International Journal of Science and Research (IJSR)
ISSN: 2319-7064
SJIF (2022): 7.942

Brief Study of Clay as an Adsorbent of Metals in Aqueous Medium

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Abstract: ***Heavy metals are discharged into water from various industries. They are found to be toxic to human and aquatic animals even at low concentration and the removal of heavy metals from wastewater is a serious problem. So clay is used as an adsorbent for the removal of heavy metals from wastewater because of its low cost, availability and eco - friendly nature by using different methods. Intercalation and pillaring of clay minerals are chemical processes through which modification could be achieved and also, activation, structural transformation and disruption of clays could be achieved by thermal treatment. In the present study adsorption properties of calcined clay minerals are discussed in comparison with their raw clay.***

Keywords: Heavy metals, wastewater treatment, clay adsorbent, calcined clay, adsorption properties.

1. Introduction

Clay and Clay Minerals

The term "clay" refers to a naturally occurring fine grained soil materials containing clay minerals. Clay is a soft, moist, earthy materials which is made by the decomposition (breakdown) of rocks through the action of weathering, which is generally develop plasticity when wet, due to a molecular film of water surrounding the clay particles, but become hard, brittle and non - plastic upon drying or firing [1]. Most of the pure clay minerals are white or light - coloured, but natural clays show a variety of colours from impurities, such as a reddish or brownish colour from small amounts of iron oxide [2].

Clay is widely distributed all over the world and contains a large amount of different types of oxides such as Al and Mg oxides. Such soils have strong physical and chemical adsorption capacity due to the soil particle with large surface area, and carry a negative charge [3]. Clay is the oldest known as ceramic materials [4].

Composition of Clay Minerals

The clay minerals constitute nearly 40% of the minerals in sedimentary rocks of the crust of the earth. Half of these materials belong to a single species illite. The other half consists of montmorillonite, chlorite and mixed layer chlorite - montmorillonite, kaolinite, septachlorite, attapulgite and sepiolite in the order of relative abundance. The kaolinite is the most common clay minerals need special attention. The outline of the kaolinite structure was first proposed by Pauling [1930] and was later developed by successive workers.

Kaolinite is a 1: 1 layered silicate with a tetrahedral Si_2O_5 and an octahedral sheet with Al^{3+} as the octahedral cation. In kaolinite, the charge in each layer is completely balance and therefore no interlayer ions are necessary for charge balance. However, in some samples of kaolinite, substitution of octahedral Al^{3+} with Fe^{2+} and/or Ti^{4+} has been reported.

The structural formula of kaolinite is given as $Al_4Si_4O_{10}(OH)_8$ with an average composition of 46.5% SiO_2, 39.5% Al_2O_3 and 14% H_2O. Successive layers in kaolinite are superimposed on each other in a way such that the O - atoms at the base of one layer form pairs with OH - groups at the top of the outer layer [5].

Uses of Clay

At present, the world population increases and for that reason, the demand of water will gradually increases and the need for improved water quality urgent [11]. Water pollution problem are caused by many industrial activities such as mining operation, industry fertilizer, metallurgy, etc. introduce heavy metals into the environment via their waste influents [12].

Heavy metal ions in water are toxic to human and aquatic animals even at low concentration become a severe environmental problem. They are usually stable and non - biodegradable within the ecosystem [13].

The duration (persistence) of heavy metals, such as Cu (II), Hg (II), Pd (II), Cd (II) and Cr (IV) in water, environments has led to multiple health problems in humans and animals [12].

There are various treatment techniques including adsorption, precipitation, ion exchange and reverse osmosis have been employed to eliminate or reduce these toxic heavy metal concentration in water and waste water.

For the removal of toxic heavy metals, the adsorption process is the most common one and is widely used for the removal of heavy metals from wastewater because of its low cost, availability and eco - friendly nature. Adsorbent such as clay minerals and modified clays are efficient for the removal of heavy metal ion from wastewater [14].

Furthermore pretreatment of clay can improve the adsorption capacity of heavy metal and the natural clay used as an adsorbent in this study has an excellent adsorption capacity of 1133.10 mg^{-1} for AR88 dye. The process of clay pre treatment enhances the pore volume and the pore volume distributions of the surface and subsoil's differ from the other clay soils examined in that the clay pore peal is

centered around 6 nm, and the clay pre treatment also enhance the surface area, and the amount of surface acidsites. In this way, clay minerals can become more organophilic and hydroprobic, also enhancing the adsorption capacity for non - ionic organic substance after treatment or modification.

In this regard, we appreciate clay and modified clay as environmentally safe adsorbents.

2. Materials and Methods

There are many forms of treatment that can modify clay, with a goal to increase the adsorption capacity of raw clay materials. However, researchers have also present results that treatment or modification did not increase the adsorption properties. In this review, we summarized the different techniques that have been implored for modification and synthesis of novel clay materials.

Among the clay modification techniques, chemical treatment and physical method (thermal treatment) are discussed below -

Chemical Treatment

This process involves the use of both organic and minerals acid, base (alkalinization), salts and metal oxides for modification of clay achieved through pillaring and intercalation. Chemical treatment is a widely used technique for activation and fictionalization of clays.

Physical Method (Thermal Treatment)

Physical method of clay modification could be achieved either by calcination or microwave heating. These methods are applied in order to disrupt the chemical structure of the clay minerals. The clay material is usually subjected to a very high temperature capable of breaking some chemical bonds and altering the arrangement of molecules in the lattice structure of the clay.

Calcination

This involves the exposure of the materials to high temperature capable of breaking the bonds of the components contained in the substance. This can also be referred to as conventional heating method of activation. Clays are strongly dependent on temperature, and the high temperature treatment of clays destructs the crystalline structure of the clay minerals. Conventional heating technique have been regarded as one of the most adopted for the preparation and activation of adsorption materials among others in which heat is transferred via convection, conduction and radiation mechanisms. In the conventional heating of materials, the outermost parts experience the energy before the interiors, stimulating a thermal gradient and the inner and the outer surface of individual particle. This result to heterogenous microstructure of materials at high heating temperature, high energy consumption and time wasting as limitations compared to other techniques. It could also result to overheating of the materials causing substrate and reagent degradation.

3. Literature Review

Adeyemo A. A. et. al., (2017) had studied the effective use of the sorption properties (high surface area and surface chemistry, lack of toxicity and potential for ion exchange) of different clays as adsorbents for the removal of different types of dyes (basic, acid, reactive) from water and wastewater as potential alternatives to activate carbons has recently received wide spread attention because of the environmental - friendly nature of clay minerals and discussed about the efficiencies of raw and modified/activated clay adsorbent and ways of improving their efficiencies to obtain better results and also acid modified clay resulted in higher rate of dye adsorption and an increased surface area and porosity (49.05 mm^2 and 53.4%) and base - modified clay has lower adsorption capacities, while $ZnCl_2$ - modified clay had the least rate of adsorption with a surface area of 44.3 mm^2 and porosity of 43.4%. the aim of the study is to explores the grey areas of the adsorption properties of the raw clays and improved performance of activated/modified clay materials with particular reference to the effects of pH, temperature, initial dye concentration and adsorbent dosage on the adsorption capacities of dyes and also various challenges encountered in using clay materials are highlighted and a number of future prospects for the adsorbents are proposed.

Rao R. A. K. et. al., (2012) have studied the adsorption studies of Cd (II) on ball clay and reported that ball clay can be used as an effective adsorbent for the removal and recovery of Cd (II) from aqueous solution then the adsorption capacity was studied by heating it at different temperature and was found that the sample heated at 200^0C showed maximum adsorption capacity toward Cd (II) ions. This research was focused on the effect of pH, time, temperature, adsorbent doses and initial Cd (II) concentration by batch experiments and the equilibrium data of Cd (II) adsorption were explained well by Langmuir and Freundlich adsorption isotherms. The kinetics data for the adsorption process obeyed pseudo - first - order and pseudo - second - order models at lower initial concentrations of Cd (II) and Cd (II) desorption was performed using batch process with various desorbing solutions and 100% desorption was achieved with HCl solutions.

Chouikhi N. et. al., (2019) had studied the adsorption of CO_2 on modified clay minerals and found that the clay minerals are inexpensive materials, with an abundant availability around the world and it can also used as an inexpensive source to synthesize economically competitive zeolites, which present a high microporosity and high CO_2 adsorption capacity. Clay is efficient for several applications such as the adsorption of CO_2 and thanks to its chemical and morphological variety and also reported that the Pillared clays and clays modified by the hydrothermal treatment show an important specific surface area and pore volume and the improvement of the textural properties also leads to an improvement in the CO_2 capture capacity.

Xei S. et. al., (2018) had studied the adsorption and desorption behavior of Cu (II) in silty clay, a series of experiments were conducted in this study and several impact factors including pH, organic matter, temperature and

coexisted ions Zn (II) were considered and it was found that the adsorption process reached equilibrium and the data can be fitted well by the Elovich model and the double - constant model for the kinetic sorption process. The isothermal adsorption results showed that the adsorption rate reached a peak value when the initial concentration was about 20mgL^{-1} and the decrease of H^+ can increase the adsorption activity of Cu (II) and reduce the ability of the desorption of Cu (II) ions. And then the thermodynamic analysis revealed that the adsorption process of Cu (II) was spontaneous and endothermic. The Freundlich model agreed the best with the experimental data compared with other three models (Langmuir, Temkin and Henry adsorption models) were used for analyzing the adsorption isotherm of Cu (II) and the result of the competitive adsorption exp. indicated that the competitive capacity of Cu (II) was greater than the Zn (II) in low - permeability media such as silty clay and the existence of binary metals can weaken the adsorption force between the single metal and the soil surface.

Shiqing Gu et. al., (2019) had studied the clay minerals adsorbents for heavy metal removal from wastewater and was found that clay minerals have been used as good adsorbent attributed for the existence of different types of active sites located at surface, such as ion - exchange sites, Lewis acid sites and Bronsted sites and this study introduced clay - based adsorbent in details for the removal of heavy metals from aqueous media, and different mechanisms of the corresponding adsorption process were discussed.

Lukman S. et. al., (2013) had studied the adsorption and desorption of heavy metals onto natural clay material and found that the initial pH plays a significant role in competitive adsorption and desorption of the investigated heavy metals onto clay minerals and the local clay used in this study has proved to be a candidate adsorbent for heavy metal removal in waste water streams.

Renu et. al., (2017) had studied the heavy metal removal from wastewater using various adsorbents and reported that the adsorption process is widely used for the removal of heavy metals from wastewater because of its low cost, availability and eco - friendly nature and both the commercial adsorbents and bio adsorbents are used for the removal of heavy metals from wastewater, with high removed capacity. The aim of the study is to compile scattered information on the different adsorbents that are used for heavy metal removal and to provide information on the commercially available and natural bio adsorbents used for removal of chromium, cadmium and copper, in particular.

Adekeye D. K. et. al., (2019) had studied the clay soil modification techniques for the adsorption of Heavy metals in aqueous medium and found that clay minerals have shown excellent potential for the removal of metal pollutant without any modification, but in many studies, their removal capacities were improved through different modification techniques. Treatment techniques such as chemical, physical (thermal), mechano chemical and fortification with organic biomasses and composities have been successfully applied to modify clay soils with the aim of improving the heavy metals adsorption capacity of the soils.

Mohammad K. U. et. al., (2017) had studied the adsorption of heavy metals by clay minerals, with special focus on the past decade and found that clays and their minerals are abundant and cheap materials successfully used for decades as an adsorbent for removing toxic heavy metals from aqueous solution and presented an outline of the structure, classification and chemical composition of various clay minerals, and a descriptive analysis of their adsorption behavior and confirmed that both natural and modified forms of clay minerals have excellent feasibility in removing different toxic aquatic metal pollutants.

Sarkar B. et. al., (2019) had studies the modified clay minerals for environmental applications and found that the physicochemical properties of clay minerals like charge density, surface area, ion exchange, and swelling capacity make the materials useful for low cost remediation of contaminated aqueous systems and soils and modification or functionalization of clay minerals can achieve a defined property of target a specific type of contaminant.

4. Conclusion

Clay is an inexpensive, locally available, and effective adsorbent materials and many types of heavy metals are discharged into water from various industries. They can be toxic or carcinogenic in nature and can cause severe problems for humans and aquatic ecosystems. Thus, the removal of heavy metals from wastewater is a serious problem. The aim of our study is to use a clay adsorbent for the removal of heavy metals from aqueous solutions by using two types of methods such as chemical method and physical method (thermal treatment), chemical method including pillaring and intercalation, physical method including calcination and microwave heating. In future, a continuous effort is also needed for the removal of heavy metals from wastewater by using various types of adsorbents to clean up contaminants in the environment.

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