



Application of Eco-Friendly Geopolymer Composite in Wastewater Treatment

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ABSTRACT

Seeing as heavy metal pollution from industrial activities and technological development is a serious threat to the environment due to their toxicity, biodegradability, and bioaccumulation, heavy metal removal from wastewater is one of the most important stages of industrial and municipal wastewater treatment. In the previous 150 years, the worldwide amount of metal pollution has increased by more than 4,000 times. Heavy metals, whether in the form of metallic elements or organic materials, can have a substantial impact on human society's health. Adsorption is a process that can be utilized in wastewater treatment that is environmentally friendly. However, the use of known and expensive adsorbents such as activated carbon has prompted researchers to look for acceptable alternatives. Much research has been done on the physical and chemical properties of geopolymers for use in the treatment of heavy metals as an alternative to activated carbon. The purpose of this paper is to investigate the adsorption of heavy metals using geopolymers.

Keywords:

Wastewater Treatment, Absorbent, Geopolymer, Eco-Friendly Composite.



1. Introduction

Waste management and water quality are two major concerns in modern society. The continued advancement of technology in urbanization and industrialization has resulted in a global increase in garbage accumulation and the release of heavy metals into waterways. Various activities, such as industry, disposal systems, agriculture, and so on, are responsible for the dangerous heavy metals. Heavy metals accumulating in sewage streams harm the human body and cause death. Chemical deposition, ion exchange, adsorption, membrane filtration, coagulation and flocculation, flotation, and electrochemical are all utilized in wastewater treatment [1-3]. Adsorption, which includes proven adsorbents such as activated carbon, is one of the most common ways to remove heavy metals. However, since activated carbon is very expensive to build and repair, most people choose another option [4,5]. Researchers have recently focused on low-cost adsorbents, which are usually industrial, agricultural, and food wastes that are produced in large quantities [6]. Geopolymer is currently being studied for wastewater treatment and replacement of traditional adsorbents. In 1979, geopolymer materials were identified as a suitable alternative to Portland cement and concrete composites [7]. Geopolymer can be considered a cost-effective zeolite made of solid aluminosilicate and highly alkaline hydroxide [8,9]. They have become options for various applications due to their unique geopolymer structure, which is very suitable mechanically, chemically, and thermally. The purpose of this paper is to evaluate the potential of geopolymer in wastewater treatment to remove harmful heavy metals.

2. Available Technologies for Refining Heavy Metals

Physical, chemical, and biological techniques such as metal deposition, ultrafiltration, biological systems, oxidation, and electrolytic processes with solvent extraction, ion exchange, membrane filtration, and adsorption are all used in wastewater treatment to remove metals. In terms of metal removal, physical and chemical operations are more expensive than biological treatment. However, biological treatment is inefficient and time-consuming. Table 1 summarizes the advantages and disadvantages of traditional physical and chemical treatment.

3. Adsorption

The resulting adsorption process is a promising and cost-effective solution for long-term purification. Heavy metals can be removed in this process, even at low concentrations, making adsorption a more practical treatment [11]. In addition, the adsorption process is recommended for the production of high-quality treated effluent and gives design and performance flexibility. Due to the reversibility, the adsorbents used can be regenerated using the appropriate desorption technique [1]. The amount of adsorbent that can be absorbed by the adsorbent is a function of the characteristics of the adsorbent, its concentration in solution, as well as a function of temperature, and pH. Solubility, molecular structure, molecular weight, polarity, and hydrocarbon saturation are the most relevant features of the adsorbent in this scenario. To obtain adsorption isotherms for an adsorbent, a constant amount of adsorbent must be retained in a constant volume of solution, and the amount of activated carbon must be changed. In this instance, more than ten containers are usually required, and when powdered activated carbon is employed, the sample must reach equilibrium within seven days. When using granular activated carbon, it must be crushed in order to reduce adsorption times. The amount of adsorbent left in the solution phase is measured at the end of the test [2]. There is no specific mechanism in the adsorption process, but adsorption isotherms are used to explain the mechanism by which the adsorbed ions interact on the adsorbent surface. The following table is to prove the reaction between the adsorbent and the adsorbent.



Table 1. Advantages and disadvantages of conventional heavy metal treatment technologies including physical and chemical processes [10].

Disadvantages	Advantages	Methods
High energy costs and by-products	Rapid process to remove toxic pollutants	oxidation
Adsorbents need to be reconstituted or disposed	Proper removal of a wide range of heavy metals	Ion exchange
Production of thick and expensive sludge	Proper removal of heavy metals	Membrane filtration technologies
Adsorbents need to be reconstructed	Flexibility and simplicity of design, ease of operation, and insensitivity to toxic pollutants	Absorption
High production of sludge and formation of large particles	It is economically possible	Coagulation / flocculation
High energy costs and the formation of large particles	Fast and efficient process for specific metal ions	Electrochemical treatment
Short half-life	Applied in gaseous mode; Volume change	Ozonation
Production of by-products	Lack of sludge production	Photochemical
High production of sludge	It is economically possible	Electrosynthetic coagulation
Sludge production	Effective and able to treat all types of waste without the need for input energy to activate the hydrogen peroxide	Fenton Reagents
This technology has not yet been established and commercialized	Possible in the removal of some metals	Biological treatment



Table 2. One-component system adsorption models [10, 11].

Naming	Equations	Types of mechanisms
q_e : Equilibrium capacity of metal adsorption, C_e : Equilibrium concentration of the substance dissolved in the solution, q_{max} : Langmuir constant corresponding to maximum absorption capacity (single layer capacity), b : Adsorption bond energy	$q_e = \frac{q_{max} b C_e}{1 + b C_e}$	a) Adsorption isotherms i) Langmuir isotherms
q_e : The mass adsorbed from the adsorbed material to the unit mass of the adsorbent at the equilibrium point k_f : Freundlich capacity factor C_e : Equilibrium concentration of adsorbent in soluble phase after adsorption (concentration in soluble phase in equilibrium) (mg / lit) n^{-1} : Frech Leach Frequency Parameter	$q_e = K_f C_e^{\frac{1}{n}}$	ii) Freundlich isotherms
q_e and q_t adsorption capacity at equilibrium, at time t , k_1 the equilibrium constant of the adsorption reaction	$\frac{dq_t}{dt} = k_1(q_e - q_t)$	b) Adsorption kinetics
K_c : Equilibrium constant C_A : Solid phase concentration in equilibrium C_e : Equilibrium concentration T (K): Absorption temperature R : gas constant (314/8 J / mol.K) ΔG° : Gibbs Free Energy ΔH° : Enthalpy change ΔS° : Entropy change	$K_c = \frac{C_A}{C_e}$ $\Delta G^\circ = R T \ln K_c$ $\ln k_e = \frac{\Delta S^\circ}{R} - \frac{-\Delta H^\circ}{RT}$	c) Thermodynamic parameters

4. Heavy Metals

Heavy metals have major environmental effects due to their properties. They accumulate in the organs of living organisms and cause a variety of diseases and disorders, which are described in Table 3 [12]. Iron, aluminum, arsenic, cadmium, copper, manganese, mercury, nickel, silver, and zinc are some of the heavy metals in waste leachate. It is difficult to decompose heavy metals and enrich them in different environmental conditions. The heavy metal in the leachate has been shown to cause secondary contamination [13].



Table 3. Sources and effects of heavy metals [12].

effects	Sources	Heavy metals
Mental disorders, anemia, osteoarthritis, hypertension, nausea/vomiting, hyperactivity, schizophrenia, insomnia, autism, stuttering, postpartum psychosis, inflammation and enlargement of the liver, heart problem, cystic fibrosis	Water pipes, copper water heaters, frozen vegetables and canned vegetables using copper to produce ultra-green dye, hot water heaters with instant gas, hormonal pills, pesticides, insects Herbicides, fungicides, copper cookware	Copper
Dermatitis (inflammation of the skin), myocarditis (inflammation of the heart muscle), encephalopathy (brain injury), pulmonary fibrosis, lung cancer, nose and bone, headache, dizziness, nausea and vomiting, chest pain, rapid breathing	Silver effluent treatment plants, plating, zinc-based casting, and storage battery industries	Nickel
Skin rashes, respiratory problems, hemolysis (destruction of red blood cells), acute and renal failure, weakened immune system, kidney and liver damage, genetic modification, lung cancer, pulmonary fibrosis	Steel and textile industry	Chromium
Nausea, encephalopathy (brain injury), headache and vomiting, learning difficulties, mental retardation, hyperactivity, dizziness, kidney damage, congenital malformations, muscle weakness, anorexia, liver cirrhosis, thyroid dysfunction, insomnia, fatigue, analysis Movement of neurons, schizophrenia-like behavior (youthful insanity)	Industries such as mining, steel, automobiles, batteries, paints, pollutants caused by increasing industrialization	Lead

5. Geopolymer

Aluminosilicate, also known as alkali activating geopolymer, is a large set of quasi-ceramic materials produced by the geosynthetic reaction of aluminosilicate materials in the presence of alkaline solution at low temperatures (less than 100 ° C) [14-16]. The structure of geopolymers consists mainly of a silica-oxygen-aluminum polymer framework with alternating silica and four-sided aluminum, which is bounded in three directions and shares all oxygen atoms. Geopolymers include fly ash, dolomite, expanded clay, natural zeolite, kaolinite, and many more. Due to their interesting properties, geopolymers have been studied and considered. The tendency of geopolymers to drastically reduce the mobility of most heavy metal ions in the geopolymer structure, the rapid growth of compressive strength, acid and fire resistance, low permeability, and good resistance to freezing and thawing cycles are just a few of their characteristics. [17 - 21]. Theoretically, any alkali can be used in polymerization reactions. Most research has been on the effects of sodium (Na +) and potassium (K +) ions. Although both NaOH and KOH can be used in



the activation process, the dissolution rate was higher when NaOH was used [8]. This is due to the smaller size of Na⁺, which can better stabilize silicate monomers and dimers in solution and increase the dissolution rate of minerals. Espearham et al, concluded that KOH-activated geopolymer was superior to NAOH-activated geopolymer in long-term compressive strength (28 days) [22]. Raw materials (alumina silicate), powdered with alkaline solutions (KOH or NaOH), and sodium silicate are mixed to make geopolymers. When using ferronickel slag as raw material, a mixture of 82% slag, 6% H₂O, 3% KOH, and 9% Na₂SiO₃ is recommended to produce a homogeneous mortar. The homogeneous dough is then poured into a mold. In most cases, the samples are kept at room temperature for a short time before processing and, if necessary, cooked for 1 or 2 days at a maximum temperature of 80 ° C. The specimens are then placed in the mold for 7 or 28 days to witness the development and increase of structural bonds. Geopolymers harden rapidly and have high initial strength, and after 28 days the final compressive strength reaches 100 MPa. Because they have less porosity than cement or mortar, they have better mechanical quality than cement or mortar [23-31].

Fly ash: A common polymerization adsorbent. This substance is produced as a by-product of coal combustion in thermal power plants [32]. Fly ash is a readily available waste that has been shown to be useful in the removal of heavy metals. On the other hand, fly ash is more adsorbable when processed or activated, in which case it is called a geopolymer. Due to the low cost and availability of fly ash as the main raw material, fly ash-based geopolymers are more commercially common. There is a significant tendency to recycle waste and convert it into usable and valuable materials [33]. Coal fly ash is one of these materials. Large-scale wind ash disposal has become a severe environmental and economic problem [8]. Converting fly ash to geopolymer, which not only removes heavy metals but also helps prevent the accumulation of waste, is one way to deal with it. Dolomite has been around for more than six decades. Dolomite is a relatively inexpensive and common mineral found around the world (often found in India, Indonesia, Turkey, and China). Dolomite, which has properties comparable to limestone, is sometimes referred to as magnesium limestone in the trade. It has a crystalline structure consisting of layers of magnesium and calcium carbonate [34]. As a result, dolomite, like limestone, is useful for removing heavy metals.

6. Geopolymer

pH, amount of adsorbent, initial concentration, contact time, and temperature are all important parameters in the adsorption of heavy metals to adsorbents [35]. The following equation [19] can be used to describe heavy metal removal efficiency:

$$\text{Removal efficiency}(\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (1)$$

In this formula, C₀ (mg / L) is the initial concentration and C_t (mg / L) is the concentration at time t (minutes). The following equations are used to calculate the quantity of adsorption (mg / g) q_t at time t and the concentration at equilibrium (mg / g) q_e:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

$$q_e = \frac{(C_0 - C_t)V}{m} \quad (3)$$



pH effect: The surface charge of the solution, the degree of ionization, and the adsorbed species are all affected by pH. As the pH of the solution rises to a certain point, more metal adsorption occurs, then diminishes as the pH climbs further. The pH equation is written as follows:

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

Concentrations of protonated and non-protonated surface groups are denoted by [A-] and [AH] and carbonyl groups are represented by pKa equilibrium constants. According to the studies of Al-Zboon, K et al, The adsorption effect increases from 1% to 90.66%, because the pH of the solution increases from 1 to 5 and then decreases significantly at pH = 6, as a result, pH = 5 is determined as the zero point load [18].

Effect of adsorbent amount: One of the most important factors affecting the absorption capacity of heavy metals by adsorbents is the amount of adsorbent used. Usually, as the amount of adsorbents increases, the adsorption capacity increases to the allowable level. If the amount of adsorbent increases, the adsorption capacity will be constant. In his study, Wang examined the amount of adsorbent from 0.5 g to 2.0 g and observed that copper removal increases with an increasing amount of adsorbent [5].

Effect of initial concentration: Adsorption rate is greatly affected by the initial concentration of heavy metals. In general, with an increasing initial concentration of heavy metals, the adsorption capacity also increases. An important force is the effect of the initial concentration to overcome all mass transfer resistances between solid and water phases. Many studies have shown that the removal efficiency of heavy metals is proportional to their concentration and with increasing initial concentration, the removal efficiency decreases [36]. The interaction of the factor group between the solution and the adsorbent surface causes adsorption capacity if adsorbed on the adsorbent. To maintain balance, a certain period of time is required, after which the absorption process is completed. Cadmium removal using a zeolite-based geopolymer takes 7 hours to reach equilibrium contact time [3]. On the other hand, the contact time of fly ash-based geopolymer to remove lead to reach equilibrium is 120 minutes and then remains constant [18].

Temperature effect: The nature of the being heat catcher or exotherm is determined by the adsorption equilibrium, which is influenced by the temperature used. The adsorption capacity of adsorbents increases with increasing temperature. This is due to the activation of the adsorbent surface and the expansion of pores. According to Javadian research, cadmium removal increases when the temperature is between 25 and 45 degrees Celsius [3].

7. Conclusions

Geopolymers' usefulness in wastewater treatment has just recently been investigated. Fly ash has attracted the most attention in the removal of heavy metals among other geopolymer adsorbents since it is a cheap and readily available waste. The Langmuir and Freundlich isotherms are commonly used to describe the adsorption capacity of adsorbed heavy metals. pH, adsorbent quantity, starting concentration, contact time, and temperature are all factors that affect adsorption capability. The adsorption capacity of a specific point before fixation is typically increased by increasing the amount of adsorbent, contact time, and initial concentration. Some compounds and their absorption, however, may differ. According to the studies, using geopolymer adsorbents as a



substitute for pricey activated carbon is effective in extracting heavy metals from wastewater. The majority of research is focused on the treatment of industrial wastewater rather than leachate. In addition, only a small amount of study has been done on geopolymer adsorbent combinations.

8. References

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