista, J., & Levec, J. (2001). Integrated ion exchange/catalytic process for efficient removal of nitrates from drinking water. *Chemical Engineering Science, 56*(4), 1551–1559.

Rabaey, K., Van de Sompel, K., Maignien, L., Boon, N., Aelterman, P., Clauwaert, P., et al. (2006). Microbial fuel cells for sulfide removal. *Environmental Science and Technology, 40*(17), 5218–5224.

Rajeshwar, K., Ibanez, J. G., & Swain, G. M. (1994). Electrochemistry and the environment. *Journal of Applied Electrochemistry, 24*(11), 1077–1091.

Reimers, C. E., Girguis, P., Stecher Iii, H. A., Tender, L. M., Ryckelynck, N., & Whaling, P. (2006). Microbial fuel cell energy from an ocean cold seep. *Geobiology, 4*(2), 123–136.

Rivas, B. L., & del Carmen Aguirre, M. (2007). Nitrite removal from water using water-soluble polymers in conjunction with liquid-phase polymer-based retention technique. *Reactive and Functional Polymers, 67*(12), 1487–1494.

Ruixia, L., Jinlong, G., & Hongxiao, T. (2002). Adsorption of fluoride, phosphate, and arsenate ions on a new type of ion exchange fiber. *Journal of Colloid and Interface Science, 248*, 268–274.

Samatya, S., Kabay, N., Yuksel, U., Arda, M., & Yuksel, M. (2006). Removal of nitrate from aqueous solution by nitrate selective ion exchange resins. *Reactive and Functional Polymers, 66*, 1206–1214.

Samatya, S., Yuksel, U., Yuksel, M., & Kabay, N. (2007). Removal of fluoride from water by metal ions (Al^{3+}, La^{3+} and ZrO^{2+}) loaded natural zeolite. *Separation Science and Technology, 42*(9), 2033–2047.

Samatya, S., Mizuki, H., Ito, Y., Kawakita, H., & Uezu, K. (2010). The effect of polystyrene as a porogen on the fluoride ion adsorption of Zr(IV) surface-immobilized resin. *Reactive and Functional Polymers, 70*(1), 63–68.

Saremi, M., & Mahallati, E. (2002). A study on chloride-induced depassivation of mild steel in simulated concrete pore solution. *Cement and Concrete Research, 32*, 1915–1921.

Sarkar, S., & SenGupta, A. K. (2008). A new hybrid ion exchange-nanofiltration (HIX-NF) separation process for energy-efficient desalination: process concept and laboratory evaluation. *Journal of Membrane Science, 324*, 76–84.

Sivasankar, V., Ramachandramoorthy, T., & Chandramohan, A. (2010). Fluoride removal from water using activated and MnO_2-coated tamarind fruit (tamarindus indica) shell: batch and column studies. *Journal of Hazardous Materials, 177*, 719–729.

Solangi, I. B., Memon, S., & Bhanger, M. I. (2010). An excellent fluoride sorption behavior of modified amberlite resin. *Journal of Hazardous Materials, 176*, 186–192.

Soldatov, V. S., Sokolova, V. I., Medyak, G. V., Shunkevich, A. A., & Akulich, Z. I. (2007). Binary ion exchange equilibria in systems containing NO^{-}, Cl^{-} and SO_2^{-} on fibrous anion exchangers with tetraalkylammomium groups. *Reactive and Functional Polymers, 67*, 1530–1539.

Spiegler, K. S., & El-Sayed, Y. M. (2001). The energetics of desalination processes. *Desalination, 134*(1–3), 109–128.

Strukul, G., Pinna, F., Marella, M., Meregalli, L., & Tomaselli, M. (1996). Sol–gel palladium catalysts for nitrate and nitrite removal from drinking water. *Catalysis Today, 27* (1–2), 209–214.

Sujana, M. G., & Anand, S. (2011). Fluoride removal studies from contaminated ground water by using bauxite. *Desalination, 267*(2–3).

Sun, Y. B., Fang, Q. H., Dong, J. P., Cheng, X. W., & Xu, J. Q. (2011). Removal of fluoride from drinking water by natural stilbite zeolite modified with Fe(III). *Desalination, 277*(1–3), 121–127.

Suzuki, T., Akizawa, Y., Ono, N., Masuda, H., Shindo, T., Nagamachi, M., et al. (1991). The transfer of mofezolac into the inflammatory site and the hypothalamus in rats. *Japanese Pharmacology and Therapeutics, 19*(1), 33–40.

Swain, S. K., Dey, R. K., Islam, M., Patel, R. K., Jha, U., Patnaik, T., et al. (2009). Removal of fluoride from aqueous solution using aluminum-impregnated chitosan biopolymer. *Separation Science and Technology, 44*, 2096–2116.

Tahaikt, M., El Habbania, R., Haddou, A. A., Acharya, I., Amora, Z., Takya, M., et al. (2007). Fluoride removal from groundwater by nanofiltration. *Desalination, 212*(1–3), 46–53.

Tahaikt, M., Haddou, A. A., El Habbani, R., Amor, Z., Elhannouni, F., Taky, M., et al. (2008). Comparison of the performances of three commercial membranes in fluoride removal by nanofiltration. Continuous operations. *Desalination, 225*(1–3), 209–219.

Tang, Y., Guan, X., Su, T., Gao, N., & Wang, J. (2009). Fluoride adsorption onto activated alumina: modeling the effects of pH and some competing ions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 337*, 33–38.

Tchobanoglous, G., Burton, F. L., & Stensel, H. D. (2003). *Wastewater engineering: treatment and reuse*. New York: McGraw-Hill.

Tokunaga, S., Haron, M. J., Wasay, S. A., Wong, K. F., Laosangthum, K., & Uchiumi, A. (1995). Removal of fluoride ions from aqueous solutions by multivalent metal compounds. *International Journal of Environmental Studies, 48*(1 Sect.A), 17–28.

Tor, A., Danaoglu, N., Arslan, G., & Cengeloglu, Y. (2009). Removal of fluoride from water by using granular red mud: batch and column studies. *Journal of Hazardous Materials, 164*, 271–278.

Tsuji, M., & Abe, M. (1986). Possible radiochemical separations of anionic radionuclides by amorphous hydrous titanium dioxide. *Journal of Radioanalytical and Nuclear Chemistry Articles, 102*(2), 283–294.

Tsuji, M., & Abe, M. (1991). Selective uptake of toxic elements by an amorphous titanium dioxide ion exchanger. *Journal of Radioanalytical and Nuclear Chemistry, 149*(1), 109–118.

Vaiopoulou, E., Melidis, P., & Aivasidis, A. (2005). Sulfide removal in wastewater from petrochemical industries by autotrophic denitrification. *Water Research, 39*(17), 4101–4109.

Viswanathan, N., & Meenakshi, S. (2010). Enriched fluoride sorption using alumina/chitosan composite. *Journal of Hazardous Materials, 178*, 226–232.

Wajima, T., Umeta, Y., Narita, S., & Sugawara, K. (2009). Adsorption behavior of fluoride ions using a titanium hydroxide-derived adsorbent. *Desalination, 249*(1), 323–330.

Warshawsky, A. (1974). Polystyrene impregnated with β-diphenylglyoxime, a selective reagent for palladium. *Talanta, 21*(6), 624–626.

Wild, S. R., Rudd, T., & Neller, A. (1994). Fate and effects of cyanide during wastewater treatment processes. *Science of the Total Environment, 156*(2), 93–107.

Yang, H., & Cheng, H. (2007). Controlling nitrite level in drinking water by chlorination and chloramination. *Separation and Purification Technology, 56*(3), 392–396.

Zhang, Z., & Pinnavaia, T. J. (2002). Mesostructured γ-Al_2O_3 with a lathlike framework morphology. *Journal of the American Chemical Society, 124*(41), 12294–12301.

Zhang, L., De Schryver, P., De Gusseme, B., De Muynck, W., Boon, N., & Verstraete, W. (2008). Chemical and biological technologies for hydrogen sulfide emission control in sewer systems: a review. *Water Research, 42*(1–2), 1–12.

Zhang, J., Xie, S., & Ho, Y.-S. (2009). Removal of fluoride ions from aqueous solution using modified attapulgite as adsorbent. *Journal of Hazardous Materials, 165*, 218–222.

Zhao, Y., Li, X., Liu, L., & Chen, F. (2008). Fluoride removal by Fe(III)-loaded ligand exchange cotton cellulose adsorbent from drinking water. *Carbohydrate Polymers, 72*, 144–150.

Zhu, P., Wang, H., Sun, B., Deng, P., Hou, S., & Yu, Y. (2009). Adsorption of fluoride from aqueous solution by magnesia-amended silicon dioxide granules. *Journal of Chemical Technology and Biotechnology, 84*, 1449–1455.