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Review

Using zeolitic adsorbents to cleanup special wastewater streams: A review

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ABSTRACT

Extensive mining, massive urban waste landfills, nuclear accidents and urban runoff discharge huge volume of special wastewater streams to the water bodies. Appropriate measures should be considered for treating these high volume contaminated water streams in order to maintain water quality as safe as possible. Natural zeolites are abundant and inexpensive inorganic adsorbents are outstanding candidates for water and wastewater treatment. Zeolites and their modified forms are introduced as inexpensive, ubiquitous and green adsorbents that exhibit high performance for removing cations, anions and organic molecules from aqueous medium. This paper reviews the latest achievements on zeolite-based processes for treating these special wastewaters and discusses advantages and disadvantages of using zeolites for wastewater remediation processes.

1. Introduction

Population growth and industrial development increase the demands for fresh water, in which, consequently cause soil and water pollution [1]. Anthropogenic activities lead to serious negative influences on human health and the environment because of producing huge amounts of special industrial wastewaters. Special industrial wastewater streams can be categorized as acid mine drainage (AMD) (because of extensive mining activities); landfill leachate (LL) (because of huge urban waste landfills); nuclear fallout (NF) (because of nuclear activities in open and unshielded facilities such as nuclear explosion and nuclear accidents) and polluted urban runoff (UR), which is runoff of rainwater created by urbanization. Although the nuclear accidents happen rarely because of the high safety measures, however, contaminated waters resulted from nuclear accidents and NF should be treated with special techniques because of extremely high risk associated with the radioactive materials. Discharging these types of wastewaters to the fresh water bodies without proper precautions will result serious environmental and health-related problems.

Nowadays, minerals are excavated from earth crust to fulfill over-growing demands of the industrialized generation to wide range of materials from metallic to non-metallic compounds, in which ultimately the quality of surface and groundwater are exacerbated as results of mining activities [2,3,4,5]. Nowadays, landfilling of non-recyclable urban solid waste is considered as a reasonable and clean method to manage the overgrowing volume of urban waste produced by civilized societies [6,7]. Landfills, however, produce huge volume of toxic leachate that contains various contaminants including heavy metals cations, anionic species, organic molecules and pathogens that are polluting soil and groundwater [8,9,10,11]. Nuclear fallout (also called Black Rain), happens when the radioactive material transferred into the upper atmosphere as a result of nuclear tests, nuclear power plant accidents (e.g. Three Mile Island, Chernobyl and Fukushima Daiichi disasters). They are called “falls out” because they come from the sky to the earth after the incident. These radioactive materials are very dangerous and long lasting pollutants that contaminate air, water and soil. Furthermore, medical and industrial applications of nuclear and radioactive materials including nuclear power stations, which are important sources of power generation, produce different radioactive waste streams [12,13,14,15,16]. Because of different nature of the radioactive irradiations and radioisotopes, this class of industrial waste should be categorized as special wastewater stream. Although frequency of nuclear accidents and

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following NF is low, however, given the dangerous nature of radioactive materials, they has significant and long lasting consequences on the public health. It can be concluded that proper remediation of nuclear wastewater is of paramount importance. Fast population growth and developed civilization increases the exposed land areas without proper vegetation and enhances surface runoff volume. In addition, further runoff washes out pollutants and carries them to the water bodies [17,18].

"Active" and "passive" treatment techniques can be considered as two general approaches for cleanup of contaminated water and wastewater streams. Adding chemicals and using energy are examples of active treatment techniques, whereas, wetland, permeable barrier and adsorption media are known as passive treatment methods. Adsorption [19,20] and ion exchange [21,22] are known as suitable remediation techniques for capturing heavy metal from polluted water. Possible applications of natural, synthetic and modified zeolites for removal of heavy metal cations and ammonium [22,23,24,25,26,27], anions [28,29], and molecules such as volatile organic compounds (VOC) [30,31,32,33,34] from contaminated solutions are studied extensively. Chronological trend of papers published on "water treatment technologies by using zeolite" is shown in Fig. 1. It can be seen that utilization of this category of porous adsorbents, as promising candidates for treating different wastewater streams is growing fast. Wastewater treatment using other natural inorganic materials such as lignite [35], chitosan [36], pumice [37] and LECA [38] are also reported. This trend ascertains that naturally occurring materials should be considered as effective adsorbents for water purification purposes.

Natural zeolites are ubiquitous minerals, which are found worldwide in massive deposits with volcanic and sedimentary origins [39,40,41,42,43]. Zeolites are hydrated aluminosilicates of the alkaline (e.g. Na^{+}, K^{+}) and alkaline earth elements (e.g. Ca^{2+} and Mg^{2+}) with a rigid three dimensional and open structure (like honeycomb) consisting of pores, channels and cages. Hydration and dehydration, molecular sieving (i.e. adsorbing molecules based on their size) and ion-exchange (i.e. exchanging of the loosely attached cations in zeolite pores and channels with cations from surrounding environment) are the most important properties of the natural and synthetic zeolitic materials [44,45,46,47]. High selectivity and reasonable adsorption capacity of zeolites for heavy metals can be attributed to their unique structural chemistry (e.g. Si/Al ratio, pore size) and high specific surface area [48,49,50]. Although the dominant mechanism for cation capturing by zeolitic aluminosilicates is ion-exchange, however, cations can be trapped by zeolites by means of other mechanisms including precipitation onto the solid phase and adsorption as well as combinations of these mechanisms [51].

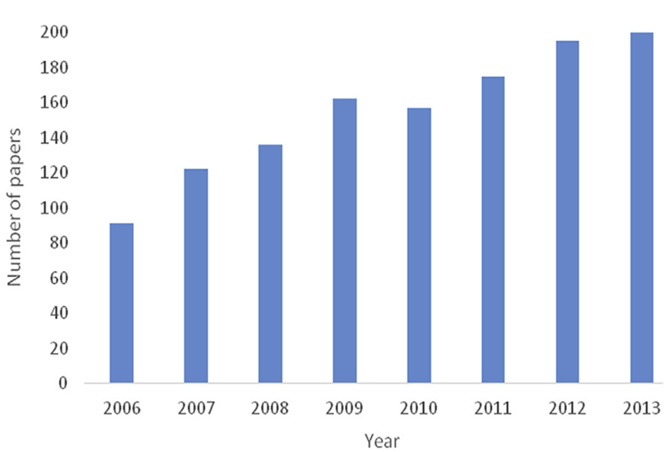

Fig. 1. Increasing trend of scientific publications on wastewater treatment using zeolite (Scopus.com, Last accessed September 20, 2014).

According to the structural database of the international zeolite association (IZA), as of July 2014, 218 unique zeolite Framework Type Codes (FTC) have been identified, and over 60 naturally occurring zeolite frameworks are known. The Si/Al ratio plays the central role in zeolite adsorption performance [52,53,54,55,56,57]. Larger Si/Al ratio results in higher thermal and physical stability. Nevertheless, zeolites with lower Si/Al ratio exhibit higher cation exchange capacity because the more aluminum in the structure the more cationic sites will be created. It is reported that some zeolites containing higher amount of silica exhibit better ion exchange performance [58]. Among natural zeolites, edingtonite and ferrierite have the lowest (i.e. Si/Al = 1.5) and highest (i.e. Si/Al = 6.14) silicon to aluminum ratios, respectively. Zeolites with lower Si/Al ratio urge to be hydrophilic media, while higher ratio makes the zeolite more hydrophobic (organophilic) [59]. Zeolite pore size is another decisive parameter in pollutants removal. It has been asserted that zeolites with medium and large pore size are more effective for adsorption and catalysis applications. During the course of ion exchange process, in which cationic pollutants present in the environment replace with the zeolite exchangeable cations, the zeolite structure remains almost intact [60]. The mobile alkaline and alkaline earth cations presenting in the zeolite structure are harmless to the environment, which makes zeolitic adsorbents eco-friendly candidates for wastewater treatment applications [61]. Among natural zeolites that are abundant with huge commercial deposits worldwide, natural clinoptilolite from heulandite (HEU) family has shown very premising and efficient performance in wastewater treatment processes. Natural clinoptilolite with Si/Al ratio of 4–5 exhibits a very high physico-chemical durability and relatively high cation exchange capacity with abundant deposits all around the globe [62,63,64].

Most of natural zeolites occurring in form of zeolitic-rich tuffs, which are usually a zeolitic phase that is accompanied with other impurities. It is noteworthy that using natural zeolite-tuffs with low zeolite content as adsorbent may demote water quality in some case. It is important to make sure that natural zeolite does not contain any water-soluble impurities that may contaminate the treated water with other pollutants. Therefore, synthetic zeolite manufactured with high purity such as Na–P and LTA zeolites with lower Si/Al are very attractive candidates for some of the wastewater treatment applications. Synthetic zeolites are more expensive compared to the similar natural counterparts, however, because of higher cation exchange capacity (CEC) and faster reactions kinetic, and therefore higher removal efficiency, they have been used widely [65]. Different modification methods including thermal activation, surface modification and making uni-cationic form of a zeolite can improve its adsorption performance in treating different wastewater streams. Zeolite thermal treatment ameliorates its performance particularly for molecular adsorption such as volatile organic compounds (VOCs) and for ammonia adsorption, because it will evaporate water and other volatile molecules existed in the zeolite pores and cavities and evacuate space for binding more pollutants [66,67]. Thermal activation should be executed under controlled condition, because extreme thermal treatment may collapse zeolite structure and diminish available binding and adsorption sites [68,69]. The effect of wide range of physico-chemical modification processes on the zeolite performance are studied. It is reported that exposing zeolites to microwave radiation led to increasing adsorption rate. Zeolite heat treatment (e.g. calcination) increased its adsorption rate in comparison to the untreated parent zeolite. Zeolite surface modification by cationic surfactants showed enhanced adsorption performances for anionic species such as chromates and arsenates [70,71,72,73,74].