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Review on Adsorption of Heavy Metal in Wastewater by Using Geopolymer

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Abstract. Rapid development of advanced technology in Malaysia gave impact increasing in the accumulation of heavy metal every day in our daily life through wastewater. Long term exposure of human bodies to heavy metals susceptible to receives various infections and diseases. From an environmental and economic perspective, adsorption is acceptable process that can be applied in wastewater treatment. However, usage of activated carbon most acknowledged and costly adsorbents lead people to find an alternative to activated carbon. Several studies of physical properties of geopolymer make them gain attention to replace an activated carbon in the treatment of heavy metal. This paper review adsorption of heavy metal by using geopolymer.

1 Introduction

Nowadays, management of waste and quality of water is two of the important proposition in human life. Accretion of technologies in urbanization and industrialization lead to increase in percentage accumulation of waste all around the world and release of heavy metal in the water streams. These harmful heavy metals are an output from varieties activities such as industrial, waste disposal, agricultural and others. Accumulation of heavy metal in wastewater streams acts against human bodies and cause to death. Technologies used in the treatment of wastewater include chemical precipitation, ion-exchange, adsorption, membrane filtration, coagulation-flocculation, flotation and electrochemical [1-3].

Adsorption is one of a common treatment applied in the heavy metal removal involves adsorbents such as undoubtedly activated carbon. However, production and regeneration of activated carbon are very costly and tend to encourage people to find another alternative [4, 5]. Recently, studies of low cost adsorbent are intensively gain an attention to the scientist

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were usually waste product from industrial, agricultural and food production which produced abundantly [6].

Currently, geopolymer gain new interest to treat wastewater and replacing the conventional adsorbent use which normally used in the production of cement. First identification of geopolymeric materials as an alternative to conventional Portland cement and concrete composites in 1979 [7]. Geopolymer can be viewed as an economic zeolite which produced by reacting solid aluminosilicate with highly alkali hydroxide [8]. A unique structure of geopolymer which good in mechanical, chemical and thermal making them as alternatives for a variety of application [9]. The purpose of this review is to evaluate the potential of geopolymer used to remove dangerous heavy metal in wastewater treatment in the recent studies.

2 Current technologies available for treatment methods of heavy metal

There a diverse of technologies in the treatment of wastewater in term of metal removal that are divided into physical, chemical and biological process such as metal precipitation, ultra filtration, biological systems, oxidation, solvent extraction electrolytic processes, ion exchange, membrane filtration and adsorption. Physical and chemical treatment is more costly compared to biological treatment in removing metal however biological treat are lack effectiveness and timely process. Advantages and disadvantages of physical and chemical current treatment were simplified as in Table 1.

Table 1. Advantage and disadvantages of current treatment technologies for heavy metal involving physical and chemical processes [10].

Methods	Advantages	Disadvantages
Oxidation	Rapid process for toxic pollutants removal	High energy costs and formation of by products
Ion exchange	Good removal of a wide range of heavy metals	Adsorbents requires regeneration or disposal
Membrane filtration technologies	Good removal of heavy metals	Concentrated sludge production and expensive
Adsorption	Flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants	Adsorbents require regeneration
Coagulation/flocculation	Economically feasible	High sludge production and formation of large particles.
Electrochemical treatment	Rapid process and effective for certain metal ions	High energy costs and formation of large particles.
Ozonation	Applied in gaseous state; alteration of volume	Short half life
Photochemical	No sludge production	Formation of by-product
Irradiation	Effective at lab scale	Require a lot of dissolved O_2
Electrokinetic coagulation	Economically feasible	High sludge production
Fentons reagents	Effective and capable of treating variety of wastes and no energy input necessary to activate hydrogen peroxide	Sludge generation
Biological treatment	Feasible in removing some metals	Technology yet to be established and commercialized

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3 Adsorption

Adsorption process gained is a promising method for a long term treatment and economically proven. In the process, heavy metals can be removing and minimizing the heavy metals even at a low concentration enhances the application of adsorption as one practical treatment [11]. Moreover, adsorption process tender to produce high quality treated effluent and offers flexibility in design and operation. Adsorbents used can be regenerate by suitable desorption process because of its sometime reversible characteristic[1].

Parameters that should considered in this treatment include the characteristic of physical and chemical of the adsorbents and adsorbate, temperature, contact time, pH and the concentration of adsprbate in liquid. There is no specific mechanism in the adsorption process but sorption isotherms are used to explain to describe the mechanism occurred on how adsorbate ions interact on the surface of the adsorbent. Table 2 showed adsorption model that are usually used to prove the reaction between adsorbate and adsorbent.

Table 2. Adsorption models of the single-component system [10, 11].

Types of mechanism	Equations	Nomenclature
a) Adsorption isotherms i) Langmuir isotherms	$q_e = \frac{q\,max\,bCa}{1+bCa}$	q_e is equilibrium metal sorption capacity, *Ce* is equilibrium solute concentration in solution, *q max* and *b* are Langmuir constants related to maximum sorption capacity (monolayer capacity) and bonding energy of adsorption.
ii) Freundlich isotherms	$q_e = K_f C_e^{1/n}$	K_f is a biosortion equilibrium constant, q_e is the sorption capacity, *n* is a constant indicative of biosorption intensity.
b) Adsorption kinetics i) Pseudo-first order	$\frac{dqt}{dt} = k_1\,(q_e - q_t)$	q_e and q_t are the sorption capacity at equilibrium and at time *t*, k_1 is the rate constant of pseudo -second
ii) Pseudo-second order	$\frac{dqt}{dt} = k\,(q_e - q_t)^2$	q_e and q_t are the sorption capacity at equilibrium and at time *t*, *k* is the rate constant of pseudo -second
c) Thermodynamics Parameters	$K_c = \frac{CA}{Ce}$ $\Delta G^o = Rt\ln K_c$ $\ln ke = \frac{\Delta S°}{R} - \frac{-\Delta H°}{RT}$	K_c is the equilibrium constant, C_A is the solid phase concentration at equilibrium, C_e is the equilibrium concentration T(K) is the adsolute temperature, *R* is the gas constant (8.314 J/mol K), ΔG^o is the Gibbs free energy ΔH^o is the entalphy change, ΔS^o is the entrophy change

4 Heavy Metal

Heavy metal poses impact to serious environmental problem due to their characteristic that accumulates in living organism, causing various disease and disorder which in the Table 3 [12]. Heavy metal that can be found in the landfill leachate such as iron, aluminium, arsenic, cadmium, copper, iron, manganese, mercury, nickel, silver and zinc. Heavy metal are not easy to break down and easy to enrich in different ambient mediums. It has been proven that heavy metal of leachate may lead to secondary pollution [13].

Table 3. Sources and effects of heavy metals.

Heavy Metal	Sources	Effects
Copper	Water pipes, Copper water heaters, Frozen freens and canned greens using copper to produce an ultra green color, alcoholic beverages from copper brewery equipment, instant gas hot water heaters, hormone pills, pesticides, insecticides, fungicides, copper cooking pots.	Mental disorder, anaemia, arthritis, hypertension, nausea/vomiting, hyperactivity, schizophrenia, insomnia, autism, stuttering, postpartum psychosis, inflammation and enlargement of liver, heart problem, cystic fibrosis.
Nickel	Effluents of silver refineries, electroplating, zinc base casting and storage battery industries.	Dermatis, myocarditis, encephalopathy, pulmonary fibrosis, cancer of lungs, nose and bone, headache, dizziness, nausea and vomiting, chest pain, rapid respiration.
Chromium	Steel and textile industry	Skin rashes, respiratory problems, haemolysis, acute and renal failure, weakened immune systems, kidney and liver damage, alteration of genetic material, lung cancer, pulmonary fibrosis.
Lead	Industries such as mining, steel, automobile, batteries and paints. Pollutant arising from increasing industrialization.	Nausea, encephalopathy, headache and vomiting, learning difficulties, mental retardation, hyperactivity, vertigo, kidney damage, birth defects, muscle weakness, anorexia, cirrhosis of the liver, thyroid dysfunction, insomnia, fatigue, degeneration of motor neurons, schizophrenic-like behaviour.
Mercury	Industries like chloro-alkali, paints, pulp and paper, oil refining, rubber processing and fertilizer, batteries, dental fillings adhesive, fabric softeners, drugs, thermometers, fluorescent light tube and high intensity street lamp, pesticides, cosmetic and pharmaceuticals.	Tremors, birth defects, kidney damage, nausea, loss of hearing or vision, gingivitis, chromosome damage, mental retardation, tooth loss, seizures, cerebral palsy, blindness and deafness, hypertonia – muscle rigidity, minamata disease.

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5 Geopolymer

Geopolymer or alkali-activated aluminosilicate is a diverse group of ceramic-like materials produced by geosynthetic reaction of aluminosilicate minerals in the presence of an alkali solution at low temperature (less than 100 degree celcius) [14-16]. It consists of a polymeric silicon-oxygen-aluminium framework with alternating silicon and aluminium tetrahedral joined together in three directions by sharing all the oxygen atoms [17]. Fly ash, dolomite, expanded clay, natural zeolite, kaolinite and many are example of geopolymers. Geopolymers had interesting properties that are encouraged to investigated and developed. The major nature of geopolymers are tendency to drastically decrease the mobility of most heavy metals ions contained within the geopolymeric structure, quick compressive development of strength, resistance to acid and fire, fat setting, low permeability and good resistance to freeze-thaw cycles [18-20].

Theoretically, any alkali can be used in geopolymerization reactions; however most of the studies have focused on the effect of sodium (Na+) and potassium (K+) ions. Both NaOH and KOH could be used in the activation process, but the extent of dissolution was higher when NaOH is used; this is due to the smaller size of Na+ which can be better stabilize the silicate monomers and dimmers present in the solution, enhancing the minerals dissolution rate [8]. Rios conclude that geopolymer treated with NaOH is better than treated geopolymer by KOH [21].

Fly ash. Fly ash is a familiar materials used as geopolymerized adsorbents. It is a complex and abundant anthropogenic material which by product of coal combustion in thermal power plants [22]. Fly ash is a waste substance that are easily to found and had been reported that could be effective for removal of heavy metals. However, it is shows lower adsorption capacity unless it is treated or activated called as geopolymer. Fly ash based geopolymer are growing in commercial potential due to their reliance on cheap and readily available waste fly ash as the main feedstock. There is a significant trend in recycling of waste materials and converting it to usable and valuable materials [23]. One of these materials is coal fly ash. The disposal of the large amount of fly ash has become a serious environmental and economic problem [8]. One approach to deal with fly ash is converting to geopolymer which not only effective to heavy metal removal but also help to reduce the waste accumulation.

Dolomite. Dolomite has been a subject of interest for over six decades. Dolomite material is available very cheaply and in abundance around the world (important occurrences are found in India, Indonesia, Turkey and China). Dolomite which has similar properties to limestone is sometimes known as magnesium-limestone in industry. Its crystal structure consists of alternative layers of magnesium and calcium carbonate [24]. Therefore, dolomite had a characteristic to remove heavy metals as effective as limestone.

6 Factor affecting adsorption of heavy metal by geopolymeric adsorbents

Some factors are influence in the process of adsorption of heavy metal into adsorbents such as pH, adsorbent dosage, initial concentration, contact time and temperature [25]. Removal efficiency of heavy metals can be described as following equation [19]:

$$\text{Removal efficiency (\%)} = \frac{(Co-Ct)}{Co} \, x\ 100 \qquad (1)$$

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Where Co (mg/L) is the initial concentration and Ct (mg/L) is the concentration at time t (min).

Adsorption amount at time t, qt (mg/g) and at equilibrium, qe (mg/g) are determined using following equations :

$$qt = \frac{(Co - Ct)V}{m} \quad (2)$$

$$qe = \frac{(Co - Ct)V}{m} \quad (3)$$

Effect of pH: The surface charge of the solution, degree of ionization, and the adsorbate species influenced by the pH of the solution. Most of the metal adsorbed increase with the increasing of pH of the solution until certain point and followed by reduction if further increasing of pH. The equation of pH can be written as :

$$\text{pH} = \text{pka} - \log \frac{[AH]}{[A-]} \quad (4)$$

where, [A-] and [AH] represent the concentration of deprotonated and protonated surface groups and the equilibrium constants pKa resembled the carbonyl groups.
Study by al-Zboon show that adsorption efficiency increase from 1% to 90.66% as pH of the solution increase from 1 to 5 and slightly decrease at pH 6 [18]. Therefore, pH 5 is indicated as zero point charge.

Effect of adsorbent dosage: Dose of adsorbent also is one of the main points to determine the capacity uptake of heavy metals by adsorbents. Usually, increase in the dose of adsorbents will increase in the adsorbed capacity until its reach a limit. If further increase the dose, the adsorption capacity will be constant. Wang study adsorbent loading from 0.5 g until 2.0 g, removal of copper increase with increase of adsorbent loading [5].

Effect of initial concentration: Adsorption dosage gain a strong effect by initial concentration of heavy metals. Generally, adsorption capacity increased with the increased initial concentration of heavy metals. Playing as important driving force, initial concentration influence in overcome all mass transfer resistance between solid and aqueous phases. Several studies have shown that removal efficiency of heavy metal is concentration dependent and there exist decreasing trend if further increase initial concentration [26].

Effect of contact time: The interaction of functional group between the solution and the surface of adsorbent result in the adsorption capacity if adsorbate into adsorbent. Specific time needed to maintain equilibrium interaction therefore the adsorption process undergo completion. Cadmium removal using zeolite based geopolymer achieve equilibrium contact time at 7 hours [3]. However, fly ash-based geopolymer for lead removal gain equilibrium contact time at 120 min and thereafter, its remain constant [18].

Effect of temperature: The natures of the processes either exothermic or endothermic are depends on the adsorption equilibrium that affected by the temperature used. The uptake capacity of the adsorbates increases with the rises of the temperatures. This happens due to the enlargement of pores and activation of the sorbent surface. Research by Javadian shows removal of cadmium was increase with temperature range from 25ºC to 45ºC [3].

7 Summary

The role of geopolymers in the wastewater treatment has been investigated a few years ago. Among other geopolymeric adsorbents, fly ash is the most interested in the removal of heavy metal because of they are reliance on cheap and readily available waste. Adsorption capacity of heavy metals adsorbed usually modeled by Langmuir and Freundlich isotherm. Factors that influence of adsorption capacity are pH, adsorbent dosage, initial concentration, contact time and temperature. Normally, increase of dosage, contact time and initial concentration will increase the uptake capacity to a certain point before constant. However, some materials and adsorption may be different. From reviews, it can be conclude that usage of geopolymeric adsorbent as alternative to costly activated carbon are effective to remove heavy metal from wastewater. Most of research focused on the industrial wastewater instead of improvement in the leachate treatment. Moreover, there has been limited research of mixture of geopolymeric adsorbents.

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