Chemical Engineering Journal 241 (2014) 443–456

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Review

Interaction of anionic pollutants with Al-based adsorbents in aqueous media – A review

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HIGHLIGHTS

- Different Al-mineral adsorbents have been reviewed for anions adsorption.
- Mechanisms of anions adsorption on Al-minerals are also discussed.
- Effect of experimental conditions on anions removal by Al-adsorbents is discussed.

ARTICLE INFO

Article history:
Received 1 August 2013
Received in revised form 15 October 2013
Accepted 17 October 2013
Available online 1 November 2013

Keywords:
Adsorption
Anionic pollutants
Aluminum minerals
Adsorption mechanism
Review

ABSTRACT

Many anionic pollutants (e.g., fluoride, nitrate and nitrite, bromate, phosphate, arsenate and arsenite, selenate and selenite, perchlorate) have been detected in surface and groundwater in different parts of the world and strict measures are being taken to minimize their concentrations and to control their mobility in aqueous media. Mineral surfaces, in general, have shown enhanced uptake of many anionic pollutants. Various phases of aluminum (Al) oxides, hydroxides and oxyhydroxide are increasingly being employed as adsorbents for the detoxification of water and wastewater contaminated with anionic pollutants. Understanding the structural properties and morphology of adsorbents is important in order to gain knowledge about the governing mechanism behind the adsorption of anions by these adsorbents. The adsorption ability of aluminum oxides, hydroxides and oxyhydroxide depends on several key factors including properties of the adsorbent (surface area, pore size, pH_{pzc}, porosity) and that of the adsorbates. This paper provides an overview of the physical and chemical properties of various aluminum oxides, hydroxides and oxyhydroxides and their application in water and wastewater treatment with the focus on the removal of anionic pollutants. Furthermore, the performance of these minerals and that of the synthetically prepared hybrid adsorbents (containing Al-minerals) for the adsorption of various anions has been reviewed with an emphasis on the behavior of adsorbent-water interface in presence of the anionic pollutants.

Contents

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http://dx.doi.org/10.1016/j.cej.2013.10.065

1. Introduction

Water is the prime necessity of life but due to the overuse of the natural water resources and increasing pollution of surface and groundwater due to anthropogenic activities, the world's supply of drinkable water is decreasing at an alarming rate. More than one-third of the Earth's accessible renewable freshwater is used for agricultural, industrial, and domestic activities leading to water contamination with numerous synthetic and geogenic compounds in varying concentrations. Although most of these compounds are present at low concentrations, many of them raise considerable toxicological concerns, particularly when present as components of complex mixtures. The international and national environmental protection agencies including United States Environmental Protection Agency (US EPA) and World Health Organization (WHO) have repeatedly established permissible limits for hazardous and emerging contaminants in the past few decades to control the quality of drinking water. In view of the aforesaid problems, research has been focused on the development of effective, low-cost and robust technology for water treatment for several decades now. One of the major classes of aquatic pollutants that have spread in global waters and cause large-scale health and environmental problems is the anionic pollutants. Nitrate, fluoride, phosphate, perchlorate, bromate and arsenate are some of the major anionic pollutants that have been found responsible in contaminating the water resources. Some of them may be present simultaneously in contaminated water. Potentially harmful concentrations of these anions have been found in numerous drinking water sources [1–3] leading to the severe health related problems in human beings. Many of these anions are present in water in trace levels, but some of them may remain undetected, thus increasing the possible health risks. As compared to the removal of other aquatic pollutants (e.g. metals, organic pollutants), the removal of anions is often a challenging task due to their physico-chemical properties, which play an important role during their removal from aqueous phase. The internationally accepted standards and guidelines for these anions in drinking water are quiet low (in the range of μg/L to a few mg/L) as proposed by WHO and are revised from time to time. In addition, the European Union and the US EPA have also issued similar health and environmental standards [4,5]. Table 1 lists the current status for potentially toxic inorganic anions and metallic anions, their permissible concentrations in water, along with some information about the main sources of pollution and the potential health risks caused by their ingestion in drinking water.

Various treatment technologies including precipitation, coagulation [6], reverse osmosis [7,8], electrodialysis [9,10], adsorption [7,11] and biological methods [12] have been extensively studied to come up with the best process that is efficient, cost-effective and draws less energy for its operation for the removal of anionic pollutants from water. Among the above mentioned processes, adsorption is one of the widely used processes that have been employed for a wide variety of aquatic pollutants including anions. The adsorption of anions at the solid–liquid interface and its effect on the fate and mobility of anions in the environment is directly controlled by diverse properties of the pollutant and the adsorbent. The mobility of metallic anions also depends on the speciation and complexation with natural organic material [13]. The adsorption of anions onto adsorbents mostly occurs through ligand exchange or by ion-pair formation with positively charged surface sites.

Although extensive research has been made on large number of adsorbents but only four main classes of generic adsorbents has dominated the commercial use of adsorption: activated carbon, zeolites, silica gel, and activated alumina [14]. Among these, activated carbon is a universal adsorbent that has been widely used as an all-purpose adsorbent in water treatment applications since 1930s [15]. Activated carbon is usually prepared from source material, such as coal, coconut shells, lignite, and wood and is a disorganized form of graphite, due to impurities and the method of preparation (activation process). The large micropore and mesopore volumes and the resulting high surface area are the major advantages associated with the activated carbon adsorbents. Although activated carbon has the ability to adsorb diverse types of pollutants (both organic and inorganic pollutants) [16–22], adsorption on activated carbon has not been found to be selective for target pollutants.

Zeolites are also important class of adsorbents that comprise of a broad range of porous crystalline solids [23]. They are based essentially on tetrahedral networks which encompass channels and cavities. Although previously, zeolites were thought to be consisting only of open and fully crosslinked framework structures of corner-sharing SiO_4 and AlO_4 tetrahedra but in recent years extensive isomorphous substitution of framework atoms and numerous structural analogues of aluminosilicate zeolites have also been researched on and used as adsorbents for a range of pollutants [24–26]. Zeolites are capable of undergoing reversible base-exchange reactions and are used as ion-exchange beds in domestic and commercial water purification systems, softening, and other applications. One major disadvantage associated with the use of zeolites as adsorbents is their capital cost.

Silica gel has also been extensively used in the adsorption process but mostly as a desiccant. This quality is due to its relatively weak bonds with water as well as its large pore volume and mesoporosity. The surface hydroxyl groups or silanols (Si–O–H) mainly participate in adsorption process (for water and organic compounds) [14] through hydrogen bonding. Other than the conventional silica gel, ordered mesoporous silicate/aluminosilicate have also been synthesized by various procedures and tested for water treatment process. MCM-41, MCM-48, MCM-41 analogue materials and disordered silica xerogels are the main synthetic silicates among other ordered mesoporous materials that have been commercially used as adsorption media and catalyst [14,27,28]. The major disadvantage with the use of silica adsorbents for water treatment is the associated cost of the adsorbent. Other than the above mentioned adsorbents, there exist several categories of adsorbents that have been investigated for water treatment including several agro-industrial wastes which have been examined for their potential for the removal of anionic pollutants from water and wastewater [11,29–34].

Among different classes of adsorbents, aluminum oxides and hydroxides/oxy-hydroxides are present abundantly as minerals and have been widely used as adsorbents for the removal of various aquatic pollutants. The surface structure of these compounds explain their surface chemical behavior to a great extent but environmental conditions also play a major role in affecting their response towards the foreign substance in aqueous media. Activated alumina is one effective aluminum compound that has been categorized by US EPA as the Best Available Technology (BAT) for the removal of various aquatic pollutants including arsenic, fluoride, uranium and selenium. It is highly porous and has