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Adsorption of heavy metals on bentonite and modified bentonite clay, factors, kinetic and thermodynamic studies / a review

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Abstract- This review dealt with environmental pollution with a number of pollutants, especially pollution with heavy elements, and because of its significant effects on the environment in general and on humans in particular, despite its presence in low quantities. How to treat it in several ways, but the most effective and least economical is adsorption technology considering that heavy elements are adsorbed materials used Bentonite clay as the adsorbent surface to remove it from aqueous solutions. Several studies also dealt with the possibility of improving the adsorption properties of bentonite clay by modifying and activating it with several experimental materials and conditions. Also, they discussed the possibility of applying the most famous kinetic models and isotherms models in addition to calculating thermodynamic functions for adsorption of heavy elements on bentonite or modified bentonite clay

Keyword : Bentonite ,Heavy metal , Adsorption .

1. Introduction

Although nature, with all its components, contains water, soil, air, and plants on a small percentage of heavy metals, this leads to a growing concern and danger to the environment and human health, due to the extensive waste and uses of chemicals in various industries. [1, 2, 3]. As a result of these industries, wastewater is exposed to pollution with a wide range and with different concentrations of heavy metals [4]. Here, the possibility of heavy metals entering the human body directly through the food chain increases, which causes a serious health risk, especially if it is present in a high concentration that exceeds the limits permissible [5].

Heavy metals are characterized by being stable and have the ability to biologically assemble within the bodies of living organisms where this accumulation impedes the activity and functioning of vital functions in the human and animal body [6].These elements can cause many

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diseases including kidney and organ damage, nervous dysfunction, heart disease, allergies, asthma, respiratory problems, and cancer, as well as cardiovascular effects [7]. Heavy elements are found in water bodies with two images, whether in the form of free ions or in a way that is associated with organic or inorganic ligands to form coordination complexes [8].

Heavy metals pose a threat to living organisms, including humans, because they cross toxic inorganic pollutants found in soils, water bodies and groundwater, and among these elements (Pb, Cr, As, Cd, Ni, Zn and Fe).

In order to control pollution with heavy elements, different regulatory bodies have set maximum limits for the disposal of toxic heavy metals in aquatic systems In spite of this, the metal ions in the water stream are present at a much higher concentration than specified, which leads to health risks and environmental degradation, and therefore, the removal of these ions is very important to protect public health.

2- Adsorption

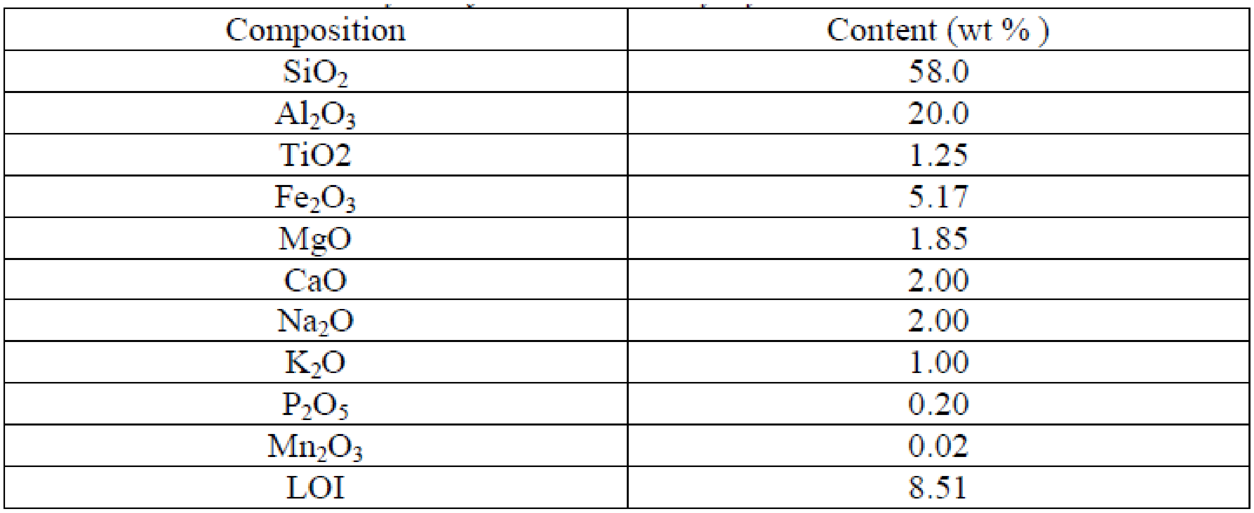
Several techniques including chemical precipitation, ion exchange, solvent extraction, electrolysis, membrane processes, and adsorption are used to remove heavy metals from wastewater [9-13]. A disadvantage of these methods or techniques is that they are costly or ineffective. Of all the suggested methods, adsorption is one of the most common methods. As it is considered an effective, economical and easy way to purify wastewater, especially in the treatment of liquid wastes. Various materials such as bio-absorbent materials, activated carbon, natural and industrial zeolites and clay minerals have been used as adsorbents to remove heavy metals from water and wastewater. Adsorption is a phenomenon occurring at the surface, which is a chemical-physical purification process as the adsorbate particles move from their solution to the adsorbent surface. The adsorption of heavy metal removal is more efficient compared to other removal methods such as sedimentation, ion exchange, or other processes. The advantages of absorbent materials include being inexpensive and available especially with natural clay available all over the world. Therefore, these absorbent surfaces are effective and highly efficient alternatives compared to traditional treatment techniques and other absorbent surfaces [15].

3-Bentonite

Bentonite is a raw material consisting mainly of montmorillonite and related clay minerals from the Smectite group, which has a large surface area per unit weight and a high cationic exchange capacity (CEC). Bentonite is known to be a good adsorbent for heavy metal ions. Organicphilic bentonite has also been used as a suitable material suitable for organic compounds [16-18]. Bentonite clay consists of a number of oxides which are listed in Table 1[19].

Smectites have a typical layered silicate structure consisting of an octahedral sheet sandwiched between two tetrahedral sheets. The interlayer space - an essential characteristics of clay minerals from this group- is easily accessible to water and another polar liquids. Smectite group minerals have a good ability to exchange cations due to the presence of aqueous cations such as Ca^{2+}, Na^{+}, K +, etc., in their surface surfaces, and these cations can be easily exchanged by heavy metals to compensate for the negative charge. A reverse and balanced process, which varies with the nature and concentration of mineral ions in the solution, the pH, and the presence of other ions in a solution that competes with heavy metals in the adsorption places.

Table 1. Component analysis of Bentonite Clay by XRF



Composition	Content (wt %)
SiO_2	58.0
Al_2O_3	20.0
TiO2	1.25
Fe_2O_3	5.17
MgO	1.85
CaO	2.00
Na_2O	2.00
K_2O	1.00
P_2O_5	0.20
Mn_2O_3	0.02
LOI	8.51

Bentonite is seen as the most efficient adsorbent for removing heavy metals (arsenic, cadmium, chromium, iron, lead and zinc) from aqueous solutions due to its natural clay properties of high surface area, low cost and good cation exchange ability, and a desire to adsorb organic and inorganic ions as many researchers have used ore Bentonite to remove heavy metals from water and wastewater. Montmoril-lonite ($Al_2O_3.4SiO_2.H_2O.nH_2O$), Silicate metal from the phyllosilicates group is the primary component of bentonite, clay minerals are groups of alumino silicate with sizes located in the colloidal part of the soil Which has a particle size of less than 0.002 mm [20, 21].

They are organized into: montmorillonite, smectite, kaolinite, illite and chlorite. It is known for its frequent use in the field of adsorption and purification because it has a coherent structure and a large surface area [22-25].

The clay soil is preferred in the adsorption field due to its high ability to exchange positive ions [26]. The composition of the slurry has a negative charge resulting from the replacement of the silicon ion (Si^{4+}) with the aluminum ion (Al^{3+}) and this leads to the giving of the acidity characteristic of bronsted on the surface of the slurry by the destruction of water molecules. The acidity characteristic increases the adsorption capacity [27].

Lewis acidity, in turn, is caused by exposure to the trivalent Al^{3+} ions after the structural rupture of the Si-O-Al bonds by the removal of hydroxyl from some of the sites of bronsted acid [28)].The bentonite retention property can be used to isolate mining waste of high $^{-1}$mineral content. According to its relatively low hydraulic portability (10^{-7} to 10^{-11} cm. S), good absorbing properties, low solubility and its ability to act in a plastic way, which makes it self-locking in certain conditions, In addition to being used as a physical barrier, it can also be used as a chemical barrier with the aim of making it difficult to spread minerals from pollution sources to water and underground bodies. The remaining filtration fluids are always produced in security burials due to the natural humidity of the stored waste. Bentonite, in conjunction with artificial bushings, can be effective in the environmental industry to avoid the spread of minerals in the environment. In addition to its very high absorptive capacities of minerals, it provides distinctive properties in terms of physical separation of waste residues buried from groundwater circulation. It acts as an efficient supplement to the synthetic bushings in insulation alternatives to toxic waste. Bentonite works along with protecting the artificial bushings financially, and reduces the risk of pollutants spreading into the environment as it is a natural lining that acts as a complement barrier.

4-Mineralogical Characterization

We will discuss here a group of studies using several techniques in the diagnosis of bentonite before and after modification, including One of these techniques is the X-ray diffraction (XRD) technique, which is used to know the crystallinity of materials and crystalline levels and their effect on the modification process, and in a study that includes modifying bentonite clays with manganese ions, where a technique was used through the Figure (1) Figure (1) shows the XRD spectra of crude bentonite clay before and after modification with Mn^{2+}. As these spectra indicated that relative changes occurred as a result of modification. A slight decrease in the peak of montmorillonite was also observed. The results of the quantitative XRD analysis indicated that their percentage of two minerals are both montmorillonite (70.24%) and quartz (21.24%). These percentages are before the adjustment for bentonite, but after the adjustment, the quantities of montmorillonite and quartz decreased from 70.24 to 66.34% and 21.24 to 17.32%, respectively. This is due to the exchange of Mg^{2+}, Na^{+}, K^{+} and Ca^{2+} cations to Mn^{2+} ions during the modification [29].

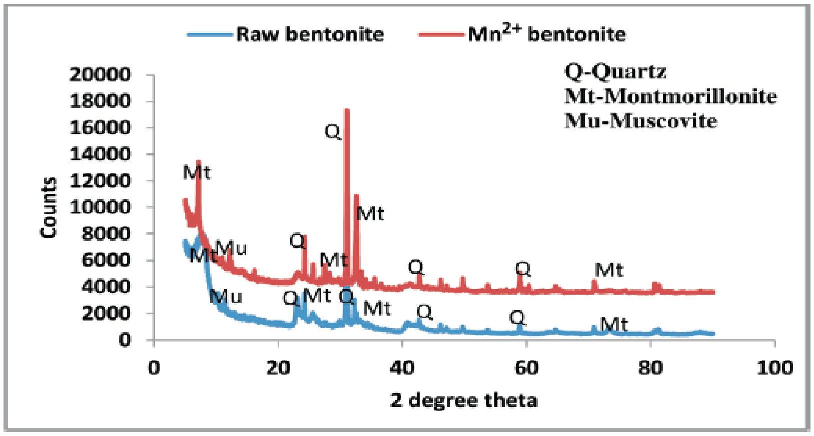


Figure1. X-ray diffraction spectra for raw and Mn^{2+}-modified bentonite clay.

Among the techniques or measurements useful in the field of adsorption and knowledge of the surface properties of adsorption surfaces is the technique of measuring the surface area by the (BET) method for adsorption- desorption of nitrogen gas represented by figure (2), Which demonstrate adsorption isotherm-adsorption ofN_2 gas for both activated and bentonite clays According to the above figure, we note that it follows the fourth class according to the classification of the IUPAC isotherm [30]. It also shows a high adsorption near the saturation pressure. The porous properties includes surface area (47,74) m^2 / g and particale size (10, 8) nm were determined from the conventional analysis of nitrogen isotherm for natural and acid activated bentonite respectiviely . Depending on the adsorption behavior of nitrogen gas according to the above figure, it can be concluded that the slurry before and after activation with acid has a porous nature at the meso-level and with a pore diameter ranging in the range (2-50) nm and this is in agreement with other studies [31, 32].

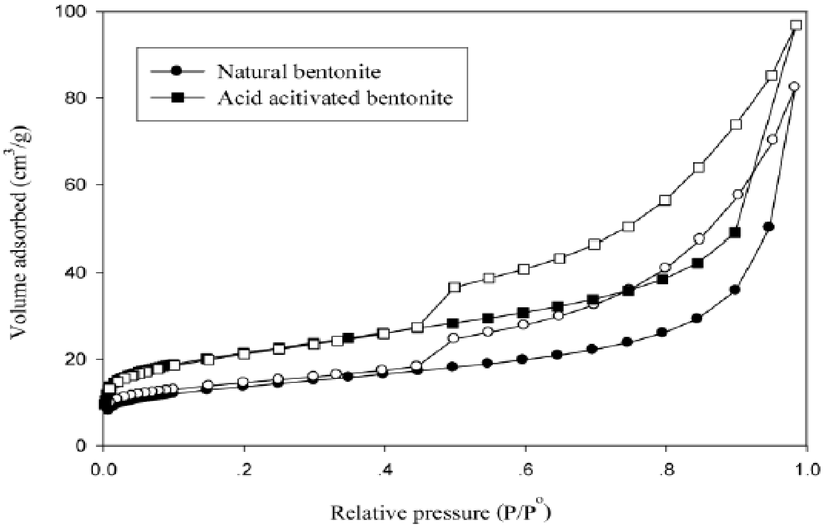


Figure2. IUPAC isotherm of N_2 at -196°C onto the before and after activation for bentonite clay.

Electron microscopes, including the scanning electron microscope, are useful diagnostic tools for adsorbent surfaces, as they provide us with information about the morphology of the surface, its dimensions, and the changes that occur as a result of the modification processes and this is what we observe in the following study which includes the modification of bentonite (BT) with ethylene glycol polymer (PEG) and diagnosed with the (SEM) technique, represented by the (figure 3A) ,Figure (3A) shows the SEM images of BT bentonite before and after polymer modification, where it is observed the presence of homogeneous tissue with microscopic dimensions with a diameter ranging from 1-4 micron. There are also needle-shaped structures that represent polymer growth in the uniform tissue (figure. 3b), indicating the inclusion of PEG particles.

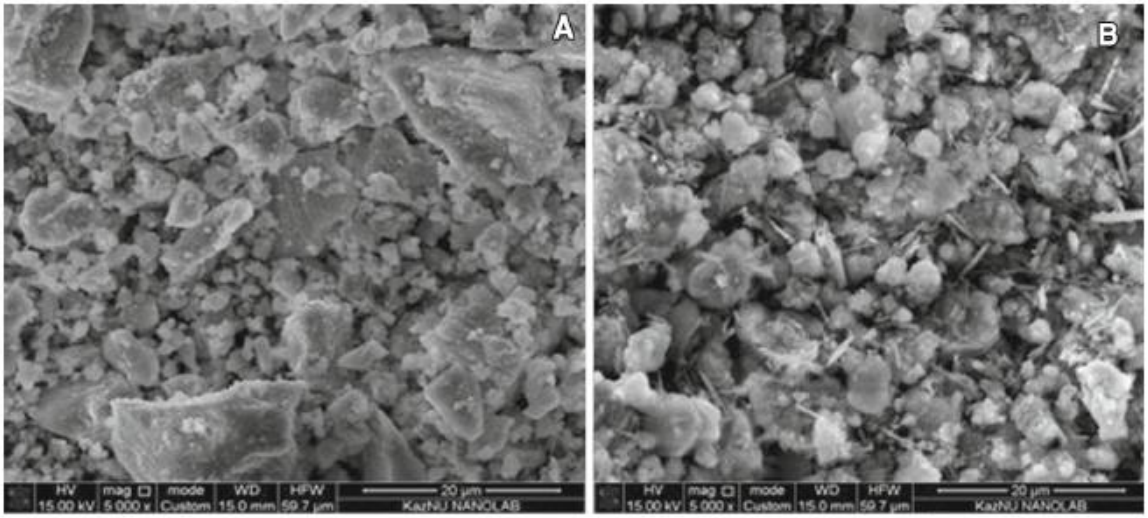


Figure 3. SEM images of both BT and BT–PEG adsorbents

It is also possible to use the infrared technique to diagnose the modified bentonite to find out the effective groups and their appearance, displacement or disappearance as a result of the modification processes as in the following study, which included a spectrum (figure 4) for bentonite before and after modification,

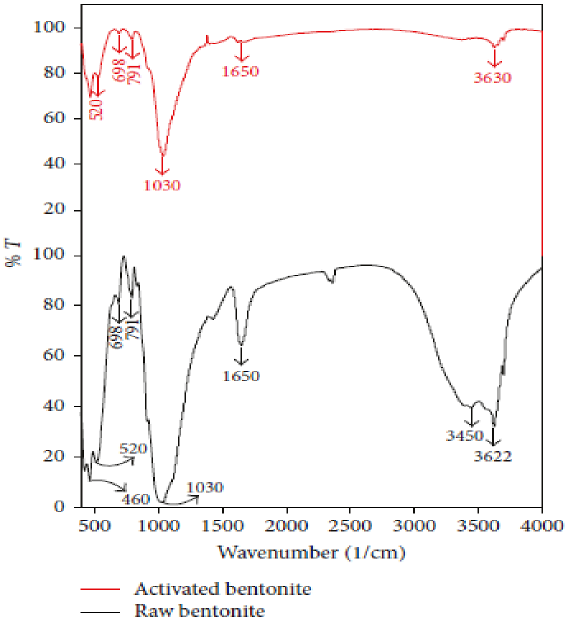


Figure 4. FTIR spectra of Jordanian bentonite before and after activation.

The natural bentonite spectrum shows peaks at 3450 and 1650 cm^{-1} which refer to the expansion and bending vibrations of the water molecule's OH groups for hydration and a peak at 3620 cm^{-1} which indicates the expansion vibration of the hydroxyl groups. There is also a strong peak at 1030 cm^{-1} due to the stretch vibration of the Si-O band.The presence of a peak at 520 cm^{-1} which is due to the stretching vibration of the Si-O-Al sphere (octahedral) and a peak at 460 cm^{-1} due to the bending vibrations of the Si-O-Si .[34, 35].After activating the bentonite with acid, we observe a decrease in the intensity of the peaks due to the expansion and flexion vibrations at 1650 cm^{-1}, which reflects the leaching of octahedral cations, such as Al^{3+} and $Mg^{2+}$from the bentonite structure, indicating the distortion of the octahedral sheet.In addition, the sharp decrease in the intensity of the peak is due to the OH-vibration at 3630 cm^{-1} and this is due to the removal of the octahedral cations. We also note a decrease in the strength of the compression at 1030 cm^{-1} due to the formation of three-dimensional networks of amorphous silica [36]. The ranges decreased at 520, 698, and 791 cm^{-1} associated with Si-O-Al vibration. This result indicates partial depletion of Al, Mg, and Fe from the clay structure indicating changes in the chemical composition. [37]. Furthermore, acid activation caused the disappearance of the stretching bands at 3450, 2360, and 1430 cm^{-1} assigned to the H-O-H stretching [38, 39].

The last method that will be presented in this review is thermogravimetric analysis (TGA) , which may be useful in diagnosing and modifying clays by providing us with information that shows the thermal stability of the studied surfaces. As a result of subjecting the raw and activated bentonite to heat treatment within the range (100-1000) °C, we obtained Figure (5). Figure 5 shows a severe weight loss of crude bentonite in the thermal range (350 - 720) °C which can be attributed to the removal of the hydroxyl group of the clay composition. While we notice that for activated bentonite there is a weight loss with a lower temperature range (410 - 645) °C, and this indicates that there is no dissolution of the clay minerals. As a result of the foregoing, we conclude that activated bentonite is more thermally stable than crude bentonite, which qualifies it to be a preferred choice for many available applications.[39].

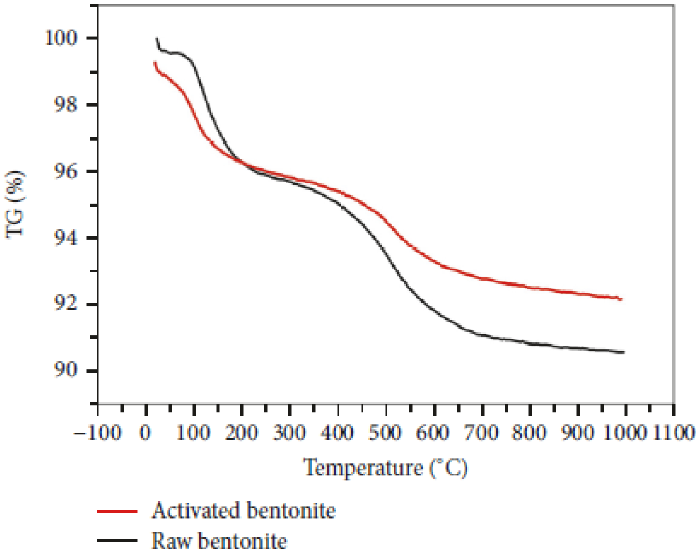


Figure 5: TGA curves of rawand acid activated Jordanian bentonite.

5-Modification of bentonite and its effect on adsorption capacity

Bentonite clay has superficial properties and the ability to ion exchange, and therefore it has varying adsorption ability to remove pollutants, especially heavy elements In order to improve this susceptibility,The quantity of heavy metal adsorbed at equilibirium (q_e) (mg/g), was determination by:

$q_e = (C_o - C_e)V/W$ ---------------(1)

where C_o and C_t are the metal concentrations (mg/L) at the beginning and equilibrium time, respectively. V is the volume of the metal solution and W is the weight of clay.

many researchers have made adjustments and activation of the bentonite surface through thermal activation or activation of various acids and bases. This is called a physical modification or chemical modification that includes the formation of polymeric, nanoparticles, or inorganic compounds with bentonite clay, So NaCl and KCl are examples of chemical activation which was used to increase a certain surface area of natural bentonite. However, much of the work did not use hydrochloric acid to revitalize natural bentonite. Hydrochloric acid is a strong acid that can improve a certain surface of natural clay. A number of researchers have studied adsorption of Pb^{2+}, Cd^{2+} and Cu^{2+}.For example, [40]studied the adsorption of Pb^{2+} and Cu^{2+} from aqueous solutions using MnO_2coated zeolite. Many studies included [41, 42] the adsorption of $Cu2^+$ using activated carbon was investigated. In another study of [43] Amberite IR-120 synthetic sulfonated resin was used To adsorb Pb^{2+}, Cd^{2+} and Cu^{2+}. Therefore, the use of these adsorbents is limited due to the high cost, so it was necessary to use alternative adsorbents that are low-cost and appropriate, including natural and acid bentonite and its ability to adsorb various minerals such as (lead, cadmiumand, copper).

Bentonite was modified with the amino acid cysteine to produce a modified cysteine bentonite (Cys - Ben). The efficacy of both modified bentonite and bentonite in adsorption of Cd (II) and Pb (II) was evaluated as indicators of heavy metals for absorption, and as a result of adsorption experiments demonstrated improved efficacy of modified bentonite adsorption is Compare us with the original bentonite ,In addition, the adsorption efficiency of modified bentonite is high for cadmium ion compared to lead ion regardless of laboratory conditions.

This research highlighted the amendment by developing an effective method for using peeled bentonite clay that is activated with thiol acid. From the results, the modified clay showed effective performance to remove major toxic ions (As^{3+}, Hg^{2+}, Cd^{2+}, and Pb^{2+}) from the water. The manufactured material is new, cheap and locally available with high absorption capacity that includes bentonite clay peeled functional peeled from Caspian, Iran. To improve absorption efficiency and denotes acid-activated bentonite (AB),The modeling clay (EAB) was peeled and then installed in toluene with the addition of a 3-mercaptopril trimethoxy silane (MPTMS) as modified (MEAB). MEAB significantly increased removal of the four target ions. This study showed thatMEAB shows identical or even better absorption capabilities compared to other

conventional absorbents and that the ability to bond heavy metal ions is about four times higher than for non-functional samples. This new functional bentonite scrub may be a good alternative to the economic advantage of getting rid of toxic, hazardous heavy metals [44].
Another study included Activate the bentonite clay with acid using H_2SO_4 and $C_2H_4O_2$ as acidic chemical agents. Use of the bentonite produced before and after activation in adsorption of iron and manganese at a temperature of 25 ° C. Both modified models showed higher adsorption efficiency than natural clay. The phenomenon of adsorption of heavy metallic clay can be illustrated on the basis of the interaction between the group of surface functions of silicate (clay) and metal ions. It is concluded that the slurry can be used as a low-cost adsorbent available locally to remove heavy metals, especially in developing countries [45].

6-Factors affecting the adsorption process

The adsorption process is affected by a number of important factors (pH, contact time, absorbent surface dose, initial concentration, temperature) which we will address through a number of studies. pH increases prefers high removal of heavy metals with increased acidity which facilitates absorption due to increased penetration of Presence of excess hydrogen ions at a low pH. When the pH of acid increases to the neutral range, the adsorption range increases.On the other hand, the more the pH increases, the more the removal pattern will shift from adsorption to removal by precipitation [46]. Therefore, the increase beyond pH 8 causes the dominant removal mechanism for heavy metals to be precipitation, electrostatic gravity, and surface complexity [47].

In a batch equilibrium study [48],For a specific study, it dealt with the batch adsorption process and focused the effect of pH on adsorption of a number of heavy elements as it showed the complete adsorption of chromium from pH 3 to 5. Zinc was also adsorption at pH more than 7, copper at pH greater than 4, and cadmium At pH (6 and 9) and lead at pH 7.7. However, no $AsO4^{3-}$ anion removal ratio has been recorded. Another factor is the adsorption dose and its direct effect on the adsorption ability due to the fact that a greater quantity of adsorbents use the number of effective sites available to increase adsorption and thus increase the adsorption efficiency. According tostudy [49], adsorbent dose of 0.5 g/l was associatedwith 85% adsorption of heavy metals. Increasing the dose to0.8 g/l increased the percentage adsorption to 92%.

Also among the factors affecting the adsorption process, as the ionic strength of the wastewater affects the adsorption of heavy metals by clay because the solution with a high ionic strength Creates a challengewith these ions with heavy metals for absorption. Therefore, the greater the ionic strength of the wastewater, the less the adsorption of heavy metals [50].

This study deals with the ability of a certain type of natural bentonite clay to remove lead from contaminated water through the adsorption process on the clay surface at a certain temperature range. A group of high concentrations (24.3, 56.85, 146.55, 269.99, 284.72, 418.86, 465.61, 658.80 mg / l) were tested from each solution mixed with 2.5g of bentonite clay for 60 minutes at a range of temperatures (20, 40, 60 ° C) and pH = 7 until an equilibrium adsorption. A very high clearance percentage was obtained (more than 98%), and the process was repeated, but at another dose (0.5 g) of bentonite. The results indicated that the quantity of lead adsorbed on bentonite clay as the mass of lead adsorbed ions ranged from 2.387 to 65.848 at a thermal range (20, 40 and 60) ° C and a bentonite clay dose of 2.5 g per 250 ml of contaminated water with the same primary lead concentrations. The amount of lead adsorbed ranged from 24.808 to 202.938 for a dose of 0.5 g at 20 ° C which indicates the effectiveness of bentonite clay in removing lead from Industrial wastewater. [51]

This pilot study was conducted to determine the optimum amount of clay to remove lead. Adsorption is carried out at ideal conditions with a pH of 6, and the initial metal concentration 50 mg / l as the amount of clay changes to 0.9 g. The results show that with an increase in the mud dose, the adsorption efficiency increases, and this is due to the increased surface area of adsorption, i.e. an increase in the number of effective adsorption sites. The optimal dose of clay that could be used to remove lead (Pb) was 0.3g / 50ml [52].

7-Contact time and Adsorption kinetics

In order to follow the mechanics of adsorption of heavy elements on the surface of modified bentonite and bentonite, researchers applied a number of kinetic models to it, including The pseudo-first order kinetic was expressed as

$$\mathrm{Ln}(q_e-q_t) = \ln q_e - k_1 t\text{------------------}(2)$$

Where q_t were the amounts of metal adsorbed on clay (mg/g) at time t and k_1 was the rate constant of pseudo-first order adsorption (h^{-1}). The slopes and intercepts of plots of $\ln(q_e - q_t)$ versus t were used to determine the pseudo-first order rate constant k_1 and q_e .

The pseudo-second order kinetic was expressed as:

$$t/q_1 = 1/k_2q^2{}_e + t/q_e\text{--------------------}(3)$$

where k_2 (g/mgh) was the rate constant of pseudo-second order adsorption. The slopes and intercepts of plots of t/q_t versus t were used to calculate k_2 and q_e.

Through a number of researches, the most well-known kinetic models of adsorption of heavy elements were applied to several forms of bentonite, where a kinetic study [7] in which second-level kinetics was followed and this result was corroborated by another study included the adsorption of cadmium (Cd) and zinc (Zn) on clay bentonite. It has a first order kinematic because of the weak value of the correlation coefficient, while the second order kinematic gave a better application because of the strength of the correlation coefficient value (R^2).The contact time for the adsorption process is influenced by the mechanics of adsorption, which consists of several stages that include the diffusion of adsorbent molecules, the formation of a film-like layer, the diffusion of the film, the entry of particles into the body inside the body, and then the association with the inner active sites.At equilibrium time, which ranges between 30 and 60 minutes, the maximum amount of adsorbent material will be determined to reach equilibrium concentrations after overcoming the different resistors[47]

A stock solution of Pb^{2+}, Cd^{2+} and Cu^{2+} was prepared by dissolving $Pb(NO_3)_2$,$Cd(NO_3)_2.H_2O$ and $Cu(NO_3)_2$ in distilled water,respectively.Adsorption of a number of heavy elements was carried out on the raw bentonite clay and the acid-activated bentonite through the batch system. This study showed the speed of adsorption occurring within the first 12 hours, which indicates the presence of a large number of vacant adsorption sites on the clay surface and then begins to slow down to the saturation or balance stage Which is within 36 hours.. The maximum adsorption is observed for the Pb^{2+} and Cd elements. 75 mg / g while Cu^{2+} had the lowest absorption on clay at about 25 mg / g. This indicates that the natural clay is selectively adsorbed to any of the minerals. A similar result was reported by Liu and Zhou [53], however, the adsorption power of Cu^{2+} in this work was higher than that of Liu and Zhou's work.

In another study, first and second class kinematic models were used to determine the mechanism for determining the rate of fluoride absorption on modified bentonite + Mn^2. The results showed that the fluoride ion adsorption on bentonite Mn^{2+} did not follow the kinetic model from the first order while the high correlation coefficient in each of the adsorbed doses. This means that the absorption of fluoride on modified bentonite clay Mn^{2+} follows the kinematic model of the second order, and this indicates that the adsorption is from the chemical type.[54]The constants were calculated from from kienatic models show pseudo-first-order model applies for adsorption of Pb^{2+} and Cd^{2+} ions on pristine BT, better correlationcoefficients were obtained for the polyethylene glycol (PEG)–bentonite (BT) composite using the pseudo-second-order model, which thus explains showthe adsorption process better [55].

8- Isothrems and Thermodynamic of adsorption

Isothermal adsorption represents the mathematical relationship between the amount of adsorbed material on the adsorbent surface at equilibrium and the concentration of the adsorbent substance when equilibrium in the solution at a constant temperature. The adsorption data were analysed with the Langmuir and Freundlich isotherm models. The Langmuir equation suggests that the sorption occurs at the solid surface that is made up of elementary sites, each of which can absorb one sorbatemolecule, *i.e.* monolayer sorption. It was also assumed that every sorption site is equivalent andthe ability of the sorbate to get bound there is independent of whether or not the neighbouring sites areccupied].The linear version of Langmuir equation is:

$Ce / qe = 1/Q_ob + Ce/Q_o + 1$ ---------------------------(4)

where Q_o is the maximum adsorption at monolayer(mg g^{-1}), Ce is the equilibrium concentration of metal (mg L^{-1}), qe is the amount of metal adsorbedper unit weight of composite, b is the Langmuir constant related to affinity of binding site (L mg^{-1}) and isa measure of energy of adsorption. A leniearizedplot of Ce / qe against Ce gives Q_o and K_L. In general for good adsorbents, high value of Q_o and low values of b are required.

The Freundlich isotherm is an empirical equation and is one of the most widely used isotherms for thedescription of multi-site adsorption where the adsorbent surface is heterogeneous in nature. Mathematically,it is expressed as:

$\ln q_e = \ln K_f + 1/n \ln C_e$ ---------------------(5)

where q_e is the amount of metal ion adsorbed (mgg^{-1}) onto chitosan biopolymer bentonite composite. The parameters of Freundlich isotherm, K_f and nindicating the sorption capacity and intensity, respectively. Linear plots of log q_e versus log C_e for the different initial metal ion concentrations gives K_f and n. The Freundlich constant nvalue indicate the favourability of the adsorption process with values < 1 for poor adsorption, 1-2 formoderately good and 2-10 represent the beneficial adsorption.

The Langmuir parameters and correlation coefficients of metal adsorption were calculated for the studied metals namely nickel and lead. Langmuir constant Q_o, represent the maximum monolayer adsorption capacity of the bentonite. The values are10.8 mg g^{-1} and 9.4 mg g^{-1} for Cd (II) and Ni (II), respectively. The Langmuir isotherm described the sorption data of Cd and Ni on bentonite and based on the maximum adsorption capacity values the sequence of metal sorption was found to be Ni (II) >Cd (II).Cu(II)has the highest K_f and n values over Zn(II), Cd(II)and Ni(II). Cu (II) with the highest n value means it has highest affinity towards the functional groups of the composite and stronger bond results in higher K_f. According to Freundlich adsorption theory, the n values between 1 and 10 indicate beneficial adsorption, and in this study the n values are more than unity for all the four metals which demonstrates the beneficial adsorption.[56]

In this study, more than one isotherm model was applied to the adsorption balance data for copper using calcined bentonite clay and sodic-treated clay, according to the correlation coefficients. It was found that the Langmuir isotherm model was better than Freundlich isotherm model. Consequently, the maximum adsorption amount according to the Isotherm Langmuir model is (1.612, 2.453) mmol / g for both calcined clay and sodium treated steel respectively, which indicates the efficiency of the adsorbed surfaces.[57]

Also, the temperature has a significant effect on the adsorption process, as with increasing temperature the amount of adsorbed material decreases, which indicates that the adsorption process is of an emitting nature of heat, and this leads to preference for adsorption at lower temperatures. As for the amount of adsorbed material increases when the temperature increases, indicating that Adsorption is endothermic and this indicates a preference for adsorption process at high temperatures. This is confirmed by experiments of adsorption of heavy metals on bentonite clay [58]. In addition, the free energy change in Gibbs decreased with increasing temperature, which indicates that absorption is preferred at a degree Higher heat.The standard Gibbs energy (ΔG) was calculated from the relation:

$\Delta G = -RT \ln K_e$------------------(6)

The values of equilibrium constant (K_e) ,The values of the entropy (ΔS) and enthalpy (ΔH) changes of thesorptionprocess were calculated by plotting of ln K_e vs. 1/T according to the van't Hoff equation:

$\ln K_e = (1/R)(\Delta S + \Delta H / T)$ --------------------(7)

The change in the free press capacity is a measure of the automaticity of the adsorption process. From the results, it was found that the negative ΔG values at 25 ° C for adsorption of elements (Cd (II) and Pb (II) are negative. This indicates that the adsorption of mineral ions on the organic bentonite is automatic, which It increases with a decrease in temperature, and this indicates electrostatic attraction between adsorption sites and metal ions. As for the entropy ΔS, which we obtained from the same study is negative for each of the metal ions, which indicates a decrease in the randomness as a result of adsorption. As for the enthalpy values ΔH (- 5.97 and -2.27) $KJ.mol^{-1}$ for Cd (II) and Pb (II) respectively indicates that the adsorption nature of both elements is exothermic.

The thermodynamic parameters were calculated for the adsorption of copper and nickel on bentonite clay **,** the value of the ΔH is positive value, that indicates, the adsorption is endothermic. Also, the results are shown with increasing temperature, the ΔG decreases which indicatethat the adsorption process is favorable at high temperature. The value of the ΔS is positive values, which indicate, the process becomes more random at the interface of the clay - metal ions solution through the adsorption for metal ions on clay [58].

Conclusion

We conclude from this study the great potential of bentonite and modified bentonite clay and the adsorption of heavy elements because of the properties of clay that belong to its porous structure in addition to the ability to ion exchange and large surface area and these lead to many effective adsorption sites. Also, the possibility of applying the frendlich and langmuir isotherms for a number of studies also this study demonstrated the possibility The application of second order kinetics is greater than the first order kinetics as shown by thermodynamic functions for the spontaneity adsorption process of heavy elements on the modified and activated bentonite or bentonite clay accompanied by heat emission and an increase in randomness for a number of selected studies.

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