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Review Paper

Promising application of natural zeolites: for waste water treatment - a review

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Abstract

The presented review shows that, due to their unique properties such as, thermally stable, can survive both in acidic and basic conditions and have the capacity to exchange with other cation, Zeolites have a great potential as effective sorbents for a large number of water treatment applications. Moreover Zeolite modification extends markedly their applications. Number of different methods can be used for zeolites modification. The most common method for modification is to use organic surfactants. Low price and wide range of use in (waste) water treatment increases popularity of oxide modification. Growing interest in zeolite application in water purification is observed worldwide since natural zeolites offer the possibility for removing contaminants in water and wastewater such as inorganic cations and anions as well as microorganisms.

Keywords: Adsorption, pollution, ion exchange, micro porous, zeolite modification.

Introduction

Water is one of the most abundant substances on nature necessary to sustain life for living organisms. However its availability is limited due to explosion and population explosion. Nowadays it is polluted in different ways. The contamination of water bodies by different pollutants commonly referred as water pollution. When pollutants are discharged in to water bodies without proper treatment chiefly causes environmental degradation. This practice severely affects living organisms which are living in aquatic environment[1].

Mostly water pollution is caused by man-made due to increasing industrialization and human activities, such as agricultural and industrial wastes, run off, dumping and disposal. Other sources of water pollution comprises marine dumping, radioactive waste, oil spills and synthetic toxic chemicals like endocrine disrupting substance (EDS) that causes genetic disorder to aquatic organisms. Besides, factors such as runoff, toxic sediments or deposition of airborne particles also cause water pollution[2].

This shows water pollution has many different causes which lead to its difficulty to solve these problem[3]. The types of chemicals which are dumped in to water bodies and its locations highly determine the effect of water pollution. Some of the effects take account of noxious drinking water and animal's foods, disturbance of Lake Ecosystem that cannot maintain complete biological diversity, deforestation due acidic rain and so on. However, the aforesaid effects are caused by various contaminants[4]. For instances, aquatic areas nearby cities and towns are mainly polluted by dangerous chemicals dumped from manufacturing industries and garbage by individuals, health centers, schools and market places[3,5]. Therefore, to improve the existing methods and investigation of new water purification technologies stimulated the water treatment industries to employ diversified uses and necessities. But, these classical water treatment methods are featured with a high degree of automation and mechanization, production of secondary high sludge, expensive in cost, lack of reusability, ineffective to remove the wastes and etc. due to these drawbacks there is a great demand of using advanced treatment methods[6].

Therefore, the principal objective of this review paper is to provide general overview about application of natural zeolites for treatment of wastewater. The need to choose this adsorption method for waste water treatment is inexpensive (economically efficient), easily harmless for human beings and of the environment, synthesized and regenerated to make effective. So, because of the above mentioned facts natural zeolite as adsorbents has been a debate of many studies due to their unique properties and possible modification methods in waste water treatment.

Pollution of water

Water is one of vibrant natural resource on the earth and a source of life for all living organisms. It covers roughly 98% of the earth crust in the form of saltwater. This makes unusable for using drinking due to its massive salt concentration. However, the rest 2% is fresh water, but, natural circumstances makes difficult for utilization. Hence, 1.6% stored in the form of ice caps and glaciers in the North and South pols; 0.36% is stored in the form of underground water. These situations significantly reduced the amount of usable water to 0.36% which solely accessible from lakes and rivers. On top of that, the existing fresh water are becoming polluted and reached the level of unusability because of excessive human made intervention and uncontrolled industrial effluents. As per the finding of researches on the field clean water systems are contaminated particularly with compounds of chemicals and manufacturing are the pressing problems of our environment. In support of this fact, a research published on Nature exclusively showed that 80% population across the globe are labeled as a potential threat to fresh water security. The frequent flow of contaminants from human activities and industrial wastes chiefly toxic metals, textile dyes, organic chemicals, toxic organic and inorganic ions, and detergents are massively decreased the amount of fresh water universally[7].

Because of the growing level of demands and industrialization all over the world new chemical compounds is frequently being invented and available for market. Thus, it is mandatory to develop a testifying mechanism to reduce their potential level harmfulness, unless, they will toxicates the entire aquatic systems sooner or later. In addition, water borne diseases like pathogenic microorganisms are omnipresent across the world. Due to lack of proper controlling mechanisms, these pathogenic microorganisms are entered in to water systems through different water pipes as well as various industries such as tanning and meat packaging factories. However, the presence of these pollutants might have undesirable effects on living organism. Therefore contamination of water is a big concern nowadays and mainly happened with natural catastrophe such as earthquakes, hurricanes, floods, and volcanoes. In the future, insufficiency of water leads to political and social insecurity and by far to a serious hydro-political war unless the invention of new ways of clean water supply. Therefore, conducting awareness campaign publicly may win the hearts and minds of governments and other stakeholders globally to craft rules and regulations on contamination of water. Hence the development of wastewater treatment technologies is basic concern worldwide[8].

Treatment of water is a process that changes the natural behavior of water or its chemical composition. That means it is not only elimination of various wastes, but, also upgrading on its natural quality by adding certain ingredients. Scientifically, the treatment mechanisms can be categorized as follows[9]: i. Mechanisms which aimed to purify its turbidity, color and odor. ii. Methods those focused on ensuring epidemiological safety (chlorination, ozonization and ultraviolet irradiation).

Parameters of water quality: After domestic and industrial usage, considerable amount of water is discharged without treatment. This leads to have an effect on the environment. When the level of water contaminants reaches beyond the allowed concentrations, it is known as water pollution and the agents are called the pollutants (contaminants). In conclusion, expansion of industries and population growth are major causes for water pollution globally[7].

Water is polluted when a specific concentration is found beyond its limit and is measured by the following parameters[7]. i. Physical parameter: These comprises physical properties of water: such as an odor, color, taste, turbidity, temperature and electrical conductivity. For instance, color and turbidity are visible which makes water unfit for drinking. ii. Biological parameters: Includes matters such as, fungi, algae, protozoa, viruses and bacteria. These pollutants may cause the reduction of survival of plant and animal in water bodies. iii. Chemical parameters: These comprise total dissolved solids: such as sulphates, carbonates, fluorides, chlorides and metal ions.

Characteristics and types of zeolites

Zeolites are inorganic materials which are characterized by its crystalline, micro porous and aluminosilicate hydrated tetrahedral structure. Their general formula can be written as Mx/n $[(AlO_2)x(SiO_2)y]$.wH2O,. where M is an alkali or alkaline earth cation, w is the number of water molecules, n is cations valency, x, y are the number of aluminates or silicates[10]. In their structure tetrahedral silicates ($[SiO_4]^{4-}$) and aluminates ($[AlO_4]^{5-}$)ions are connected by oxygen sharing which enables them as naturally abundant adsorbents. Axel Fredrik Cronstedt, who was the Swedish mineralogist, discovered these materials in 1756 in the form of collection of minerals "Zeolite". Their name is derived from the Greek word: zeo means boil and litha is stone. According to Axel Fredrik Cronstedt observation they lost water, when they are heated. And further heating in a blowpipe leads them to the formation of frothy mass[11].

The cation-exchange character of these inorganic materials is their unique property. Mean that they can remove dissolved cations by exchanging with substituted cations (see Pabalan and Bertetti, this volume). For example well known living organism contaminant NH_4^+, can be substituted and detached with Na^+, K^+, Mg^{2+}, Ca^{2+} or H^+ ions.

Nowadays, over 50 types of zeolites are known which differ in their physico – chemical properties. Mean that the variation is due to their source and the environmental situations in place during its development[12]. So, these materials can be categorized as natural and synthetics. However, synthetic zeolites are applicable widely. When we use zeolites it is necessary to remind that they are not similar. Hence they differ with their physic-chemical characters. Also their composition and structure are considered as their difference. Some times their cation selectivity, pore size, strength and density can vary zeolites depending on our choice. Here we have to take a serious attention when we select zeolites for a specific application[13]. The most useful types of zeolites are: Clinoptilolite $(Na,K)_6[Al_6Si_30O_{72}]\cdot 20H_2Op)_6$, mordenite, phillipsite, chabazite $(CaO.5,Na,K)_4[Al_4Si_8O_{24}]\cdot 12H_2O)$, stilbite $(NaCa_4[Al_9Si_{27}O_{72}]\cdot 30H_2O)$, analcime $(Na_{16}[Al_{16}Si_{32}O_{96}]\cdot 16 H_2O)$ and laumontite $([Al_8Si1_6O_{48}]\cdot 18H_2O)$[21]. From these clinoptilolite is widely used and it is chiefly abundant naturaly[14]. Beyond their classifications the characteristic properties of zeolites are: they can absorb vapors and gases, have low density and large void volume, high degree of hydration, ability to exchanger cations; have nano sized pores, are catalysts and have Stable crystal structure[7].

Application of natural zeolites

The values of all commercially useful zeolites heavily depend on the following properties, namely, ion exchange capacity, adsorbing efficiency, and catalytic property.

Asan adsorbent: Sieving in molecular level is the most important consideration on adsorption efficiency of zeolites. When diameter of chemical species is so large these minerals can filter effectively "sieved." This property can be used for effective separation of species according to their size and shape. Their cavity is highly dependent on the strong interaction with polar molecules such as water results from strong electrostatic field with in zeolite's cavity.

Because of the polarizing power of these electric fields, non-polar molecules are adsorbed strongly. As a result, excellent separations can be achieved with no stericinterruption[15]. Adsorption efficiency which depends on molecular sieving, electronic fields and polarizing power are reversible in theory and practice. This situation allows the reusability of zeolites. This shows the cost effectiveness of zeolites economically[16].

As Ion Exchanger: Natural zeolites referred as cation exchangers due to the negative charge on their structure. Due to mobile nature of cations, zeolites are the most important materials to exchange their cations for the surrounding fluids. Indeed, due to a competition between cations of zeolites phase and fluid phase zeolites are more preferable among available cations. The most efficient remover of water hardness is sodium zeolites A.

It is mainly due to their connection via oxygen ions with secondary silicates and aluminate which lead also being linked into zeolites' structure. Substitution of Si by Al defines the negative charge of the zeolites structure, which is replaced by s - block metal ions.

This replacement is not only restricted to Silicon (Si) and Aluminium (Al) but also for atoms of iron, boron, chromium, germanium, and titanium[11].

Therefore, because of their unique structure and linkage of silicates and alumunate, these inorganic materials are highly porous with typical pore sizes and shapes[15].

As Catalyst: Very active catalysts are formed by zeolites. In zeolites catalysis, electrostatic attraction phenomena are very important and "shape selective catalysis" describe strongly their steric effect. When certain products, reactants or transition states are kept from forming within the pores selective reactions can be made[16].

Mechanism for waste water treatment by natural zeolites

Natural zeolites are promising materials for wastewater treatment. This is because zeolites undergo ion-exchange, adsorption, and they can also be purified and modified to catch wastewater contaminants. Particularly, numerous studies have proved the capacity of natural zeolites to remove metal cations from polluted water. The reason why natural zeolites are more promising than other cation exchangers like organic resins are, due to their abundance, excellent selectivity, which is followed by the discharge of environmentally friendly transferable cations to the surroundings, as well as their compact size allow simple and cheap maintenance[11]. Moreover, the unique three-dimensional porous structure gives these natural materials are more selective for this application.

Water treatment efficiency of either natural or modified zeolites can be affected by their type and quantity, particle size distribution, the initial concentration of contaminants, temperature, pressure, pH, conductivity, reaction time and the presence of anions. Standard procedures (column or batch process) are used for the water treatment with natural zeolites. Owing to the unique properties of natural zeolites they get rid of impurities at low concentrations for conservation of water if the treatment is carried out in the column process when compared with other chemical and biological processes[13].

Generally natural zeolites have good ion-exchange capacity worldwide. Luckily, clinoptilolite, mordenite phillip site and chabazite are selective for NH_4^+even at higher concentration of competing cations. In addition, Clinoptilolite and Mordenite are selective for Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Cr^{3+}, Mo^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, which are very toxic even at low concentrations. Therefore, natural zeolites can be taken as novel adsorbents for waste water treatment[17].

Modifications of natural zeolites

Generally speaking, natural zeolites can be customized by using chemicals and heating or by both methods. The modification process could result cation migration and also highly affected their position and hole size. Pore manufacturing is well-known process and widely used technique in zeolites modification with some sort of sorbent properties manipulation. This in turn brings a concurrent contact in ion exchange and adsorption in zeolites. So, these natural materials can be modified with the following inorganic solutions.

With inorganic salts: It is quite possible to qualify properties and efficiency of zeolites in water treatment by using chemical modification with a mix of Sodium Chloride (NaC)l, Calcium Chloride($CaCl_2$), Barium chloride ($BaCl_2$), Ammonium chloride (NH_4Cl) and Iron chloride ($FeCl_3$) and/or hexadecyltri-methyl ammonium bromide. As described in Figure-1, successful modification of zeolites requires the presence of high concentrated solutions. In zeolite arrangement reaction sites are basically occupied with water molecules in the creation of hydration spheres around exchangeable cations (Figure 1-A). As shown in Figure 1-B, the mixing of zeolites with other solutions like Sodium chloride (NaCl), results for the exchange of cations like Hydrogen ions (H^+) or Sodium ions (Na^+) with sodium (Na^+), Potassium (K^+), Calcium (Ca^{2+}), Magnesium (Mg^{2+}). Moreover, to get rid of anions, the surface of zeolites should be modified with a solution of inorganic salts like Iron chloride. This leads to the creation of oxi-hydroxides to form stable complexes. This method may bring a lower or higher impact on the formation of adsorption sites and change of negative to positive surface charge (Figure-1-C). Besides, Table-1 shows the specific surface area of zeolites before and after treatment with inorganic salts.

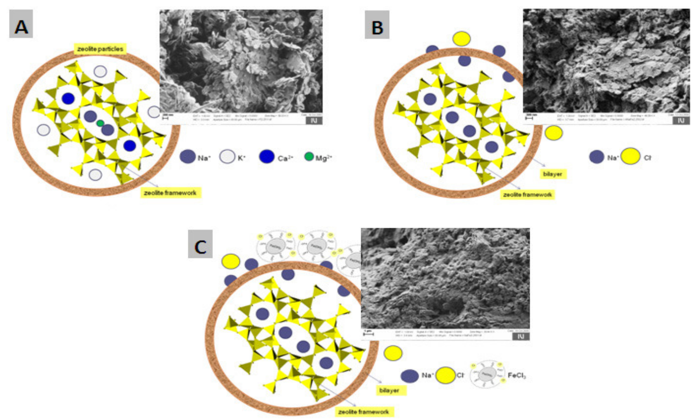

Figure-1: SEM image of natural zeolites before and after modification[18].

Table-1: Surface area of zeolites before and after treatment[18].

Type of Zeolite	Surface area, m^2/g
Natural Clinoptite	24
Natural Clinoptite	16
NaOH-Clinoptite	19
NaFe-Clinoptite	91
NaFe-Clinoptite	51
Natural mordenite	42
Hexadecyltri-methyl ammonium-mordenite	6
Hexadecyltri-methyl ammonium –mordenite	5

This approves the hypothetical assumption of the appropriate location of Sodium (Na^+) ions and possibilities of metal ions exchange with zeolites structure.

Modification by acidic/basic solutions: The most common and simple method to modify zeolites structure and its properties can be done by using either inorganic base such as sodium hydroxide (NaOH), calcium hydroxide ($Ca(OH)_2$) or acid solutions of hydrochloric acid (HCl) and nitric acid (HNO_3). This method is becoming more effective based on the content of chemicals, structure, purity, and other laboratory situations. One major consequence of treatment of zeolites by acid solution is the suspension of amorphous materials which slabzeolites pore. More than 90% of the dissolution of natural zeolites in this solution arises as a result of either by acidic or basic character of the aluminates or silicates of zeolites with H^+ or OH^- ions in the solution. Zeolites which have high composition of silica can interact with acidic and basic aqueous solution are slowly dissolved and acid-resistants[8]. Dealumination process can be progressively removed Aluminium -ions from zeolites' surface. This reaction favors lower pH and degree of protonation to detach aluminium hydroxide. When the concentration of cations is high, zeolites can exchange cations with hydrogen ion but highly affected by the acidity of the solution and cation hydratation enthalpy[4]. Treatment of zeolites with Hydrochloric acid results to DE cationization, removal of aluminium ions and rarely deformation of their structure. Hydrochloric acid has various effects on zeolites. For instance, if some natural zeolites are carried out under similar conditions it leads to weak decationization and almost no dealuminization[18].

When identical natural zeolites are treated with acids they heavily depend on their nature and the amount of exchangeable cation and impurities. In addition, the efficiency of modification is influenced by zeolites reaction time, heating temperature, pre-treatment with water or other solutions, such as ammonium chloride (NH_4Cl)[18].

Waste water treatment with natural zeolites

The applications of zeolites for a wide range of industrial processes heavily depend on its chemical and physical properties. For example, they can be used as ion exchange media because of their capacity for replacing or absorbing ions dissolved in water. Their structural architecture enables them to be utilized as water softeners to oust calcium and magnesium ions from hard water. The zeolites absorb these elements and release Na^+ ions to the water. Zeolites can also be employed to treat radioactive waste such as Sr-90, Co-60 and Cs-137 in aqueous solutions and to treat ammonium from sewage water[17].

Treatment of drinking wastewater: Currently, there is a rapidly emerging crisis involving the access to clean water because of massive release of various pollutants by industries to the environment. Therefore, there is a great demand for the development of novel, efficient, and inexpensive technologies for the treatment of polluted waters, soils, and the air. The common pollutants are dyes, heavy metals, pesticides, pharmaceuticals, phenols, insecticides, and detergents. Human health and aquatic ecosystems are highly affected by these contaminants. Hence, to have a health being and aquatic life water which is free of toxic substances and pathogens disease causing organisms is essential[7]. In this regard, natural zeolites are important to treat and trap pollutants to purify waste water through ion-exchange and adsorption[19].

Elimination of cations: In zeolites' structure the negative charge is produced through exchange of aluminum (Al^{3+}) by silicon (Si^{4+}) ion. Negativity increases with higher substitution of aluminum atom. Also, on the pore surfaces of zeolites negatively charged ions are balanced by positively charged ions. The surrounding cations which are held together by weak electrostatic force easily exchange with other certain cations in solution. Therefore, cations such as ammonium (NH_4^+), heavy metals in wastewaters, Cs^+ and Sr^{2+} in nuclear wastewaters can be easily exchanged. For example, in grey water Ammonium is the well-known cation which affects human and animal health[20].

Table-2: Removal of some pollutants by using zeolites[21].

Type of the Pollutant	Performance of Zeolites to remove the pollutants
Cs^+	80–100% is removed with batch and 40–80% in dynamic flow method
NH_4^+	30–98% removal with batch process
$Mn^{2+,}$	67% more reduced by K-clinoptiloclite
Chromium, Iron, Manganese, Copper, Cadmium, Nickel, Lead and Zinc	10–100%
PO_4^{3-}	90% removed using acetylpyridinium – modified - zeolite
Chemical oxygen demand(COD) and biological oxygen demand (BOD)	75% Chemical oxygen demand(COD) and 100% by phillipsite columns
Hg^{2+}	Nearly 50% Hg^{2+} is removed by Na-clinoptilolite and heulan

Removal of microorganisms: Natural zeolites are extremely bi dispersive porous materials. Furthermore, they have channels in their surface. As a result of this unique structure, some can pass through the channel trough the accessible adsorptive space. Similarly, the large mineral particle of the zeolites is available for obeying microorganisms like bacteria[22].

Removal of anion contaminants: By the very nature containing negative charge on their structure zeolites almost cannot trap anions. However, it is possible to increase their sorptive efficiency by doing modification[21].

Removal of phenols: Phenols are commonly known as lethal compounds and extracted from different industrial sources mainly from dyes, pesticides, paper wastes, plastics, pharmaceutics, rubber, and petroleum processing. For instance, the SMZ (mixed with HDTMA) having higher BET surface area and higher amount of HDTMA and also displayed greater retention of bisphenol A because of electrostatic interaction of positively charged end of HDTMA with dissociated hydroxyls of bisphenol A, coordination of the oxygen atoms of bisphenol A by HDTMA positive charges, and the adsorption of uncharged bisphenol A via hydrophobic partitioning into HDTMA layers[23].

Removal of Humic acids: Humic acid are common compounds in practically all soils. When they come from surface and ground waters to drinking water it results for the change in its color, odor, and presence of dangerous chemicals. Many scholars showed that humic acid was highly adsorbed by surfactant modified zeolite (SMZFA) and the maximum adsorption capacity was comparable or higher than for activated carbons and clays. Humic acid adsorption by SMZFA was improved at acidic pH and in the presence of inorganic electrolyte. Since the inner pores in zeolite fraction and oxides in non-zeolites part hold inorganic cations and oxyanions (e.g. phosphate). SMZFA is a potential wide-range adsorbent for water treatment to remove various contaminants with fundamentally diverse chemical properties[26].

Treatment of industrial wastewater: It is known that most industries are placed nearby water sources. These sources contain a wide range of pollutants from toxic ionic species, to extremely poisonous organic compounds, which are very harmful to humans and the environment. Most of these pollutants are non-biodegradables and thus damage the growth of crops. Those factories that produce chemicals and materials such as sodium hydroxide, plastics, pesticides and fungicides release heavy metal like mercury and other toxic wastes near water sources. Mercury, toxic metal pollutant can enter in to the food chains through bacteria, algae, fish and finally into the human body. This toxic metal can have minor symptom of depression and irritability. Furthermore its acute poisoning effect can cause paralysis, insanity, blindness, birth defects and even death[8].

Also dyes in wastewater come primarily from textile, printing, food and leather processing industries. In water environments dyes decrease sunlight infiltration and thus influence photosynthesis. Some dyes are dangerous or cancerogenic. The adsorption of dyes by natural and modified clinoptilolites was recently inspected in, showing that natural zeolitesare not a suitable adsorbent for azo dyes due to the exclusion of the dye anions from the adsorbent pores. Zeolites modified with a typical quaternary amine surfactant (HTAB) adsorb anionic dyes[8].

Conclusion

Natural zeolites are hydrated aluminosilicate materials that are abundant and environmentally friendly. So, this review shows that, due to their unique structure and ropertiesas thermally stability, their survival both in acidic and basic conditions, easily available, inexpensive and having the capacity to exchange with other cation, zeolites have a great potential as promising sorbents for a large number of water treatment applications. Moreover, Zeolites modification extends markedly their applications. Number of different methods can be used for zeolites modification. The most common method for modification is to use organic surfactants. So, growing interest in zeolites applications in water purification is observed worldwide.

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