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Review of fluoride removal from water by adsorption using soil adsorbents – an evaluation of the status

Enos W. Wambu, Willis O. Ambusso, Charles Onindo and Gerald K. Muthakia

ABSTRACT

The fate of excessive fluoride in water is cause for serious public health concerns worldwide. Water defluoridation using various technologies therefore continues to attract disproportionate research interest from around the world. Defluoridation studies using soil adsorbents, in particular, have remained the focus of intense research efforts since the last few decades. So as to assess the research status in this area, soil adsorbents commonly reported for water defluoridation over the last few decades were reviewed. This paper presents a compilation of defluoridation capacities and a summary of requisite parameters for water defluoridation using soil adsorbents. Comparison of defluoridation efficiencies of soil adsorbents is also presented, and the fluoride adsorption kinetics and adsorption equilibrium characteristics of adsorbents discussed. The results indicate that the soil adsorbents that have attracted highest research interest in this regard include hydroxyapatites, montmorillonites, hydrotalcite, zeolites, pumice and kaolinites. On average, however, the minerals that have shown the highest capacities for water defluoridation are: ferrihydrites, hydrotalcite, palygorskites, boehmite/bauxite, and pumice. Fluoride adsorption for most soil adsorbents is fitted by the Langmuir and Freundlich isotherms. Most of the kinetic data, in contrast, were described by the pseudo-second order kinetics model. Water pH and temperature were the dominant solution factors that controlled fluoride adsorption onto soil adsorbents.

Key words | adsorption, defluoridation, drinking water, fluoride, literature review, soil adsorbents

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INTRODUCTION

Excessive water fluoride continues to pose serious public health concerns world over. Detrimental effects of long-term exposure to excessive dietary fluoride range from mild colorization of teeth surfaces to staining, pitting and loss of the tooth enamel, and severe crippling skeletal deformations and death may result in chronic cases (Xu *et al.* 2000). The associated non-skeletal effects include neurological, kidney, endocrine, thyroid and liver disorders, and chronic disruption of metabolic processes occurs when the fluoride doses are very high (Ayoob & Gupta 2006; Adelana *et al.* 2010). Nonetheless, fluorosis is still the most noxious effect of prolonged consumption of excessive dietary fluoride (Jha *et al.* 2013). Sustained consumption of high-

fluoride water when safer drinking water is not readily available remains the main pathway by which people get exposed to excessive fluoride.

At the moment, technologies used in defluoridation of water include reverse osmosis and nanofiltration, dialysis and electro-dialysis and adsorption (Mohapatra *et al.* 2009a). However, adsorption appears to be the most appropriate solution because it is cost-effective, simple to operate and it produces high-quality treated water (Deshmukh & Attar 2008; Ingallinella *et al.* 2011; Malakootian *et al.* 2011; Goromo *et al.* 2012). Currently, activated alumina, rare earth oxides and activated carbon are the most plausible adsorbents for fluoride removal from water (Bhatnagar

et al. 2011; Tomar & Kumar 2013). They are, however, expensive, require a delicate balancing in adsorption parameters, and are strongly affected by the presence of competing anions such as SiO_4^{4-} , SO_4^{2-} , Cl^- , CO_3^{2-} and PO_4^{3-} in water. According to Loganathan *et al.* (2013), the alternate adsorbents desired for safe and easy treatment of high-fluoride water must not only be affordable and efficient but also simple to use and robust enough to regenerate in several cycles of reuse without considerable loss of their defluoridation capacities (DCs). Unsurprisingly, soil adsorbents have continued to attract unequalled research attention in the area of water defluoridation, especially over the last few years (El-Said & Draz 2010; Nath & Dutta 2010; Hyun *et al.* 2011; Goromo *et al.* 2012). This is because soils, ordinarily, have good natural sorptive properties, and they are chemically stable, readily available in abundance, and usable in a wide range of water conditions. As a consequence, large volumes of research data continue to accrue in the field of water defluoridation based on sorbent soil media.

To inform further research progress in these discipline areas, consolidation of the current research output by systematic critical review is desired. Such reviews are particularly useful in interrogating the research status of a given study area, and they are used to unravel important research details and expose gaps in research data that require filling so as to facilitate subsequent research progress in the particular field of study.

Water defluoridation has been the subject of intense literature reviews, especially in the most recent years (Sollo *et al.* 1978; Mohapatra *et al.* 2009a; Singh *et al.* 2014). Several of these reviews have been devoted to the use of adsorption technology in water defluoridation (Onyango & Matsuda 2006; Bhatnagar *et al.* 2011; Loganathan *et al.* 2013; Tomar & Kumar 2013), with a significant proportion of them being dedicated to fluoride removal from water by adsorption based on specific types of adsorbents such as nanofilters (Pontié *et al.* 2006), chitosan derivatives (Miretzky & Cirelli 2011) and calcium containing materials (Nath & Dutta 2015).

Despite the intense research interest being generated by soil adsorbents in water defluoridation, there has been no such review that has been devoted solely to providing deeper insight into the role of soil adsorbents in water defluoridation. Furthermore, previous reviews of water

defluoridation and of water defluoridation by adsorption have given only a casual treatment to the role of soil adsorbents in water defluoridation. As a consequence the overall direction of science, insofar as the use of soil adsorbents in water defluoridation is concerned, remains unclear. An in-depth review of fluoride soil adsorbents is therefore desirable for a deeper understanding of the role of soil adsorbents in the on-going search for robust adsorbents for easy and safe defluoridation of drinking water. This would in turn inform more focussed studies towards innovative technological approaches to management of community exposure to excessive fluoride through drinking water.

The current work was designed to provide an in-depth view of available soil adsorbents that have been reported for water defluoridation in the recent literature. It presents a compilation of DCs and parameters for optimal fluoride adsorption by various classes of soil adsorbents. The equilibrium and kinetics properties of fluoride uptake by the adsorbents are summarized and the overall status and prospects of applicability of the particular adsorbents discussed. It is hoped that the current work will provide a vantage point from which subsequent studies can be designed to engage present knowledge gaps so as to bridge scientific data and facilitate research progress towards innovative water defluoridation technologies based on the current literature data.

FLUORIDE SOIL ADSORBENTS

The classes of soil minerals that have attracted the greatest research interest for defluoridation of water in the most recent past are presented in Table 1.

Some of the minerals that have received the highest research attention in this area include the aluminosilicates, oxide minerals of Al and Fe, apatites, calcareous soil minerals, and carbonaceous geomaterials (Bhatnagar *et al.* 2011). Others are: sordic soils (Robbins 1986), red soil (Liang *et al.* 2014), serpentine mineral (Chidambaram *et al.* 2003), fired clays (Bardsen & Bjorvatn 1996) and ando soils from Kenya (Zevenbergen *et al.* 1996).

Table 1 | Soil minerals most studied for fluoride adsorption

Adsorbent	pH	Time (s)	Temp (K)	Langmuir		Freundlich		Sources
				q_m	R^2	K_f	R^2	
Hydroxyapatite	5.4	342.9	302.5	13.268	0.832	3.384	0.953	
Limestone derived apatite		1,440	303	22.22	0.997	11.11	0.758	Murutu <i>et al.</i> (2009)
Calcium hydroxyapatite	7	600	298	16.38	0.9917	3.601	0.9848	Nie <i>et al.</i> (2012)
Al ³⁺ -modified calcium hydroxyapatite	7	600	298	32.57				Nie <i>et al.</i> (2012)
Glass derived from hydroxyapatite	6.72	720	308	17.34		0.5175	0.9989	Liang <i>et al.</i> (2011)
Nano-structured hydroxyapatite	6.6	240	298	5.53	0.978	0.61	0.988	Eddy <i>et al.</i> (2011)
Hydroxyapatite	6	150		4.54	0.0015	0.161	0.9999	Fan <i>et al.</i> (2003)
Synthetic hydroxyapatite	2	120	298	0.489	0.91	0.371	0.987	Gao <i>et al.</i> (2009b)
Nano-sized hydroxyapatite	3	120	298	7.605	0.944	5.854	0.949	Wang (2011)
Apatitic tricalcium phosphate	4	90	313	15.15	0.988	4.01	0.969	Mourabet <i>et al.</i> (2012a)
Hydroxyapatite	7.5	90	303	3.12	0.992	1.45	0.981	Mourabet <i>et al.</i> (2012b)
Palygorskite	3	3,600	301	57.97	0.993	0.925	0.983	
Zirconium-modified Na-attapulgite	4.13	1,110	323	24.55	0.9935	8.2142	0.9563	Zhang <i>et al.</i> (2012a)
modified attapulgite		2,880	301	44	0.995	1.51	0.983	Zhang <i>et al.</i> (2009)
Tunisian clays (MK)	3	4320		71.94	0.991	0.34	0.983	Hamdi & Srasra (2009)
Boehmite								
Boehmite	4		298	8.27		2.15		Leyva-Ramos <i>et al.</i> (2008)
Boehmite	6.8			2.057	0.9212	0.574	0.9665	Jiménez-Becerril <i>et al.</i> (2011)
Ceramics								
Fe-impregnated granular ceramics	6.9	2880	303	1.699	0.961	0.065	0.971	Chen <i>et al.</i> (2011a)
Ceramic adsorbent				0.989	0.946	7.83	0.971	Chen <i>et al.</i> (2010b)
Fe-impregnated granular ceramics	6.9	2880	303	2.157	0.962	0.604	0.993	Chen <i>et al.</i> (2010b)
Brick powder	8	60	298			3.27	0.97	Yadav <i>et al.</i> (2006)
Bauxite								
Thermally activated titania-rich bauxite	5.5–6.5	90		4.13				Das <i>et al.</i> (2005)
Mixed Fe/Al hydroxides	6	120	303	5.16				Sujana & Anand (2010)
Reddish brown bauxite	4	120	303	22.44	0.98			Sujana & Anand (2011)
High alumina content bauxite	7		293	3.125				Lavecchia <i>et al.</i> (2012)
Coals								
Low-grade coal			333	396.8				Borah & Dey (2009)
Natural lignite	8	10	298	17.9	0.979	0.00718	0.985	Pekař (2008)
Lignite	5–10	150	303	7.1	0.9786	1.1473	0.9377	Sivasamy <i>et al.</i> (2001)
Fine coke	<5	90	303	6.9	0.9969	0.6287	0.9915	Sivasamy <i>et al.</i> (2001)
Bituminous coke	<5	60	303	7.4	0.9906	0.0611	0.9592	Sivasamy <i>et al.</i> (2001)
Kaolin								
Kanuma mud	6.9	60	303	0.562	0.899	3.067	0.981	Chen <i>et al.</i> (2011c)
Kaolinite clay		100	333	0.0557		1.4		Gogoi & Baruah (2008)

(Continued)

Table 1 | Continued

Adsorbent	pH	Time (s)	Temp (K)	Langmuir		Freundlich		Sources
				q_m	R^2	K_f	R^2	
Mechanochemically activated kaolinites	3	30	323	0.782	0.989	0.091	0.996	Meenakshi <i>et al.</i> (2008)
Kaolinite	4	30	303	0.103				Agarwal <i>et al.</i> (2002)
Kaolinite			303	1.45		0.47	0.937	Sujana <i>et al.</i> (2009a)
Kaolinite-ferrihydrite			303	12.83		1.58	0.975	Sujana <i>et al.</i> (2009)
Laterites								
High nickel laterites (NH)	3.5	300	303	15.02	0.925	0.84	0.996	Sujana <i>et al.</i> (2009a)
Low nickel laterites (NL)	3.5	300	303	12.3	0.967	0.36	0.956	Sujana <i>et al.</i> (2009a)
Laterite	7.5	200	303	0.8461	0.9698	0.1328	0.9976	Sarkar <i>et al.</i> (2006)
Montmorillonites								
Montmorillonite	6	180	298	3.365	0.978	0.236	0.97	Tor (2006)
Montmorillonite	6	30	303	0.247				Agarwal <i>et al.</i> (2002)
500 °C treated Ca-montmorillonite	4	30	301	1.324	0.991	0.85	0.964	Ramdani <i>et al.</i> (2010)
None-Ca-montmorillonite	4	30	301	1.013	0.982	0.515	0.962	Ramdani <i>et al.</i> (2010)
Activated spent bleaching earth	3.5	15		7.75		0.943		Mahramanlioglu <i>et al.</i> (2002)
Montmorillonite clay	3	50	333	1.91	0.993	0.3225	0.967	Karthikeyan <i>et al.</i> (2005)
Fe(III)-modified montmorillonite	4.5	160	298	9.6957	0.9630		0.990	Bia <i>et al.</i> (2012)
Poly-aniline montmorillonite composite		30	323	6.0	0.97	0.91	0.96	Karthikeyan <i>et al.</i> (2012)
Poly-parole montmorillonite composite		30	323	12.3	0.97	4.2	0.99	Karthikeyan <i>et al.</i> (2012)
Algerian bentonites		180		9.44	0.998	1.85	0.9985	Achour & Youcef (2009)
Tunisian clays (H)	3	5,760	298	66.62	0.992	0.33	0.88	Hamdi & Srasra (2009)
Pumice								
Pumice	7	120		0.31				Malakootian <i>et al.</i> (2011)
Functionalized pumice	6	30		41	0.986	27.6	0.999	Asgari <i>et al.</i> (2012)
Pumice	3	20	297	13.51	0.978	2.15	0.995	Mahvi <i>et al.</i> (2012)
Quartz								
Quartz	6	2		0.19	0.013	80	1	Fan <i>et al.</i> (2003)
Fe ³⁺ activated quartz	6	2		1.16	0.0027	3	1	Fan <i>et al.</i> (2003)
Zeolites								
ZrO ²⁺ -loaded zeolite		1,440	303	4.13	0.9936	–	–	Samatya <i>et al.</i> (2007)
Aluminium-loaded Shirasu-zeolite P1 (A1-SZP1)	4–10	960	297	4.37	–	–	–	Xu <i>et al.</i> (2000)
Natural stilbite zeolite modified with Fe(III)	6.94	120	–	2.31	0.996	0.988	0.926	Sun <i>et al.</i> (2011)
Al ³⁺ loaded zeolite		1,440	303	2.35	0.9955	–	–	Samatya <i>et al.</i> (2007)
La ³⁺ loaded zeolite		1,440	303	2.63	0.9978	–	–	Samatya <i>et al.</i> (2007)
Al-loaded zeolite		960	297			0.380189		
Al ³⁺ -exchanged zeolite fluoride-9	5		313	39.52		4.16	0.99	Onyango <i>et al.</i> (2004)

(Continued)

Table 1 | Continued

Adsorbent	pH	Time (s)	Temp (K)	Langmuir		Freundlich		Sources
				q_m	R^2	K_f	R^2	
La ³⁺ -exchanged zeolite fluoride-9	4		313	54.28		0.45	0.996	Onyango <i>et al.</i> (2004)
Others								
Raw marine sediments	6.2	60	298	200	0.834	115.584	0.937	El-Said & Draz (2010)
Waste mud	5.5	60	293	27.2	0.993	1.22	0.974	Kemer <i>et al.</i> (2009)
Ferrihydrite			303	20.2		6.58	0.925	Wei & Xiang (2012)
Overburden from chromite mines (OMC)	3.5	300	30	15.17	0.939	0.97	0.935	Sujana <i>et al.</i> (2009)
Magnesium loaded fly-ash cenospheres	3	60	318	6	0.9912		0.7848	Xu <i>et al.</i> (2011)
Pyrophyllite	4	120	297	3.79	0.99	0.95	0.99	Goswami & Purkait (2011)
Red soil from china	6		300	2.1218	0.09728	0.326	0.9581	Zhu <i>et al.</i> (2007)
Fluorspar	6	2		1.79	0.0003	8.5	0.9999	Fan <i>et al.</i> (2003)
Synthetic siderite		180	298	1.775	0.907	0.2761	0.9963	Liu <i>et al.</i> (2010a, 2010b)
Calcite	6	2		0.39	0.0142	8.33	1	Fan <i>et al.</i> (2003)
Saline sordic soil	8.9	1,440	298	0.3475	0.999			Robbins (1986)
Plaster of Paris	7	20	303	0.366	0.996	0.151	0.945	Gopal & Elango (2007)

Aluminosilicate clay adsorbents

Over the years the aluminosilicate minerals, especially the montmorillonites (Bia *et al.* 2012), kaolinites (Wei & Xiang 2012), palygorskite-sepiolite (Shengyu *et al.* 2015) and various zeolites (Gómez-Hortigüela *et al.* 2013), have continually attracted intense interest as adsorbents in the area of water defluoridation.

Montmorillonites

Montmorillonites are 2:1 clay systems that belong to the general class of phyllosilicate clays. They are the most extensively studied minerals for fluoride adsorption among the aluminosilicates (Mahramanlioglu *et al.* 2002; Tor 2006; Achour & Youcef 2009; Ramdani *et al.* 2010; Bia *et al.* 2012). The maximum DCs for natural montmorillonites occur within the pH values of natural waters (Agarwal *et al.* 2002; Tor 2006; Ramdani *et al.* 2010) in the range of ambient tropical temperatures of 298–303 K (Agarwal *et al.* 2002; Achour & Youcef 2009; Ramdani *et al.* 2010). Even though longer equilibration intervals of 160–180 minutes have been reported for fluoride adsorption onto certain

montmorillonite adsorbents (Tor 2006; Achour & Youcef 2009; Bia *et al.* 2012), the usual equilibrium time of fluoride adsorption onto most montmorillonite adsorbents is normally in the 30–60 minutes bracket (Agarwal *et al.* 2002; Karthikeyan *et al.* 2005, 2012; Ramdani *et al.* 2010).

The DCs of natural montmorillonites are in the range of 0.265–3.365 mg/g (Agarwal *et al.* 2002; Karthikeyan *et al.* 2005; Tor 2006), which is low when compared to those of other fluoride adsorbents such as Zr-loaded garlic peel (Zr-GP) particles (Kai *et al.* 2011) and bone char (Ma *et al.* 2008). Several studies have, therefore, considered use of modified montmorillonite clays. Karthikeyan *et al.* (2012), for example, studied fluoride adsorption onto aniline modified montmorillonites (PANi-MMT) and pyrrole modified montmorillonite (PPy-MMT) and reported enhanced DCs of 6.0 and 12.3 mg/g for PANi-MMT and PPy-MMT, respectively.

The temperature and adsorption contact time for optimum fluoride adsorption using PANi-MMT and PPy-MMT were 303 K and 50 minutes, respectively. The equilibrium fluoride adsorption data for both PANi-MMT and PPy-MMT could be fitted by the Freundlich isotherm, indicating that physisorption was the preferred mode of

fluoride immobilization into PANi-MMT and PPy-MMT surfaces. Apparently, adherence of fluoride adsorption data to the Freundlich model is the usual case for organo-modified montmorillonite adsorbents. In one of the recent studies, Kaygusuz *et al.* (2015) reported an enhanced defluoridation capacity (DC) of 31.0 mg/g for alginate-modified montmorillonite clays when the tests were conducted at 298 K. The fluoride adsorption onto the alginate-montmorillonite composite bead, as for PANi-MMT and PPy-MMT, was a physisorption process. The kinetic data for fluoride adsorption onto the biopolymer-clay composite could then be described by the Elovich adsorption kinetics model.

In related work, Mahramanlioglu *et al.* (2002) had earlier investigated fluoride adsorption onto spent beaching earth (SBE) – a montmorillonite clay waste from edible oil processing industries. The DC of the acid-treated SBE was 7.752 mg/g and the maximum fluoride adsorption using acidified SBE was recorded in acidic media with a pH value of 3.5. Unlike the adsorption of fluoride onto PANi-MMT and PPy-MMT, however, fluoride uptake by acidified SBE surfaces was rapid and the time required for the attainment of the adsorption equilibrium was just 15 minutes. Furthermore, the equilibrium fluoride adsorption data for SBE was fitted by the Langmuir adsorption isotherm, indicating that fluoride uptake by acidified SBE surfaces was a chemisorption process. Utilization of SBE for water defluoridation is particularly desired because it represents value addition, which could preclude the associated disposal costs and environmental concerns accruing to generation of the bulky and noxious SBE waste by edible oil industries (Wambu *et al.* 2009).

Bia *et al.* (2012), on their part, have explored fluoride adsorption from water using Fe(III)-enhanced montmorillonite clays. The DC for the Fe(III)-modified montmorillonite, which was recorded at a pH value of 4.5 and temperatures of 298 K, was 9.6857 mg/g and the equilibrium time for fluoride adsorption using the Fe(III)-enhanced montmorillonites was 160 minutes. It was observed that the rate of fluoride adsorption onto Fe(III)-modified montmorillonites increased with increasing fluoride concentration, but it decreased with increasing pH of the solution adsorption mixture. Fluoride adsorption onto Fe(III)-modified montmorillonite could, therefore, be a diffusion-controlled process. Clearly, the

modification of montmorillonite surfaces with Fe(III) did not only enhance the DC of the adsorbent, but the affinity of the montmorillonite surfaces for labile water fluoride as well.

From the available literature, it is clear that surface-modified montmorillonites depict superior DCs in the range of 6.0–31.0 mg/g compared to 0.2–3.6 mg/g DCs, which have normally been reported for unmodified montmorillonites. Surface modification, therefore, presents a real prospect for the use of montmorillonites in the treatment of high-fluoride water. However, montmorillonites are relatively reactive minerals; they tend to have a narrow fluoride adsorption edge because they solubilize in acid media when the solution pH is lower than 4, and their sorptive surfaces easily get poisoned by hydroxyl ions in strongly alkaline media.

The overall DCs and the fluoride adsorption kinetics and adsorption mechanisms for the montmorillonites are dependent on the mode of surface treatment of the adsorbents. Whereas fluoride adsorption onto metal cation-intercalated montmorillonites is generally slow and chemisorptive in nature, a rapid physisorption reaction is the preferred mechanism of fluoride uptake by montmorillonite surfaces that have been intercalated by reactive organic molecules. Even so, montmorillonite clays are not very well distributed around the world for easy procurement and use in water defluoridation, and their current use as bleaches in edible oil processing presently supersedes their proposed use for water defluoridation (Murray 2007).

Kaolinites

Kaolinites, like montmorillonite, have attracted high research interest in the area of water defluoridation in recent years (Hyun *et al.* 2005; Schaller *et al.* 2009; Reich *et al.* 2010). Unlike montmorillonites, however, kaolinites are generally more widely distributed around the world (Murray 2007). They are more stable in water (Clozel *et al.* 1994) and therefore usable in a wider range of water conditions than montmorillonites (Sugita *et al.* 2005; Meenakshi *et al.* 2008; Ibrahim *et al.* 2010).

Even though Kau *et al.* (1997) had reported exceptionally high fluoride retention capacity of 18 meq/100 g for a sample of South Carolina kaolinites, current research data

indicate that kaolinites normally have limited DCs of less than 1.0 mg/g over a wide range of adsorption conditions (Srimurali *et al.* 1998; Gogoi & Baruah 2008). This shows that kaolinites do not generally represent very prospective media for water defluoridation.

Attapulgite/palygorskite

Like the montmorillonites and kaolinites, attapulgite (syn. palygorskite) belong to a class of aluminosilicates that have most frequently been considered for water defluoridation. Available literature shows that palygorskites normally have remarkable DCs in the range of 24.55–71.94 mg/g (Hamdi & Srasra 2009; Zhang *et al.* 2009, 2012a; Feng *et al.* 2012; He *et al.* 2013). However, like the other aluminosilicates, palygorskites require surface enhancement to improve their DCs. A number of studies have, therefore, considered surface-enhanced palygorskite adsorbents for defluoridation of water. Zhang *et al.* (2009), for instance, evaluated fluoride uptake by an attapulgite adsorbent enhanced with magnesium and aluminium salts. Other examples of studies have considered fluoride adsorption onto zirconium-modified Na-attapulgite adsorbent (Zhang *et al.* 2012a) and iron-modified attapulgite adsorbent (He *et al.* 2013).

The usual adsorption parameters for optimum fluoride removal from water using metal enhanced palygorskite are temperatures of about 323 K, a pH range of 3.7–7.5 and equilibration time of about 110 minutes (Zhang *et al.* 2009). The pH range of optimum fluoride removal from water using attapulgites shows that the adsorbent surfaces are relatively stable in acidic media and that fluoride uptake by the adsorbent is liable to OH⁻ anionic interference under alkaline conditions. As would be expected, the phosphate, sulphate and carbonate ions are the major interferent ions in water defluoridation using cation-exchanged palygorskite. It has been shown, however, that the cation-exchanged attapulgite can be regenerated for up to 6–10 cycles of reuse by treatment in strong alkalis or by calcination at high temperature (Zhang *et al.* 2009, 2012a; Feng *et al.* 2012; He *et al.* 2013). Nevertheless, like montmorillonites, palygorskite clays are not well distributed globally and their current use as bleaches for edible oils processing clearly surpasses the desire to apply them to water defluoridation (Murray 2007).

Zeolites

Zeolites belong to the tectosilicate class of clay minerals consisting of a continuous framework of silicate tetrahedral units, SiO₄⁴⁻, each sharing all the four oxygen atoms at the vertices (Bohn *et al.* 2001). Like the other aluminosilicate minerals, zeolites have frequently been studied for water defluoridation (Payne & Abdel-Fattah 2004; Onyango *et al.* 2010, 2004). However, natural zeolites typically have limited fluoride uptake capacities of just 0.36–0.54 mg/g because they possess a negative intrinsic zeta potential over their mineral surfaces in a wider pH range of values (Teutli-Sequeira *et al.* 2013). The negative potential of the zeolite surfaces can however be reversed by impregnating the zeolite structure with multivalent metal cations or a combination of cations such as with Al³⁺ (Xu *et al.* 2000; Onyango & Matsuda 2006), Al³⁺ and La³⁺ (Onyango *et al.* 2004), Na⁺, Ca²⁺, La³⁺ and Eu³⁺ (Díaz-Nava *et al.* 2002), Al³⁺, La³⁺ and ZrO²⁺ (Samatya *et al.* 2007), and Fe³⁺ (Sun *et al.* 2011) so as to improve the anionic adsorption capacities of the mineral. The capacity of common metal cations to enhance the DCs of zeolite surfaces decrease in the order:

ZrO²⁺ > Eu³⁺ > La³⁺ > Al³⁺ > Fe³⁺ > untreated zeolites > Ca²⁺ ≈ Na⁺ (Díaz-Nava *et al.* 2002; Onyango *et al.* 2004).

Fluoride adsorption onto metal-exchanged zeolites occurs rapidly over the exposed adsorbent surface in the first 15 minutes. It then follows a gradual diffusion of the fluoride particles into the inner-core adsorptive sites of the porous zeolite structure, and the time required for attainment of the final equilibrium is about 24 hours (Díaz-Nava *et al.* 2002; Samatya *et al.* 2007). The reaction of fluoride with zeolites surfaces is relatively independent of changes in pH, and high fluoride adsorption using metal-exchanged zeolites is normally achieved over the entire pH range of 4–10. In the same way, fluoride adsorption onto zeolites is not strongly affected by the presence of co-ions such as the Cl⁻, NO₃⁻, SO₄²⁻ and CH₃COO⁻ ions (Xu *et al.* 2000). It shows that zeolite adsorbents are stable and they can, therefore, be used to sorb fluoride from water over a wide range of water conditions.

The typical DCs of modified zeolite adsorbents are in the range of 2.3–4.5 mg/g (Xu *et al.* 2000; Samatya *et al.* 2007; Sun *et al.* 2011). This is, however, contrary to the remarkably high DCs of 39.58 mg/g and 54.28 mg/g that

were reported by Onyango *et al.* (2004) for Al^{3+} - and La^{3+} -intercalated zeolite adsorbents, respectively. The low DCs that characterise zeolite adsorbents show that high amounts of adsorbent are required to treat substantial amounts of water, inevitably resulting in high volumes of undesirable fluoride-laden zeolite sludge. For environmental considerations, zeolites do not, therefore, present the prospective adsorbents desired for easy defluoridation of household water.

Ceramics and mixed mud adsorbents

Fluoride adsorption onto ceramic adsorbents has been studied by Yadav *et al.* (2006) and Chen *et al.* (2010a, b) among others. The adsorbents derived from ceramic products normally depict limited DCs in the range of 0.989–2.157 mg/g, and the highest fluoride removal from water using the ceramic adsorbents is achieved at pH values of 6.9–8.0 and temperatures of 298–303 K. The time for attainment of equilibrium is about 60 minutes for brick powder (Yadav *et al.* 2006) and 48 hours for granular ceramic adsorbent (Chen *et al.* 2010b). The equilibrium fluoride adsorption data for the two ceramic adsorbents could be described by both the Langmuir and the Freundlich isotherms, which reflected surface heterogeneity in the clay surfaces of the adsorbents. The time-dependent fluoride uptake by granular ceramics was consistent with the pseudo-second order kinetics model. It indicated that surface reactions were the rate-determining step in fluoride uptake by the adsorbent (Chen *et al.* 2010b). However, the fluoride adsorption data for brick powder could be fitted by both the Lagergren kinetics and intraparticle diffusion models, indicating that surface adsorption as well as intraparticle diffusion contributed to the rate-determining step (Yadav *et al.* 2006).

In related work, a number of workers have investigated adsorption of fluoride on red soil (Zhu *et al.* 2007), zirconium oxide-modified sintered mud (Lv *et al.* 2013) and waste mud (Kemer *et al.* 2009). Both the sintered mud and red soil of China had a very low DC of 0.6 mg/g and 2.1218 mg/g, respectively. However, the waste mud obtained from a Cu–Zn mine-industry in Turkey showed a high DC of 27.2 mg/g. The pH, temperature and contact time for fluoride uptake by waste mud and the red soil of China were 5.5–6, 30–60 minutes and 298–303 K,

respectively. The equilibrium adsorption data for the red soil (Zhu *et al.* 2007), modified sintered mud (Lv *et al.* 2013) and waste mud from mine industries (Kemer *et al.* 2009) were fitted by the Freundlich isotherm, indicating that physisorption was the preferred adsorption mechanism for fluoride immobilization into these adsorbents. However, the equilibrium data for sintered mud and red soil could also be fitted by the Langmuir isotherm, indicating heterogeneity in the sorptive surfaces of the adsorbents. Both fluoride adsorption onto the waste mud and onto sintered mud could be described by a pseudo-second-order rate kinetics model, and the data for sintered mud was also correlated by pore diffusion models.

Oxide minerals

The major groups of oxide minerals of interest to water defluoridation include Al- (Vithanage *et al.* 2014), Fe- (Huang *et al.* 2011), Mn- (Sivasankar *et al.* 2011), Ti- (Das *et al.* 2005) and other trace metal hydr(oxides) (Chang *et al.* 2011).

Aluminium-based oxides minerals

The Al oxide minerals of greatest interest to water defluoridation studies include: bauxite (Das *et al.* 2005), boehmite (Jiménez-Becerril *et al.* 2011) and gibbsite (Vithanage *et al.* 2014).

Bauxite

Bauxite is a laterite mineral formed from intense weathering process under oxidizing conditions. It is one of the most widely distributed aluminium hydr(oxide) minerals among the humid tropical climates of the world. Rather than being a pure mineral, bauxite is, in fact, an assembly of aluminium (hydr)oxide minerals, which include: gibbsite, $\text{Al}(\text{OH})_3$; boehmite, $\text{AlO}(\text{OH})$ and diaspore, HAIO_2 , alongside clays, silt and iron (hydr)oxide minerals. Examples of bauxite minerals that have attracted the highest research interest in water defluoridation studies, especially in the recent past, include: refractory grade bauxite (Das *et al.* 2005), titania rich bauxite (Sujana & Anand 2010), mixed Fe/Al hydroxides (Sujana & Anand 2011), reddish brown bauxite

(Lavecchia *et al.* 2012), high alumina bauxite (Mohapatra *et al.* 2004) and calcined bauxite (Thole *et al.* 2012).

Fluoride adsorption onto bauxite involves stoichiometric interactions of fluoride ions with Al^{3+} and other cationic centres in the bauxite mineral structure. Water defluoridation using bauxite is, as a result, favoured by conditions that enhance the formation of free F^- ions in water. For this reason, the highest fluoride adsorption using bauxite occurs in acidic media of pH range of 5.5–6.5 (Sujana *et al.* 1998; Das *et al.* 2005), which coincides with the pH values of highest concentration of F^- ions in aqueous phase of fluoride solutions at room temperatures. Fluoride adsorption onto bauxite is therefore relatively independent of co-ions including the NO_3^- , NO_2^- , Cl^- and SO_4^{2-} (Das *et al.* 2005). It has been shown that the efficacies of bauxite adsorbents to remove fluoride from water decrease with increasing temperature (Sujana *et al.* 1998; Mohapatra *et al.* 2004), which shows that fluoride adsorption onto bauxite surfaces could be exothermic in nature. As for zeolites, the rates of fluoride adsorption onto bauxite surfaces are characterized by initial rapid phases in the first 5 minutes followed by a gradual approach to the adsorption equilibrium after about 120 minutes.

Ordinarily, the DCs of bauxite adsorbents average 3.1–5.2 mg/g (Coetzee *et al.* 2004; Onyango & Matsuda 2006; Thole *et al.* 2012). However, these bauxite DCs have been shown to increase with decreasing particle size of the adsorbents and the outstanding DC of 170 mg/g, reported by Farrah *et al.* (1987) for the mineral may relate to the small particle sizes of gibbsite minerals, which are primary mineral constituents in the bauxite samples.

Boehmite

Boehmite is another Al-based hydr(oxide) mineral that has attracted the highest research interest for water defluoridation lately. The adsorption capacities of boehmite are about 2.057 mg/g and, like for bauxite, the highest DCs for boehmite occur in pH values of 4.5–7.5. Unlike for bauxite, however, fluoride uptake by boehmite is slow and it may extend up to 24 hours before the equilibrium is established. The equilibrium adsorption data for fluoride adsorption onto boehmite is fitted by both Langmuir and Freundlich isotherms, which indicates a heterogeneous mineral surface. The adsorption kinetics data have, however, been described

by the pseudo-second-order model, which is consistent with chemisorption reactions (Jiménez-Becerril *et al.* 2011).

Leyva-ramos (2008) has studied fluoride removal from water by adsorption using activated alumina prepared from pseudo-boehmite. The derived adsorbent had DCs of 8.27 mg/g at pH of 4 and temperatures of 298 K. The adsorption data could simultaneously be described by both the Langmuir and the Freundlich isotherms, indicating mixed adsorption mechanisms. On the other hand, Wan *et al.* (2015b) recently reported an outstanding adsorption capacity of 67.5 mg/g for a classical fluoride adsorbent based on pseudoboehmite and chitosan shell magnetic nano-particles (ACMN). The adsorbent exhibited optimum DCs in a media of pH of 7.0 ± 0.1 at 293 K temperature. The fluoride adsorption onto ACMN was, however, rapid and more than 80% fluoride adsorption could be achieved in the initial 20 minutes but the time required for attainment of the final equilibrium was 60 minutes.

Typically, Al-based adsorbents are among the most studied mineral adsorbents for water defluoridation because they generally have high affinities for fluoride ions, and they are among the most abundant minerals, especially in the humid tropical climates. Nonetheless, Al-based oxide minerals do not exhibit the highest DCs and they have a narrow sorption edge in the pH range of 5.5–6.5. For this reason, as for the montmorillonite clays, Al-oxides minerals tend to solubilize into $[\text{AlF}_x]^{(-x+3)}$ complexes in strongly acidic media and their DCs are diminished by OH^- ions in alkaline media.

Iron oxide minerals

Ferric hydr(oxide) minerals are also among the most extensively studied materials for water defluoridation (Bhatnagar *et al.* 2011). Fluoride removal from water has been evaluated for laterites (Goromo *et al.* 2012), haematite (Hiemstra & Riemsdijk 2000; Tang *et al.* 2010), goethite (Hiemstra & Riemsdijk 2000; Mohapatra *et al.* 2009b) and ferrihydrite (Sujana *et al.* 2009a) minerals among other Ferric hydr(oxide) minerals.

Laterites

The DCs of natural laterites are in the bracket of 12.0–15.0 mg/g (Maiti *et al.* 2011; Wambu *et al.* 2012) but several studies

have demonstrated improved DCs for laterite adsorbents by modification of laterite surfaces using acid-base treatment and calcination at high temperatures. However, the acid-base activated laterites (Maiti *et al.* 2011) have greater DCs of 36.3–39.1 mg/g compared to the DCs (12.0–20.0 mg/g) of thermally activated laterite adsorbents (Huang *et al.* 2011). Nonetheless, the fluoride adsorption of thermally activated laterites is concentration-dependent, whereas that of acid-base activated laterites is temperature-dependent (Maiti *et al.* 2011). As expected for a mixed mineral adsorbent, fluoride adsorption onto laterite adsorbents exhibit mixed reaction mechanisms, and the equilibrium fluoride adsorption for laterites conform simultaneously to Langmuir and Freundlich isotherms (Teutli-Sequeira *et al.* 2011). The DCs of laterites are, however, strongly affected by the presence of co-ions and the reduction in the fluoride adsorption in the presence of common anions is of the order: $\text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^-$ (Huang *et al.* 2011).

Even so, laterites are, generally, among the most promising low-cost adsorbents for water defluoridation because they have high DCs, and they are readily available and usable in a wide range of water conditions (Mohapatra *et al.* 2009a, 2009b).

Haematite

Haematite and goethite are the chief constituent minerals of laterites. Fluoride adsorption onto pure haematite (Teutli-Sequeira *et al.* 2011) and onto pure goethites (Hiemstra *et al.* 2000) has also been investigated. Available data show that fluoride adsorption onto haematite is independent of the solution pH and temperature. As a result, high DCs are achieved by adsorption using haematite over a wide pH range of 2–7 and temperature of 298–232 K (Teutli-Sequeira *et al.* 2011; Mohapatra *et al.* 2012b). The process is, however, slow and the time required for attainment of equilibrium is about 48 hours.

Goethite

Unlike haematite, fluoride adsorption onto goethite is strongly pH and concentration dependent. Hiemstra & Riemsdijk (2000) have indicated that fluoride adsorption at goethite is based on the exchange of adsorbate fluoride

particles against OH(H) of singly coordinated surface goethite groups at low and intermediate concentrations. At high fluoride concentrations, doubly coordinated OH groups get involved and fluoride precipitation then takes place when the fluoride concentrations are very high, especially in acidic pH of the media.

Tang *et al.* (2010) have therefore, indicated that the most efficient fluoride adsorption using goethite takes place in acidic media of pH values about 4, and the initial equilibrium is attainable in about 240 minutes. These results appeared to contradict those of Mohapatra *et al.* (2009b) who investigated fluoride adsorption onto synthetic goethite and reported that maximum fluoride removal, based on the synthetic samples of goethite, passed through broad maxima in a pH range of 6–8, and the time and temperature requirements for initial equilibrium to be established was about 120 minutes and 303 K, respectively. As for the natural goethite samples (Tang *et al.* 2010), however, the kinetic data of fluoride adsorption onto the synthetic goethite adsorbent was fitted by the pseudo-second-order kinetic model with R^2 values of 0.982. Similarly, the adsorption equilibrium data for synthetic nano-goethite powder was described by the Freundlich isotherm, which showed that surface reactions between fluoride particles and the goethite mineral surfaces were reversible and that physisorption was the dominant mechanism.

Ferrihydrite

Ferrihydrite is another class of iron-based minerals that continues to attract increased research attention for water defluoridation at the moment. Wei & Xiang (2012), for example, have recently studied fluoride adsorption onto ferrihydrite and kaolinite-ferrihydrite associations. The maximum DCs for the two adsorbents were found to be 20.20 mg/g and 12.82 mg/g, respectively, and optimum fluoride adsorption using the two adsorbents could be achieved in near-neutral pH values of 6.2–8.0. The equilibrium fluoride adsorption data for the adsorbent samples were simultaneously fitted by one-site Langmuir ($R^2 = 0.981$) and two-site Langmuir ($R^2 = 0.992$) models. In addition, the Freundlich model could also be fitted for the KF sample ($R^2 = 0.975$), which was consistent with the mixed surfaces in the composite adsorbent. It indicated

that chemisorption was the principal mechanism in fluoride adsorption on pure ferrihydrite samples.

In related work, Mohapatra *et al.* (2012a) reported an excellent DC of 64 mg/g for Mg-doped ferrihydrite and in one of the most recent studies, Jia *et al.* (2015) have reported an outstanding DC of 123.03 mg/g for a 2-line ferrihydrite/bayerite composite (LFBC). The maximum fluoride uptake by both Mg-doped ferrihydrite (Mohapatra *et al.* 2012a) and LFBC (Jia *et al.* 2015) occurred in neutral pH values of 7.0. The equilibrium data for fluoride adsorption onto LFBC could be fitted by both the Langmuir and Freundlich models, indicating mixed adsorbent surfaces in LFBC. However, the fluoride adsorption onto Mg-doped ferrihydrite could only be fitted by the Langmuir isotherm. This shows that intercalation of the mineral with Mg^{2+} ions increases the specific Langmuir adsorption sites in the adsorbent (Mohapatra *et al.* 2012a). However, as for the ferrihydrite/kaolinite association, which was studied by Wei & Xiang (2012), fluoride adsorption onto a ferrihydrite/bayerite composite was based on mixed reaction mechanisms as expected for a heterogeneous mineral adsorbent.

Siderite

Shan & Guo (2013) have studied modification of natural siderite fluoride adsorbents with aluminium sulphate and aluminium sol. The optimally modified natural siderite (OMNS) was obtained at the siderite: $\text{Al}_2(\text{SO}_4)_3$:AlOOH mass ratio (g) of 50:0.3:10, which was then calcinated at 450 °C for 3 hours. The solution pH did not strongly control fluoride adsorption onto OMNS, and high DCs using the modified adsorbents could be achievable in a wide range of solution pH values of 3.5–10.0. However, fluoride adsorption onto OMNS was obviously constrained by the coexistence of HCO_3^- and PO_4^{3-} . The time-dependent fluoride adsorption data for OMNS was fitted by the pseudo-second-order kinetics equation, which indicated that surface reactions were the rate determining step.

The feasibility of synthetic siderite to sorb fluoride from water has also been investigated by Liu *et al.* (2010b). The batch fluoride adsorption capacity of synthetic siderite was 1.775 mg/g at 298 K. The fluoride uptake of synthetic siderite, like that of OMNS, was independent of solution pH,

and high amounts of fluoride could be sorbed from water over the entire pH range of 4–9. The DC of the adsorbent was significantly reduced in the presence of the PO_4^{3-} and the SO_4^{2-} ions, but the Cl^- and NO_3^- ions did not significantly affect fluoride adsorption onto the adsorbent.

Other ferric hydr(oxide) minerals

Adsorption characteristics of fluoride onto schwertmannite adsorbent have been studied by Eskandarpour *et al.* (2008). High DCs of 50.2–55.3 mg/g were achieved using the schwertmannite adsorbent over a wide range of temperatures of 296–313 K, which showed that the fluoride uptake by schwertmannite was not strongly controlled by changes in the adsorption temperature. The highest DC for the material was recorded in acidic media of a pH value of 3.8. In binary-component systems, inner-sphere complex-forming species (the PO_4^{3-} and the SO_4^{2-} ions) strongly reduced fluoride adsorption onto schwertmannite, while outer-sphere complex forming species (Cl^- and NO_3^- ions) somehow increased the fluoride removal efficiency of the mineral. The adsorbent could be regenerated in two reuse cycles, which showed that fluoride adsorption onto schwertmannite was a reversible process.

As for schwertmannite, a remarkable DC of 136.98 mg/g was recently reported by Fakhri (2014) for maghemite ($\gamma\text{-Fe}_2\text{O}_3$). The optimized fluoride adsorption temperatures, adsorbent dosage, and pH for maghemite were 313 K, 0.5 g/L, and 4, respectively. The adsorption process was rapid and the adsorption equilibrium could be established in about 30 minutes. The Langmuir isotherm gave a more satisfactory fit for fluoride removal, and the kinetic data could be described by the pseudo-second-order kinetics model.

Calcareous minerals

The term calcareous is used to describe soil samples that are enriched in calcium and magnesium carbonates or soils formed by the weathering of calcium enriched rocks and fossil shell beds (Lagassé *et al.* 2012). Numerous calcareous minerals, including calcite (Turner *et al.* 2005, 2008, 2010), quicklime (Patel *et al.* 2009), marine sediments (El-Said & Draz 2010), limestone (Nath & Dutta 2010), dolomite

(Kang *et al.* 2006; Ayoob *et al.* 2008; Kagne *et al.* 2008), a number of Ca-based cementitious materials (Kagne *et al.* 2008; Ayoob & Gupta 2009) and gypsum (Gopal & Elango 2007) have been investigated for fluoride removal from water in the recent past. Fluoride adsorption onto calcareous minerals occurs over the entire mineral surface with precipitation of fluorite, CaF_2 (Turner *et al.* 2005; Sasaki *et al.* 2013). As expected for surface precipitation, therefore, water defluoridation using calcareous materials is fast and the time required for attainment of the equilibrium is just 30–60 minutes (Patel *et al.* 2009; El-Said & Draz 2010). Defluoridation of water using calcareous materials is, for this reason, controlled by factors that control solubility and the availability of both Ca^{2+} and free F^- ions at the adsorbent-solution interface. The capacity of calcareous minerals to immobilize water fluoride ions as a result increases with increasing temperatures (Yang *et al.* 1999), and it is favoured by acidic media of pH values of 5–6 (Gogoi *et al.* 2015), which correspond to the pH values of the highest F^- ions speciation in aqueous fluoride solutions (Richards *et al.* 2009). It follows that fluoride reactions with calcareous mineral adsorbents is highly pH specific, and it is not normally affected by the presence of interferent anions such as the sulphate, nitrate, and phosphate ions (Turner *et al.* 2010).

Even as Reardon & Wang (2000) reported remarkably high DCs for certain calcareous materials, most recent data (Fan *et al.* 2003; Viswanathan & Meenakshi 2010) indicate that limited fluoride adsorption capacities of about 0.39 mg/g are typical of calcareous mineral adsorbents. Nonetheless, hydrotalcite minerals and the related hydrotalcite-like compounds continue to attract increasingly high research interest in the area of water defluoridation because of their remarkable DCs when compared to those of the other calcareous mineral adsorbents (Hosni & Srasra 2011; Lv *et al.* 2012; Yoon & Kim 2013; Wan *et al.* 2015a). Like typical calcareous mineral adsorbents (El-Said & Draz 2010), the highest DCs for synthetic hydrotalcite-like compounds occur in acid media of pH values 4–6 at temperatures of 298–313 K (Hosni & Srasra 2011; Lv *et al.* 2012; Yoon & Kim 2013). The equilibrium time required for optimum fluoride adsorption onto hydrotalcite materials varies from about 60 minutes (Hosni & Srasra 2011) to as high as 1,440 minutes (Yoon & Kim 2013). The fluoride adsorption equilibrium data for hydrotalcite and

hydrotalcite-like adsorbents, as for most calcareous adsorbents, are fitted by the Langmuir adsorption isotherm, which is consistent with chemical surface precipitation mechanisms (Viswanathan & Meenakshi 2010; Gogoi *et al.* 2015) and the adsorption kinetics data conform to the pseudo-second order kinetics model.

Carbonaceous minerals

Carbonaceous minerals that have attracted the highest research interest for water defluoridation include lignite (Pekař 2008), charfines (Srimurali *et al.* 1998), coke and coal (Sivasamy *et al.* 2001; Borah & Dey 2009;), and fly ash (Xu *et al.* 2011).

Lignite

Fluoride adsorption onto lignite is generally independent of interferent anions, and it occurs optimally over a whole range of pH values of 6–12 at temperatures of about 303 K. The reaction is fast, and more than 90% adsorption is normally completed in the first 10 minutes of the adsorption process. The time required for the attainment of the final equilibrium may, however, extend to 150 minutes (Sivasamy *et al.* 2001; Pekař 2008), indicating the presence of heterogeneous adsorptive surfaces. Although initial studies have revealed very limited DCs for lignite (Srimurali *et al.* 1998), the latest results have reported appreciable DCs of 6.9–17.6 mg/g for the mineral (Pekař 2008).

Charfines

Charfines are a by-product of the process of making coke from lignite. The efficacy of fluoride adsorption using charfines has been reported to be higher than that of lignite (Srimurali *et al.* 1998), but there is a general paucity of data on the use of this adsorbent for water defluoridation and more investigations are desired to document and characterize its effectiveness as a fluoride adsorbent.

Coal

A number of defluoridation studies have been conducted based on coal and coke adsorbents. The water DCs of coal/

coke average 6.9–7.44 mg/g, which corresponds to 80% fluoride removal from water at most fluoride concentrations (Sivasamy *et al.* 2001; Borah & Dey 2009). Water defluoridation using coal occurs in acidic media, and the DC of the mineral decreases with increasing alkalinity of the adsorption media up to a pH value of 7 and it remains constant thereafter. High DCs for coal are, therefore, achievable at room temperature over a wide pH range of 4–10. Furthermore, only a little adsorbent of about 1% (mg/mL) dosage is required. The sorption process is fast, with more than 90% fluoride being sorbed in the initial 10 minutes even though, as for lignite, a more extended contact time of 60–90 minutes is then required before the final equilibrium is attained.

Fly ash

Even though the fluoride adsorption reaction with fly-ash surfaces is fast, the DCs of fly ash are normally low, and complete fluoride removal from water using fly-ash is not usually achieved even at low fluoride concentrations (Mahramanlioglu *et al.* 2002; Chidambaram *et al.* 2003). Meanwhile, Geethamani *et al.* (2013), has reported an enhanced DC of 11.6 mg/g for magnesia loaded fly-ash. Other workers have also reported that magnesia-loaded fly ash cenospheres (MLC) prepared by the wet impregnation method using a magnesium chloride solution have a greater DC of about 6.0 mg/g compared to unmodified fly ash (Xu *et al.* 2012). Like the fluoride uptake by coal, the optimum fluoride adsorption using MLC occurred in acidic media with pH values of about 3.0 and at a temperature of 318 K. The DCs of MLC, however, decreased in the presence of other anions in the order: comprehensive > dihydric phosphate > nitrate > sulphate.

Thus lignite, charfines and coal have significant capacities to sorb fluoride from water, but fly-ash does not normally have an attractive DC for easy defluoridation of water. The optimum fluoride removal using carbonaceous adsorbents is achieved at room temperature, over a pH range of 4–12.

Other soil mineral adsorbents

Pumice

Pumice is a volcanic rock mineral associated with solidified volcanic lava. It contains 60–70% silica and it has

characteristic low density and high porosity, which suits its use as an adsorbent (Mahvi *et al.* 2012). Typically, the DCs of natural pumice are in the range 7.87–13.3 mg/g (Mahvi *et al.* 2012; Salifu *et al.* 2013) but enhanced DCs of 17.83–41.0 mg/g have been reported for functionalized pumice adsorbents (Asgari *et al.* 2012; Sepehr *et al.* 2013). Maximum fluoride adsorption for pumice occurs in the range of natural pH values (6–7) of water at room temperatures (Mahvi *et al.* 2012). The fluoride adsorption onto pumice is rapid, and the time required for attainment of equilibrium is 20–30 minutes (Asgari *et al.* 2012; Mahvi *et al.* 2012).

According to Salifu *et al.* (2013), equilibrium fluoride adsorption data for aluminium oxide coated pumice (AOCP) could be fitted to five different isotherm models in the order: Generalized model > Langmuir type 2 > BET > Temkin > Dubinin–Radushkevich. Similarly, Sepehr *et al.* (2013) have reported that the equilibrium fluoride adsorption data for two pumice samples pre-treated independently with an aqueous solution of magnesium chloride (MGMP) and hydrogen peroxide (HMP) could be described by the Freundlich isotherm. It is observed that the kinetic data for fluoride adsorption onto AOCP (Salifu *et al.* 2013) and onto both MGMP and HMP (Sepehr *et al.* 2013) were consistent with the pseudo-second order kinetics model (Ho 2004), indicating that fluoride adsorption onto pumice is a chemisorption process.

Apatite and hydroxyapatite

Hydroxyapatites (HAPs), $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, are among the adsorbents that have shown the strongest affinities for labile fluoride. According to Aoba (1997), the reaction of soluble fluorides with HAPs is based on fluoride substitution in the apatite structure, which exchanges fluoride ions with OH^- ions in the mineral lattice of HAPs to form fluoroapatite, $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$. This natural exchange between aqueous fluoride and HAPs surfaces takes place in the natural pH range of water (6.0–7.5) over temperatures of 288–308 K (Nie *et al.* 2012). At the moment, HAPs are among the most studied minerals for water defluoridation (Fan *et al.* 2003; Murutu *et al.* 2009; Liang *et al.* 2011; Ma *et al.* 2011; Mourabet *et al.* 2012a, 2012b). However, fluoride uptake by HAPs is very slow and requires 10–24 hours to equilibrate (Murutu *et al.* 2009; Liang *et al.* 2011; Nie *et al.* 2012).

The DCs of natural HAp vary greatly between HAp samples (Fan *et al.* 2003; Murutu *et al.* 2009; Liang *et al.* 2011; Mourabet *et al.* 2012b; Nie *et al.* 2012). The natural DCs of HAp can, however, be enhanced by impregnating the HAp adsorbent with cationic metal particles (Nie *et al.* 2012), grafting HAp surfaces with reactive organic groups (Patankar *et al.* 2013) or by nano-sizing (Wang *et al.* 2011). Nie *et al.* (2012) reported an enhanced DC of 32.57 mg/g for Al(III)-modified HAp and showed that the fluoride adsorption data for the cation-intercalated HAp could be fitted by the Langmuir isotherm. It showed that fluoride adsorption onto the Al(III)-modified HAp was a chemisorption process.

While investigating the adsorption of fluoride from water onto nano-sized hydroxyapatite that had been intercalated with low-molecular-weight organic acids, Wang *et al.* (2011) reported a DC of 7.605 mg/g for the HAp adsorbent. The authors noted that the DC of the adsorbent increased with increasing concentrations of the reactive organic groups in the HAp surfaces. The equilibrium fluoride adsorption data for the 'organo-exchanged' HAp indicated that fluoride adsorption onto the adsorbent surfaces was physisorption in nature. Despite the results of this study, the available data indicate that HAp functionalized with reactive organic groups generally have limited DCs of 1.56–5.6 mg/g (Sairam Sundaram *et al.* 2008, 2009; Patankar *et al.* 2013; Pandi & Viswanathan 2014a, 2014b), which shows that intercalating the HAp with organic molecules does not represent an effective protocol of enhancement of HAp adsorbents for defluoridation of water.

A number of investigators have also studied the efficacy of synthetic HAp in fluoride removal from water. Larsen & Pearce (2002), for instance, developed a fluoride adsorbent by reacting calcite and brushite, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$. Between 70.5 and 98.8% fluoride adsorption could be achieved from distilled water containing 5–20 mg/L fluoride while using this adsorbent. The corresponding percentages of fluoride adsorption from background solutions containing 104 mg/L Ca^{2+} were 61.5–76.0%. Murutu *et al.* (2009) then synthesized a HAp fluoride adsorbent by calcination of limestone at 1073 K and reacting the residues with 50% orthophosphoric acid under controlled conditions at 323 K. MacDonald (2011), on the other hand, was able to prepare HAp fluoride adsorbents by reacting commercial

quicklime, CaO, with controlled amounts of 85–90% phosphoric acid, while Liang *et al.* (2011) prepared a glass-derived hydroxyapatite by etching sodium calcium borate glass using phosphoric acid.

The DCs for synthetic HAp have been found to be in the range of 11.34–22.22 mg/g. Perhaps with the only exception of synthetic HAp samples derived by reacting $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{-EDTA}$ with $\text{NH}_4\text{H}_2\text{PO}_4$, which sorbed high amounts of fluoride in acidic media with a pH value of 2 (Gao *et al.* 2009b), the solution pH (6.0–7.5) and equilibration time (10–24 hours) for optimum fluoride adsorption using synthetic HAp are similar to those for natural HAp (Murutu *et al.* 2009; Liang *et al.* 2011). The efficacies of synthetic HAp to sorb fluoride ordinarily increase with increasing temperatures, indicating endothermic processes. For this reason, while investigating hydroxyapatite nano-particles (nHAp) derived from waste phosphogypsum, Zhang *et al.* (2012b) reported a high DC of 40.818 mg/g for the adsorbent at 328 K. As for naturally derived HAp adsorbents, fluoride adsorption onto synthetic HAp, is not affected by the presence of co-ions such as the SiO_4^{4-} , SO_4^{2-} , Cl^- , CO_3^{2-} , PO_4^{3-} .

In general, HAp are clearly among the most promising fluoride adsorbents; they have high DCs, and they are stable and usable in a broad range of water conditions. Furthermore, HAp are among the most distributed minerals around the world and they can, therefore, easily be procured for use in water defluoridation. However, natural apatite minerals, from which natural HAp could be derived, are ordinarily very hard materials and are therefore difficult to prepare for water defluoridation. In addition, apatite rocks are also associated with the enrichment of natural water systems with labile fluoride (Adelana *et al.* 2010). Intensive preliminary tests are, therefore, requisite to ensure that the would-be adsorbents are free of labile fluoride before they are harvested and processed for water defluoridation.

SURFACE ACTIVATION OF SOIL ADSORBENTS

Natural soil systems ordinarily have low ion-exchange capacities because their surfaces are inherently saturated with replaceable groups which mask and neutralize the

intrinsic surface charge to maintain the surface stability of the soil. The ion-exchange properties of the soil mineral can, however, be enhanced by pre-treatments that dislodge these masking ions from soil surface sites, and unblock the porous structure of the soil systems (Falaras *et al.* 2000; Wu *et al.* 2006). This is important when the soil surfaces possess a net charge that would repel the adsorbate ions, which carry a similar charge to that of the soil surfaces. For anionic adsorption, surface charge reversal for negatively charged soil adsorbents is achieved by impregnating the soil structure with multivalent cations or by hydrothermal activation in dilute acids among other physicochemical treatments. The latter approach is, however, the more popular because it is simpler and more cost-effective (Makhoukhi *et al.* 2009; Frini-Srasra & Srasra 2010). Acid activation of soil adsorbents results in partial de-alumination of the clay structure. This increases the proportion of silica and the density of silanol (Si-OH) groups on the adsorbent surface, and increases the overall acidity and the net positive charge of the clay surface of the soil (Zhu *et al.* 2007).

Owing to a high proportion of electronegative oxygen groups in the soil structure close to the adsorbent surfaces, many soil systems tend to carry a net negative charge, which is unfavourable to fluoride adsorption. In natural systems, this keeps fluoride in the soil solutions, from where it becomes easily available for easy uptake by plants. So as to enhance the potential of the soil adsorbents for fluoride adsorption, the adsorbent soil samples are pre-treated in dilute acid solutions to improve their surface positive charge. The surface charge reversal can then be confirmed by determination of the surface pH and the PZNC of the soil adsorbents by a variety of techniques, which include the alkalimetric analysis of Fiske & Logan (1931).

INFLUENCE OF SOLUTION PARAMETERS

The solution parameters, which include the pH, temperature, adsorbate concentration and adsorbent dosage and co-existent ions, exert the strongest effects on the adsorption processes because of their influence on the surface

chemistry of the soil adsorbents and on the transport of solutes through the bulk solution to the adsorbent surface.

Solution pH

It is observed that the pH is the main parameter that controls fluoride adsorption onto soil adsorbents. It determines the aqueous speciation and reactivity of fluoride in water, and controls the availability of adsorbate fluoride particles and how they move through solution and react with soil surfaces. Moreover, the solution pH also controls ionization of reactive groups at the colloid soil surfaces, and it determines the nature and the density of the overall soil surface charge and the electrochemical adsorption potential at the soil surfaces (Sujana *et al.* 2009a, 2009b; Huang *et al.* 2011; Maiti *et al.* 2011). The solution pH of maximum fluoride adsorption varies with the type of soil. Iron enriched laterites (Sujana *et al.* 2009); kaolinites (Agarwal *et al.* 2002; Meenakshi *et al.* 2008; Weerasooriya *et al.* 1998) and, to a limited extent, certain hydroxyapatites (Gao *et al.* 2009; Wang 2011) have their maximum DC in acidic media, at pH values of 5 or less.

Maximum fluoride adsorption onto montmorillonites (Agarwal *et al.* 2012; Bia *et al.* 2012; Tor 2006), aluminium oxide minerals (Das *et al.* 2005; Vithanage *et al.* 2014), and calcareous minerals (El-Said & Draz 2010; Nath & Dutta 2010) is, however, restricted to pH values of 5–6. Some soil adsorbents, which include: pumice (Asgari *et al.* 2012; Malakootian *et al.* 2011); palygorskites (Zhang *et al.* 2009); and certain ferric oxide minerals such as haematite (Teutli-Sequeira *et al.* 2011; Mohapatra *et al.* 2012b) sorb high amounts of fluoride over an entire range of pH values from 2 to about 8. Still, fluoride adsorption onto zeolites (Xu *et al.* 2000) and onto certain carbonaceous adsorbents such as lignite and coal (Sivasamy *et al.* 2001; Borah & Dey 2009) is pH independent, and the highest fluoride adsorption using these adsorbents is observed over the entire range of pH values from 4 to 12.

The differences in pH of the highest fluoride uptake for various soil systems arise principally from the differences in the surface chemistry, which control the affinity of soil surfaces towards different fluoride species in soil solutions. Soils that have high fluoride adsorption capacities in acidic media of a pH <5 have a higher affinity for molecular

HF species, which are the dominant fluoride species in strongly acidic media. They adsorb by forming continuous hydrogen bonds with electronegative centres in the adsorbent soil surfaces. Certain soils that preferentially sorb fluoride in the pH range of 5–6 have an affinity for F^- species and the mode of fluoride adsorption is mainly complexation with positive metal centres, which include Al^{3+} , Fe^{3+} , and Si^{4+} , among many, in the lattice soil surfaces. It can be assumed that over the entire range of pH values, the soils must then contain surfaces that have a mutual attraction to either of the species.

Temperature

Temperature is another key factor that controls the adsorption equilibrium of fluoride at the soil surfaces because of its influence on the adsorption energy, adsorption kinetics and on the reaction activation energy (Biswas *et al.* 2010a). Higher temperatures enhance the rates of adsorption by enhancing faster solute transport through solution onto the adsorbent surfaces. Very high temperatures may, however, counter the adsorption fluxes from solution and reduce the rates and magnitude of uptake of a particular adsorbate by the adsorbent.

The specific effect of temperature on fluoride adsorption on particular adsorbents is, however, varied. The peak fluoride adsorption by natural montmorillonites (Karthikeyan *et al.* 2005), Fe(III)-modified montmorillonite (Bia *et al.* 2012), pumice (Mahvi *et al.* 2012), and lignite (Sivasamy *et al.* 2001; Pekař 2004) occur at room temperatures of 298 K. The highest fluoride uptake by both aniline- and pyrrole-modified montmorillonites (Karthikeyan *et al.* 2012) as well as by coal (Sivasamy *et al.* 2001; Borah & Dey 2009) are favoured by temperatures of about 303 K. It is found that the fluoride exchange reactions of HAp (Nie *et al.* 2012) and that of certain ferric oxide minerals such as haematite (Teutli-Sequeira *et al.* 2011; Mohapatra *et al.* 2012b) occur over the entire range of temperatures from 298 to 323 K before the magnitude of adsorbent uptake of the solute is affected. Fluoride adsorption onto Mg^{2+} and Al^{3+} (Zhang *et al.* 2009), Fe^{3+} (He *et al.* 2013) and ZrO^{2+} (Zhang *et al.* 2012b) metal ion-loaded palygorskite; synthetic HAp (Zhang *et al.* 2012a); calcareous minerals (Yang *et al.* 1999); and magnesia-loaded fly ash cenospheres (MLC) is favoured by higher

temperatures in the range of 303–323 K. This depicts chemical and endothermic surface reactions.

The efficiency of bauxite to sorb fluoride has however been found to decrease with increasing temperature, indicating the existence of exothermic fluoride immobilization in bauxite surfaces (Sujana *et al.* 1998; Mohapatra *et al.* 2004).

Contact time

The residence time required for attainment of equilibrium in an adsorption process is influenced by the structure of the adsorbent and the nature of the chemical interactions that occur between the adsorbate and the reactive adsorbent sites. Adsorbents with compact crystalline structures and characteristic exposed reactive surface sites tend to have more rapid adsorption rates than porous media with intraparticle surface sites. This is because in the latter case, the adsorbate particles must be transported inside the adsorbent structures by diffusion to access the reactive sites. Thus, fluoride adsorption onto pulverised calcareous minerals occurs over the entire mineral surface with surface precipitation of fluorite, CaF_2 (Patel *et al.* 2009; El-Said & Draz 2010). Water defluoridation using calcareous materials is therefore fast and, as expected for a surface reaction, the equilibrium is attained in 30–60 minutes (Sivasamy *et al.* 2001; Pekař 2008).

In less compact crystalline adsorbents such as lignite, over 90% adsorption is achieved in just 10 minutes. However, it requires up to 150 minutes to saturate the final 10% of less-exposed sites inside the adsorbent (Sivasamy *et al.* 2001; Borah & Dey 2009). Such trends are observed in fluoride adsorption onto coal, but with shorter equilibration periods of 60–90 minutes for the later phase of adsorption (Sivasamy *et al.* 2001; Borah & Dey 2009). Coal is therefore more crystalline and compact, with less porosity than lignite. Equilibration periods required for fluoride adsorption onto pumice are in the range of 20–30 minutes, but they have not been associated with the two-phase adsorption phenomenon, indicating limited porosity in the mineral (Asgari *et al.* 2012; Mahvi 2012). Although some authors have associated fluoride adsorption onto natural montmorillonites with a rapid sorption of just 20–30 minutes (Agarwal *et al.* 2002; Ramdani *et al.* 2010), natural montmorillonites (Karthikeyan *et al.* 2005), Fe(III)-modified montmorillonites (Bia *et al.* 2012), metal ion-loaded palygorskite (Zhang *et al.* 2009) and

certain aluminium oxide minerals (Sujana & Anand 2011) appear to have consistent fluoride adsorption equilibrium time intervals in the range 110–180 minutes. This indicates that these minerals may possess similarity in structural porosities.

As in fluoride adsorption onto calcareous and carbonaceous soil adsorbents, immobilization of fluoride into adsorbent zeolites (Díaz-Nava *et al.* 2002; Samatya *et al.* 2007), hydroxyapatite (Murutu *et al.* 2009; Liang *et al.* 2011; Nie *et al.* 2012), certain aluminium oxide minerals (Teutli-Sequeira *et al.* 2011) and iron oxide minerals (Sujana *et al.* 2009a, 2009b; Huang *et al.* 2011; Maiti *et al.* 2011) are characterized by an initial rapid phase of 10–30 minutes followed by prolongation of fluoride adsorption equilibria to 10–48 hours. The later phase of slow equilibration in this case can be ascribed to high structural porosity in the case of zeolites and to slow valence exchange-type reactions in the case of hydroxyapatite and oxide minerals of aluminium and iron.

Co-existent ions

Natural water systems contain dissolved species of both an organic and inorganic nature. Co-existent ions in water control the adsorption of fluoride by their competitive effect for space in the soil adsorbent surfaces and in the adsorbate flux of ions from the bulk solutions to the adsorbent surface. Co-ions tend to lower the rates and magnitude of adsorption, but the extent of this influence depends on the chemical and geometric dimension, relative concentrations and relative affinities of the individual ions for the adsorbent surface in comparison to the adsorbate ions. The influence of any particular ion, however, varies from adsorbent to adsorbent.

The soil adsorbents whose fluoride uptake is most affected by coexistent anions include iron oxide minerals (Sujana & Mohanty 2010; Huang *et al.* 2011; Maiti *et al.* 2011) and certain carbonaceous mineral adsorbents. The suppression of fluoride immobilization onto ferric oxides in the presence of common anions follows the order: $\text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^-$ (Xu *et al.* 2000). Fluoride adsorption onto zeolites (Xu *et al.* 2000), HAPs (Murutu *et al.* 2009; Liang *et al.* 2011), bauxite (Sujana *et al.* 1998; Das *et al.* 2005) and calcareous mineral adsorbents (Turner *et al.* 2010) is site-specific and selective. It is, therefore, independent of coexisting anions such as chloride, nitrate, sulphate, acetate and phosphate ions.

In general, therefore, the adsorbate concentration, adsorbent dosage, pH, temperature, and the presence of other ions control fluoride sorption processes at the soil surfaces. This influence is ascribed to the effect of these parameters on the surface chemistry of the adsorbents, on the mass transfer processes in the adsorbate solution, and on the characteristics of the electrochemical double layers close to the adsorbents' surfaces. The effect of solution parameters on fluoride adsorption onto particular soil adsorbents must, therefore, be investigated to isolate the most favourable conditions for fluoride removal from water by adsorption using the minerals.

COMPARISON WITH OTHER FLUORIDE ADSORBENTS

A comparison of the fluoride adsorption capacities, DCs, of soil adsorbents with those of other low-cost adsorbents reported in the literature is given in Table 2.

Categories of fluoride adsorbent that have most frequently been studied for water defluoridation include activated alumina, activated carbons, biosorbents and biopolymers, soil minerals and rare earth oxides. The most promising fluoride adsorbents reported in the literature appear to be nanomagnesia, calcined Mg-Al- CO_3 layered double hydroxides, Fe-Al-Ce trimetal oxide, CaO nanoparticles, and activated cerium(IV) oxide/SiMCM-41 adsorbent. However, even though the majority of the soil minerals have shown limited DCs of less than 10 mg/g, approximately 40% of soil adsorbents have shown significant DCs above this value. Comparing the best adsorbents in each category, it can be seen from Table 2 that the adsorption capacities of soil minerals are relatively low when compared with those of the other adsorbents, such as rare earth oxides, calcium oxide modified activated alumina and several nano-sorbents. However, they are higher than those of silica, activated carbons, biosorbents and biopolymers and most of the alumina based adsorbents. In general nano-sized adsorbents showed the highest fluoride adsorption capacities across all the categories of adsorbents. According to Weng *et al.* (2007), differences in the adsorption capacities of adsorbents are caused in part by variation in properties of the adsorbents such as the specific

Table 2 | Fluoride adsorption capacities of various adsorbents

Adsorbent	Type	Adsorption capacity (mg/g)	Reference
Calcium oxide modified activated alumina	alumina	101.01	Camacho <i>et al.</i> (2010)
Alum-impregnated activated alumina	alumina	40.68	Tripathy <i>et al.</i> (2006)
Aluminium hydroxide (hydrated alumina), THA	alumina	23.7	Shimelis <i>et al.</i> (2006)
Activated alumina (Al ₂ O ₃)	alumina	16.34	Ku <i>et al.</i> (2011)
Metallurgical-grade alumina	alumina	12.57	Pietrelli (2005)
Manganese oxide modified activated alumina	alumina	10.18	Camacho <i>et al.</i> (2010)
Magnesia- amended activated alumina	alumina	10.12	Maliyekkal <i>et al.</i> (2008)
Chitosan based mesoporous alumina	alumina	8.264	Jagtap <i>et al.</i> (2011)
Copper oxide coated alumina (COCA)	alumina	7.77	Bansiwala <i>et al.</i> (2010)
Hydrous-manganese-oxide coated alumina	alumina	7.09	Teng <i>et al.</i> (2009)
Aluminium hydroxide (hydrated alumina), UHA	alumina	7	Shimelis <i>et al.</i> (2006)
La(III) impregnated alumina	alumina	6.65	Puri & Balani (2000)
Alum sludge	alumina	5.394	Sujana <i>et al.</i> (1998)
Manganese-oxide-coated alumina	alumina	2.851	Maliyekkal <i>et al.</i> (2006)
Alkoxide origin alumina	alumina	2	Kamble <i>et al.</i> (2010)
Commercial activated alumina	alumina	1.73	Thakre <i>et al.</i> (2010a)
Activated alumina (Grade OA-25)	alumina	1.45	Ghorai & Pant (2004)
Conducting polypyrrole	biopolymer	6.37	Karthikeyan <i>et al.</i> (2009b)
Eichhornia crassipes biomass and its carbonized form	biosorbents	0.523–1.54	Sinha <i>et al.</i> (2003)
Glutaraldehyde-crosslinked calcium alginate	biosorbents	73.6	Vijaya <i>et al.</i> (2011)
Zirconium(IV)-impregnated collagen fiber	biosorbents	41.42	Liao & Shi (2005)
Spirogyra IO2	biosorbents	1.272	Mohan <i>et al.</i> (2007)
Fungal biomass (Pleurotus ostreatus 1804)	biosorbents	1.272	Ramanaiah <i>et al.</i> (2007)
Various grades of graphite	carbon	0.16–3.13	Karthikeyan & Elango (2008)
Manganese-oxide-coated granular activated carbon	carbon	–	Ma <i>et al.</i> (2009)
Zirconium ion impregnated coconut fiber carbon	carbon	40.016	Sathish <i>et al.</i> (2008)
Al ₂ O ₃ /CNTs	carbon	28.7	Li <i>et al.</i> (2001)
Aluminium impregnated hierarchical web of carbon fibres	carbon	17	Gupta <i>et al.</i> (2009)
Zirconium ion impregnated coconut shell carbon	carbon	6.41	Taylor <i>et al.</i> (2007)
Aligned carbon nanotubes (CNTs)	carbon	4.5	Li <i>et al.</i> (2003)
Waste carbon slurry	carbon	4.306	Gupta <i>et al.</i> (2007)
Zirconium(IV) tungstophosphate/chitosan composite	chitosan	2.025–2.142	Viswanathan & Meenakshi (2010a)
Chitosan coated silica	Silica	44.4	Vijaya & Krishnaiah (2009)
Magnetic-chitosan particles	chitosan	22.49	Ma <i>et al.</i> (2007)
Neodymium-modified chitosan	chitosan	22.38	Yao <i>et al.</i> (2009)
Titanium/chitosan adsorbent	chitosan	7.2	Jagtap <i>et al.</i> (2009)
La(III) incorporated carboxylated chitosan beads	chitosan	4.711	Viswanathan & Meenakshi (2008a)

(Continued)

Table 2 | Continued

Adsorbent	Type	Adsorption capacity (mg/g)	Reference
Lanthanum incorporated chitosan beads	chitosan	4.7	Bansiwal <i>et al.</i> (2009)
La-incorporated chitosan beads (10 wt% La)	chitosan	4.7	Thakre <i>et al.</i> (2010a)
Magnesia/chitosan composite	chitosan	4.44	Sundaram <i>et al.</i> (2009a)
Fe(III) loaded carboxylated chitosan beads	chitosan	4.23	Viswanathan & Meenakshi (2008b)
Alumina/chitosan composite	chitosan	3.809	Viswanathan & Meenakshi (2010c)
Chitosan based mesoporous Ti-Al binary metal oxide supported beads	chitosan	2.22	Thakre <i>et al.</i> (2010b)
Aluminium impregnated chitosan	chitosan	1.73	Swain <i>et al.</i> (2009)
Hydrotalcite/chitosan composites	chitosan	1.255	Viswanathan & Meenakshi (2010b)
Nanomagnesia	nano-soil	267.82	Maliyekkal <i>et al.</i> (2010)
CaO Nanoparticles	nano-soil	163.3	Patel <i>et al.</i> (2009)
Fe ₃ O ₄ @Al(OH) ₃ NPs	nano-soil	88.48	Zhao <i>et al.</i> (2010)
Nano-alumina	alumina	14	Kumar <i>et al.</i> (2011)
Fe-Al-Ce trimetal oxide	oxides	178	Wu <i>et al.</i> (2007)
Activated cerium(IV) oxide/SiMCM-41 adsorbent	oxides	114.38	Xu <i>et al.</i> (2001)
Fe-Al mixed hydroxide (Molar ratio:1)	oxides	91.7	Sujana <i>et al.</i> (2009b)
Al-Ce hybrid adsorbent	oxides	91.4	Liu <i>et al.</i> (2010a)
Magnetic alumina sol-gel (MASG) adsorbent	oxides	38	Chang <i>et al.</i> (2006)
Hydrated iron(III)-aluminium(III)-chromium(II) ternary mixed oxide	oxides	31.89	Biswas <i>et al.</i> (2010b)
Magnesia-amended silicon dioxide granules	oxides	12.6	Zhu <i>et al.</i> (2009)
Iron(III)-tin(IV) mixed oxide	oxides	10.47	Biswas <i>et al.</i> (2009)
Zirconium-iron oxide	oxides	9.8	Dou <i>et al.</i> (2011)
Magnetic alumina homogeneous precipitation (MAHP) adsorbent	oxides	8	Chang <i>et al.</i> (2006)
Granular ferric hydroxide (GFH)	oxides	7	Kumar <i>et al.</i> (2009)
Fe-Al-Ce nano-adsorbent	oxides	2.22	Chen <i>et al.</i> (2009)
Synthetic siderite	oxides	1.775	Liu <i>et al.</i> (2010b)
Bismuth aluminate (BA)	salts	7.09	Karthikeyan & Elango (2009)
Aluminium titanate (AT)	salts	3.01	Karthikeyan & Elango (2009)
Clay minerals	soil	69.44–93.45	Hamdi & Srasra (2007)
Lignite (LN)	soil	6.9–7.44	Sivasamy <i>et al.</i> (2001)
Schwertmannite	soil	50.2–55.3	Eskandarpour <i>et al.</i> (2008)
Activated titanium rich bauxite	soil	3.70–4.13	Das <i>et al.</i> (2005)
Zeolite F-9	soil	28–41	Onyango <i>et al.</i> (2004)
Al ₃ + pre-treated low-silica synthetic zeolites	soil	28.21–41.35	Onyango <i>et al.</i> (2006)
Metal ion-loaded natural zeolite	soil	2.04–4.13	Samatya <i>et al.</i> (2007)

(Continued)

Table 2 | Continued

Adsorbent	Type	Adsorption capacity (mg/g)	Reference
PPy/Fe ₃ O ₄ nanocomposite	soil	17.6–22.3	Bhaumik <i>et al.</i> (2011)
Geomaterials	soil	12.3–15.17	Sujana <i>et al.</i> (2009a)
Synthetic hydroxyapatite	soil	0.295–0.489	Gao <i>et al.</i> (2009b)
Calcined Mg-Al-CO ₃ layered double hydroxides	oxides	213.2	Lv <i>et al.</i> (2006)
aluminium hydroxide impregnated limestone (AILS)	soil	84.03	Jain & Jayaram (2009)
Nano-geothite	soil	59	Mohapatra <i>et al.</i> (2004)
Limestone (LS)	soil	43.1	Islam & Patel (2007)
Modified attapulgite	soil	41.5	Zhang <i>et al.</i> (2009)
Hardened alumina cement granules (ALC)	soil	34.36	Ayoob & Gupta (2008)
Precipitated mud	soil	27.2	Kemer <i>et al.</i> (2009)
Glass derived hydroxyapatite G-Haps	soil	17.34	Liang <i>et al.</i> (2011)
Quicklime	soil	16.67	Islam & Patel (2007)
KMnO ₄ modified carbon	soil	15.9	Daifullah <i>et al.</i> (2007)
calcined Zn/Al hydrotalcite like compounds (HTlc)	soil	13.43	Das <i>et al.</i> (2003)
Granular ceramic	soil	12.12	Chen <i>et al.</i> (2010b)
Acid–base raw laterite (TL)	soil	11.8	Maiti <i>et al.</i> (2011)
Acid treated spent bleaching earth	soil	7.752	Mahramanlioglu <i>et al.</i> (2002)
Treated biogenic apatite	soil	6.849	Gao <i>et al.</i> (2009a)
Magnesia-loaded fly ash cenosphers (MLC)	soil	6	Xu <i>et al.</i> (2011)
Lightweight concrete	soil	5.15	Oguz (2007)
Biogenic apatite	soil	4.99	Gao <i>et al.</i> (2009a)
Synthetic nano-hydroxyapatite	soil	4.575	Gao <i>et al.</i> (2009b)
Hydroxyapatite	soil	4.54	Fan <i>et al.</i> (2003)
Chemically modified bentonite clay (10% La-bentonite)	soil	4.24	Kamble <i>et al.</i> (2009)
Original waste mud	soil	4.2	Kemer <i>et al.</i> (2009)
nano-AlOOH	soil	3.259	Wang <i>et al.</i> (2009)
Nano-hydroxyapatite/chitin composite	soil	2.84	Sundaram <i>et al.</i> (2009b)
Acid-activated mud	soil	2.8	Kemer <i>et al.</i> (2009)
Hydrated cement	soil	2.6788	Kagne <i>et al.</i> (2008)
Magnesium incorporated bentonite clay	soil	2.26	Thakre <i>et al.</i> (2010c)
Magnesia	soil	2.175	Sundaram <i>et al.</i> (2009a)
Fluorspar	soil	1.79	Fan <i>et al.</i> (2003)
Al and Fe dispersed in porous granular ceramics	soil	1.79	Chen <i>et al.</i> (2011b)
Calcium chloride modified natural zeolite	soil	1.766	Zhang <i>et al.</i> (2011)
Montmorillonite clay	soil	1.485	Karthikeyan <i>et al.</i> (2005)
Algerian montmorillonite clays (with calcium)	soil	1.324	Ramdani <i>et al.</i> (2010)
nano-hydroxyapatite	soil	1.296	Sundaram <i>et al.</i> (2009b)
Nickel calcined Hydrotalcite-like Compounds, NiCHT	soil	1.202	Ez <i>et al.</i> (2007)
magnesium calcined Hydrotalcite-like Compounds, MgCHT	soil	1.185	Ez <i>et al.</i> (2007)

(Continued)

Table 2 | Continued

Adsorbent	Type	Adsorption capacity (mg/g)	Reference
Activated quartz	soil	1.16	Fan <i>et al.</i> (2003)
Hydrotalcite	soil	1.03	Viswanathan & Meenakshi (2010b)
Algerian montmorillonite clays (without calcium)	soil	1.013	Ramdani <i>et al.</i> (2010)
Laterite	soil	0.8461	Sarkar <i>et al.</i> (2006)
Cobalt calcined hydrotalcite-like Compounds, CoCHT	soil	0.842	Ez <i>et al.</i> (2007)
Calcite	soil	0.39	Fan <i>et al.</i> (2003)
Montmorillonite	soil	0.263	Tor (2006)
Bleaching powder	soil	0.1308	Kagne <i>et al.</i> (2009)
Acid activated kaolinite clay	soil	0.045	Gogoi & Baruah (2008)
Geogenic apatite	soil	0.014	Gao <i>et al.</i> (2009a)
Fired clay chips	soil	0.2	Moges <i>et al.</i> (1996)
Al ³⁺ -exchanged zeolite F-9	soil	39.52	Onyango <i>et al.</i> (2004)
La ³⁺ -exchanged zeolite F-9	soil	54.28	Onyango <i>et al.</i> (2004)
Basic oxygen furnace slag	waste	4.58–8.07	Islam & Patel (2011)
Quartz	soil	0.19	Fan <i>et al.</i> (2003)

surface area, structural chemistry, and density of surface reactive groups, besides the influence of solution parameters such as pH, temperature, concentration, and the presence of competing species in solution.

Clearly, the current work indicates that soil adsorbents are the most promising media for isolation of the robust adsorbents desired for easy treatment of high-fluoride water. This is because soil minerals generally have better sorptive DCs than most of the other categories of adsorbents including alumina-based adsorbents, activated carbons, biosorbents and biopolymers and they are chemically stable, simple to prepare and usable in wider water conditions. In addition, the current literature shows that soil adsorbents can more easily be regenerated over several cycles of reuse, and they are generally available and cheaply obtainable in large quantities from abundant natural resources.

CONCLUSIONS

In general the choice of a soil adsorbent for treatment of fluoride-contaminated water is controlled chiefly, among other factors, by the known adsorption capacities of the adsorbent

for fluoride and the related adsorbates. The availability, cost, ease of preparation, simplicity of its application, and potential environmental and health hazards are the other factors that dictate suitability of an adsorbent for defluoridation of drinkable water. Based on approximate mean DCs, which have been reported in the literature, palygorskite (~57 mg/g), pumice (~18 mg/g), zeolites (~16 mg/g), hydroxyapatite (~13 mg/g), iron-enriched laterites (~9 mg/g), bauxite (~8 mg/g) and montmorillonites (~5 mg/g) appear to be the most promising clay-based sorbents for water defluoridation. The other minerals, including kaolinites, ceramics, quartz, red soils, fluorspar, calcite and sordic soil have mean DCs of less than 3.0 mg/g and do not present very prospective sorbents for water defluoridation.

Certain potential adsorbents, which include palygorskite, pumice and montmorillonites, are not well distributed and could be difficult to procure for easy use in water defluoridation. Most distributed minerals in the humid tropical climates where high fluoride water is rampant include, laterites, hydroxyapatite, and silicate clays. The silicates and lateritic minerals are also the easiest to prepare and they are environmentally passive. This makes them first choice geomaterials for water defluoridation, especially

among the developing countries within the tropics. On the other hand, despite its exceptional DC and large abundance in nature, natural apatite is among the hardest natural materials (Levy et al. 2008) and is difficult to pulverize to usable forms for easy water defluoridation.

At the moment, the rare earth oxides and various nano-sized adsorbents appear to have the highest water DCs. However, the current work reveals that the soil adsorbents could be the most promising media for isolation, processing and fabrication of robust adsorbents for the treatment of fluoride contaminated water. On the whole, the soil adsorbents have higher DCs than most of the other categories of adsorbents including most alumina based adsorbents, activated carbons, biosorbents and biopolymers. They are stable, simple to prepare and use and they could be regenerated over several cycles of reuse not to mention that they are among, if not the cheapest materials to procure due to their ready availability in large quantities in nature.

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