Adsorption of Pollutants Using Different Types of Geological Materials: a review

Çeşitli Jeolojik Materyaller Kullanılarak Kirleticilerin Adsorpsiyonu: Yapılan Çalışmalar Üzerine Bir Araştırma

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Adsorption of Pollutants Using Different Types of Geological Materials: a review

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Abstract

The increase in the amount of pollutants in the ecosystem led to the search of low-cost adsorbents. Despite the effective capacity of conventional adsorbents, such as activated carbon, attention has been directed to adsorbents that are naturally accessible due to their low cost of removing contaminants. This study is a survey of research on the ability of geological materials and modifications to adsorb ionic metals, heavy metals, organic compounds and pharmacological contaminants. Geological materials such as bentonite, kaolinite, montmorillonite, zeolite and calcite are effective in removing pesticides, heavy metals and antibiotics from water and wastewater.

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Öz

Ekosistemdeki kirletici miktarındaki artış, düşük maliyetli adsorbanların araştırılmasına sebebp olmuştur. Aktif karbon gibi geleneksel adsorbanların etkin kapasitesine rağmen, kirletici maddeleri giderimlerinin düşük olmasına rağmen doğal olarak erişilebilen adsorbanlar dikkat çekmektedir. Bu çalışma, farklı jeolojik malzemelerin iyonik metalleri, ağır metalleri, organik bileşikleri ve farmakolojik kirleticileri adsorbe etmesi ile ilgili yapılmış çalışmaların değerlendirilmesi üzerinde bir araştırmadır. Bentonit, kaolinit, montmorillonit, zeolit ve kalsit gibi jeolojik malzemeler; pestisitleri, ağır metalleri ve antibiyotikleri su ve atıksudan uzaklaştırmada etkilidir.

1. INTRODUCTION

In our days the industrial development and human activities leads to increased pollution of environment, which subsequently influence the human health. The industrial activities cause huge amount of wastes and were discharged into soils, air and water systems [1]. Our surrounding environment usually contains many pollutants such as heavy metals [2], cationic and anionic ions, oil [1], dyes [3], gases and organics [4], which have poisonous and toxic effects on ecosystems. Removal of these contaminants requires cost effective technologies. Adsorption has long been considered as a highly efficient and low cost approach for pollution control [5]. Adsorption is the separation process in which certain components of a gaseous or liquid phase are selectively transferred to the surface of a solid adsorbent [6]. In most cases, the adsorption behavior towards a broad variety of adsorbate is well known, and recommendations for application can be derived from scientific studies. According the type of attractions between adsorbate

and adsorbent, it could be defined 4 types of adsorption [7]: Exchange (ion exchange), Physical, Chemical and Specific adsorption.

Physical adsorption is the main principle of applications, because its incremental applications and employment for controlling pollution in air are water. However, it is characterized by low enthalpy values (20– 40 kJ mol-1), due to weak Vander Waals forces of attraction. The activation energy for physical adsorption is also very low and hence it is practically a reversible process [8] which could be affected by many factors such as, temperature: Pressure, Specificity, and nature of adsorbate and the surface area of adsorbent, where the extent of adsorption increases with the increase of surface area of the adsorbent. Hence finely powdered metals and porous substances having large surface areas perform well as adsorbents. Various adsorbents have been developed for the removal of contaminants from wastewater, polluted air and soil. One may say that most of the contaminants can find proper adsorbents for their environmental remediation.

Historically many adsorbents were studied for the removal of contaminants from affected environments, such as apple pomace and wheat straw [9], activated carbon, clay and zeolite. Activated carbon has been successfully used for pollutant treatment and is the most widely used adsorbent due to its high capacity of adsorption of organic materials [10] and its effectiveness and versatility [11]. However, due to it being a limited natural resource, slow adsorption kinetics and low adsorption capacity of bulky adsorbate because of its microporous nature, disposal problems and also the high cost and difficulty of regeneration, a search for cheap, effective adsorbents derivatives has becomes important [12].

Attention has been focused on the various natural adsorbents such as zeolites, clay, which are locally available and have the effective removal capacity of contaminants at low cost [13]. Zeolite used for de-fluoridation in countries like India, Kenya, Senegal and Tanzania was Nalgonda technique. The removal of fluoride by raw red soil, raw Bauxite, raw bentonite, kaolinitic clay and raw marine sediment were also applied. Additionally, the removal of zinc by different mineral adsorbents including, raw bentonite, clinoptilolite, chabazite, vermiculite, montmorillonite, zeolite and clays were evaluated. Several adsorbents like clay and hydrotalcite, zeolites have been used to remove nitrates from water and wastewater [14].

The present work aims to summarize some examples of geological materials used as adsorbents for pollutants.

2. POLLUTANT TYPES:
2.1. Heavy metals:

The presence of heavy metals in air, soil and water is known to be harmful to living species. Mercury (Hg) has been identified to cause damage to the nervous system, kidneys, and vision. Lead (Pb) causes anemia, damage to the kidneys, nervous system deterioration, damage the ability to synthesize protein, etc. The expose of Cadmium to human cause provoke cancer, mucous membrane destruction, kidney damage, bone damage, and also affects the production of progesterone and testosterone. Arsenic (As) Causes damage to skin, eyes, and liver, may also cause cancer [15]. The WHO recommended the maximum acceptable concentration of zinc in drinking water as 5.0 mg/L [16]. Beyond the permissible limits, Zn^{2+} is toxic [17].

2.2. Dyes:

Dyes are colored compounds suitable for coloring textiles, wool, leather, paper and fibers. Today, there are more than 10,000 dyes with different chemical structures available commercially [18]. The high solubility of dyes in water results in their wide dissemination into the environment, thus making them detrimental to crops, aquatic life and human health. They may also resist light and heat, thereby reducing photosynthetic activity and negatively impacting the receiving environment [19].

2.3. Antibiotics:

Antibiotics have been proven to be powerful drugs to treat various bacterial infections, from minor to life-threatening ones [20]. The excessive use of antibiotics creates serious problems to the environment; about 30–90 % of the given dose would remain undegradable in human or animal body, largely excreted as active compound [21].

2.4. Biocides:

Thousands of biocides are available in the market, and many of them possess a broad spectrum of antimicrobial activity [15]. The disposal of waste and direct discharge of wastewater containing biocides cause serious and potentially long-lasting damage to the environment.

2.5. Inorganic Contaminant.

Fluorosis is endemic in at least 25 countries across the globe and has affected millions of people [22, 23, 24]. Fluoride is beneficial when present within the permissible limit of $1.0-1.5$ mg L^{-1} for calcification of dental enamels [25]. Similarly, excess of nitrates in drinking water causes methemoglobinemia or blue baby disease.

2.6. Gases:

The global atmospheric concentration of carbon dioxide (CO_2) has increased from 280 ppm in the pre-industrial age to more than 370 ppm now and is expected to increase above 500 ppm by the end of this century [26].

2.7. Ammonium:

Higher concentration of ammonium will cause a sharp decrease of dissolved oxygen and obvious toxicity on aquatic organisms [1].

2.8. Nitrates:

Nitrate contamination in groundwater has become an ever increasing and serious environmental threat since 1970s [27].The excessive application of fertilizers in agriculture causes the infiltration of large quantities of this ion into under ground and surface water [28]. After ingestion of plants or water high in NO^{3-}, acute poisoning may occur within 30 mins to 4 hrs. in cattle.

3. CONTAMINANTS REMOVAL BY ADSORPTION

Adsorption is one of the effective treatment methods for the removal of both organic and inorganic water pollutants. In general, natural environment-friendly geological materials such as clays, clay minerals and sandstone are considered as low cost adsorbents for removal of cationic dyes and surfactants due to their permanent negative charges and negatively ionized surfaces [29; 30].

Due to the problems mentioned previously, research interest into the production of alternative adsorbents to replace the costly activated carbon has intensified in recent years.

Zeolites and clay minerals are important inorganic components in soil. Their sorption capabilities come from their high surface area and exchange capacities. The USA, Greece, UK, Italy, Mexico, Iran, Russia and Jordan are well known for their large deposits of natural clay minerals [31].

3.1. Some Types of Clay Materials and Their Uses

Clays are distinguished from other fine-grained soils by differences in size and mineralogy. Geologists and soil scientists usually consider the separation to occur at a particle size of 2 μm (clays being finer than silts); sedimentologists often use $4-5$ μm and colloid chemists use 1 μm [32].

Depending on the academic source, there are three or four main groups of clays: kaolinite, montmorillonite – smectite, illite and chlorite. There are approximately 30 different types of ''pure'' clays in these categories, but most ''natural'' clays are mixtures of these different types, along with other weathered minerals. In addition, this choice of minerals provided various arrangements of aluminol and silanol surface hydroxyl sites [33].

3.2. Bentonite:

Bentonite is an absorbent aluminium phyllosilicate, which is essentially impure clay consisting mostly of montmorillonite. There are different types of bentonite, each named after the respective dominant element, such as potassium (K), sodium (Na), calcium (Ca) and aluminium (Al). Bentonite is usually formed from weathering of volcanic ash, most often in the presence of water. Bentonites have excellent rheological and absorbent properties [34]. For industrial purposes, two main classes of bentonite exist:

sodium and calcium bentonite. Sodium bentonite expands when wet, absorbing as much as several times its dry mass in water. Because of its excellent colloidal properties [35], it is often used in drilling mud for oil and gas wells and for geotechnical and environmental investigations. Calcium bentonite is a useful adsorbent of ions in solution [36], as well as fats and oils, and is a main active ingredient of fuller's earth, probably one of the earliest industrial cleaning agents [37]. Bentonites are environmentally safe providing dust abatement procedures which are used in processing and handling [34]. As far as adsorptive properties are concerned, bentonite clay has an overall neutral charge; it has an excess negative charge on its lattice and is characterized by a three-layer structure with two silicate layers enveloping an aluminate layer.

The adsorption of Zinc ions by raw bentonite was studied by Hajjaji and El Arfaoui, it has been detected that the adsorption capacity of Zn ions by Bentonite is about 1.1 mmol/g of bentonite and the best-fit isotherm model was Langmuir [38]. Acid-activation of the bentonite reduced the maximum uptake of Zn ions by 95% and the best-fit model of the isotherms was Dubinin–Radushkevich.

Polyacrylic acid–organobentonite nanocomposite (PAA–Bentonite) was synthesized, characterized and its performance was tested for the sorption of Pb(II) ions from aqueous solutions. The maximum sorption capacity of the nanocomposite was 93 mg g^{-1} which was approximately twice as much as that of untreated Bentonite (52 mg g^{-1}). The results also showed that PAA – Bent sorbed Pb very rapidly and a pseudo-equilibrium condition reached within 30 min. H. R. Rafiei et al concluded that PAA –Bent nanocomposite represents a new sorbent for efficient and fast removal of Pb ions from aqueous solutions, which may contribute to the improvement of waste water treatment and storm water filtration at the urban/watershed interface [39].

The adsorption capacity of copper and nickel ions waste effluent at different temperatures by bentonite from Saudi Arabia was studied. It was found that, the adsorption capacity of bentonite clay increase with temperature. In addition, the maximum capacity was 13.22 mg/g at 20°C for copper as a single. For nickel ions, the maximum capacity was 9.29 mg/g at 20°C [40].

According to the results obtained in the adsorption process study of Cd (II) and Cr (VI) on natural bentonite provided by Mahfoud Barkat et al, it was concluded that the natural Algerian bentonite could be an effective and low-cost adsorbent for the adsorption of Cd and Cr ions from aqueous solutions [41]. According to the study results, the adsorption is rapid and maximum efficiencies adsorption achieved in 120 min and the pH of solution has a positive effect, however, the temperature has an inverse effect on adsorption. The optimum conditions were found at pH 6 and 5 for Cd (II) and Cr (VI), a concentration of 50 mg L^{-1} and temperature 293.15 K. According the authors, Langmuir and Freundlich, equilibrium isotherms were used to describe the adsorption of Cd (II) and Cr (VI). Langmuir model has better correlation coefficient than Freundlich model. Thermodynamic analysis showed that the adsorption process was exothermic and spontaneous in nature. The sorption capacity of bentonite was comparable to the other available absorbents, and it was much cheaper.

The effect of the contact time on the removal of Methylene blue from aqueous solutions using acid-activated Algerian bentonite revealed that the Methylene blue adsorption was fast at the initial stage of the contact period, but became slower near equilibrium (120th–200th min). The removal efficiency of Methylene blue was minimum at pH = 3 (55.48 %) and reached maximum (91.65 %) for a pH value of 10 in the first 5 min of the adsorption process. The dye uptake was found to be relatively small at low pH values; however, increase in the pH values by 4–5 units increased the rate of adsorption considerably [42]. The adsorption capacities of the clay increased with increasing contact time and initial concentration, although it remained constant after 30 min for 10, 20 and 30 mg L^{-1}.

Raymond et al investigated Acid Green 25 removal from wastewater by organo-bentonite [43]. The so-called "organo-bentonite" was obtained by modifying the raw bentonite by mixing 10 g of bentonite with 100 ml of cetyl trimethylammonium bromide (CTAB) solution, which later employed as adsorbent for Acid Green 25 removal. The capability of surfactant modified-bentonite for adsorption of dyestuff from aqueous solution was investigated. Isotherm and kinetic experiments were carried out. It was reported the Maximum adsorption capacity of Acid Green 25 by organo-bentonite 3.723 mmol/g.

In Turkey, the removal of Reactive Red 120 (RR 120) from aqueous solutions using cetylpyridinium modified Reşadiye bentonite (CP-bentonite) was investigated with particular reference to the effects of

temperature, pH and ionic strength on adsorption [44]. It was reported that the structural arrangement of cetylpyridinium ions in the CP-bentonite sample as well as the pH, temperature and ionic strength of the bulk solution influenced the adsorption of RR 120 dye from aqueous solutions by CP-bentonite. The maximum Adsorption capacity of cetylpyridinium-bentonite was 81.97 mg/g.

In Taiwan and Indonesia, the Adsorption of Acid Blue 129 from Aqueous Solutions onto Raw and Surfactant-modified Bentonite was investigated per different temperature conditions. It was approved that the Adsorption capacity of bentonite 0.76 mmol/g, and for CTA bentonite 2.76 mmol/g [45].

In Turkey study provided by Gença and Dogan reported that the adsorption activity of ciprofloxacin on bentonite was much higher compared with that on activated carbon, pumice, and zeolite [46]. The highest removal efficiencies were calculated as 91,87 for bentonite at 20 mg/L initial concentrations. Thermodynamic of ciprofloxacin adsorption shows that adsorption is the endothermic adsorption. The negative value of Gibbs free energy change or adsorption energy $\Delta G°$ for bentonite indicate the spontaneous nature of the adsorption.

Bentonite clay was used by Fernanda Maichin and friends to adsorb and remove amoxicillin compound from contaminated water [47]. The adsorbent mixture was efficient, chemically inert, and abundant, with low cost and has a removal rate of 50% of amoxicillin in water. The adsorption processes were physical and activated depending of the temperature. The thermodynamic indicates a spontaneous, endothermic adsorption reaction with concentration results of the empirical model very close with the experimental. The adsorption modelling equations were confirmed to reduce the amoxicillin concentration from contaminated water and suggested as a possibly from common effluents from pharmaceutical industries.

Study was carried out by Mohamed El Miz et al on the adsorption of Thymol on Pillared Bentonite. Thymol (2-isopropyl-5-methylphenol, IPMP) is known for its bactericidal effect (has a lethal activity of micro-organisms) [48]. It has been shown to be an efficient acaricide molecule against the Varroa destructor, an external parasitic mite that attacks honey bee. It was reported that the Moroccan bentonite pillared possessed an important capacity for adsorbing thymol. The quantity of thymol adsorbed was 319.5 mg/g at pH 7.54 and showed high irreversibility desorption in water. The Freundlich isotherms were found to be applicable for the adsorption equilibrium data of thymol on pillared bentonite.

On the other hand Yan reported the removal of Pirimiphos-methyl which is a phosphorothioate used as an insecticide by using different types of bentonite from wastewater [49]. The authors have discussed the effects of bentonite types, dosing quantity, operation time, temperature, and pH value on the adsorption. The results clearly depict that the Na-bentonite exhibited the best adsorption under the conditions; Na-bentonite dosage of 5%, pH 3, reaction temperature of 20°C, and stirring time of 60 min. It was found that the Na-bentonite reduced the concentration of 4-hydroxy-2-diethylamino-6-methylpyrimidin from 5, 761 mg/L to 130 mg/L, and COD (chemical oxygen demand) from 12, 500 mg/L to 4, 233 mg/L.

3.3.   Kaolinite:

The kaolinite group includes the dioctahedral minerals kaolinite, dickite, nacrite, and halloysite and the trioctahedral minerals antigorite, chamosite, chrysotile and cronstedite, with a formula of $Al_2Si_2O_5(OH)_4$ [50]. The different minerals are polymorphs, i.e. they have the same chemistry but different structures. Kaolinite is a non-swelling clay [50; 33]. Kaolin deposits are classified as either primary or secondary. Primary kaolins result from residual weathering or hydrothermal alteration and secondary kaolins are sedimentary in origin. Kaolin is an environmentally safe material with no adverse health problems as long as the fine particle dust is controlled [34].

In Nigeria Adebowale et al [51] provided a modification of kaolinite with 200 µg mL^{-1} of phosphate and sulphate anions. The adsorption of four metal ions (Pb^{2+}, Cd^{2+}, Zn^{2+}, and Cu^{2+}) was studied as a function of metal ions concentration. The metal ions showed stronger affinity for the phosphate-modified adsorbent with Pb^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} giving an average of 93.28%, 80.94%, 68.99%, and 61.44% uptake capacity. From the desorption studies, Pb^{2+} ions exhibited very strong affinity for the phosphate-modified clay, followed by Cu^{2+} and Zn^{2+} ions while Cd^{2+} ions showed the least affinity. The increase in the effective cation exchange capacity from 7.8 meq/100 g for the unmodified clay to 13.5 meq/100 g for the phosphate-modified clay supported this fact. The order of desorption was: Unmodified>sulfate - modified>phosphate - modified clay.

Adsorption of Pb(II), Cu(II), Fe(III), Mn(II) and Zn(II) by sorption on kaolinite clay was investigated in Egypt. According the study results, Kaolinite clay is considered as a good ion exchanger since it is easily available at low cost and high capacity. Data show that kaolinite clay favourably adsorbs the current heavy metal ions and their adsorption are belonging to Freundlich isotherm model [52].

P-Aminoazobenzene (PAAB) is a sort of the carcinogenic aromatic amine which is commonly used as the intermediates of azo dyes. Qingfeng, Hanlie and Xiaoling [53], investigated the adsorption of PAAB on kaolinite in aqueous solution under different pHs, temperature and ionic strength. The adsorption of PAAB was found to increase with decreasing pH and ionic strength. The change in free energy ΔG after PAAB adsorption at pH 1.4 and 4.0 is -4.33 and -2.89 kJ/mol, respectively. The negative ΔG value indicated that the adsorption of PAAB on kaolinite is a spontaneous and favorable process. The enthalpy change (ΔH) at pH 1.4 is -6.93 kJ/mol, compared to -8.73 kJ/mol at pH 4.0, suggesting that the interaction between the adsorbent and the adsorbate molecules was physical rather than chemical.

Natural Raw Kaolinite clay was used by Kayode. et al [54], as an adsorbent for the investigation of the adsorption kinetics, isotherms and thermodynamic parameters of a cationic dye Basic Red 2 (BR2) from aqueous solution. The authors reported that, more than 90 percent of dye removal was achieved by using 150 mg of the adsorbent for an initial dye concentration of 100 mgL^{-1}. Due to strong electrostatic interaction between BR2 and Natural Raw Kaolinite, the pseudo-second-order very well predicted the behaviour of adsorption at different dye concentrations and the intraparticle diffusion models (up to 10 min) played a significant role, but it was not the main rate-determining step during the adsorption. The experimental data best fit with the Langmuir isotherm showing that the surface of the kaolinite particle in the removal of BR2 has homogeneous distribution of active sites within the clay, equal energy of adsorption and equivalent in nature. The enthalpy change (ΔH^0) for the adsorption process was -35.34 $kJ \cdot mol^{-1}$, an exothermic reaction, which did not indicate a strong chemical interaction between the adsorbed dye molecules and natural raw kaolinite. The ΔG^0 values were negative therefore the adsorption was spontaneous and the negative value of ΔS^0 suggested a decreased randomness at the solid/solution interface.

Algerian kaolins, activated by acid treatment was used by Soumia [55], for removal of anionic dyes from tannery wastewater. The adsorption of Derma Blue R67, Coriacide Brown 3J, and Coriacide Bordeaux 3B was highly dependent on the initial dye concentration, acid activation, and clay nature. A comparative study of adsorption evidences the high adsorption capacity of the three tanning dyes on the activated Kaolinite than activated Bentonite. Compared with standard Bentonite clay, activated kaolins have a good and high potential for adsorption removal of anionic dyes from aqueous solution.

In similar study Sadiq et al [56] investigated the removal activity reactive blue by Kaolin clay. The optimum conditions of adsorption were found to be: a adsorbent dose of 0.3 g in 100 mL of solution. The optimum contact time and pH were 60 min and 5 respectively. The best fit was achieved with the Langmuir isotherms. The efficiency of colour removed increase with increasing adsorbent dosage, and with increasing contact time. The removal efficiency of reactive blue was found equal to 71 % for kaolin clay.

Experimental study was carried out by Salman et al [57] using adsorption isotherms to explain the adsorption of formaldehyde on kaolin and bentonite clays. Bentonite shows a greater tendency to adsorb formaldehyde as compared to kaolin. Maximum adsorption capacity of kaolin and bentonite indicates that 1 g of kaolin can adsorb 3.41 mg of formaldehyde while in the case of bentonite, it is 5.03 mg of formaldehyde per gram. The authors concluded that instead of chemicals and other expensive treatments, non-hazardous clays like bentonite and kaolin can be used as formaldehyde removers from wastewaters and industrial effluents to overcome water pollution.

In the same aspects in Iran, Morteza et al [58] concluded in their study that existing kaolin particles in soil can retain and attenuate nitrate pollution to prevent groundwater contamination which in turn can help to achieve sustainability in groundwater use. They remarked that easy availability of various types of clay kaolin and their ability to adsorb and retain nitrate will create more interest to develop new natural adsorption method of pollutant removal from solution.

3.4.   Montmorillonite/Smectites:

Montmorillonite is a very soft phyllosilicate mineral that typically forms in microscopic crystals, forming clay [59]. Montmorillonite, a member of the smectite family, has 2:1 expanding crystal lattice. Chemically, it is hydrated sodium calcium aluminium magnesium silicatehydroxide $(Na,Ca)_x(Al,Mg)_2(Si_4O_{10})(OH)_2nH_2O$. Potassium, iron and other cations are common substitutes and the exact ratio of cations varies with source [59]. The basic structural unit is a layer consisting of two inward-pointing tetrahedral sheets with a central alumina octahedral sheet. However, some montmorillonites expand considerably more than other clays due to water penetrating the interlayer molecular spaces and concomitant adsorption. The amount of expansion is largely due to the type of exchangeable cation contained in the sample.

Researchers in Ondokuz Mayis university investigated the removal efficiency of Cu(II) from industrial leachate by biosorption of montmorillonite. The initial conditions were at pH 6, adsorbent dosage 10 mg/L, and contact time for 10 min using raw montmorillonite with the Cu(II) removal results of 80.7%. At the same conditions, removal efficiency was increased to 88.91% when modified montmorillonite was used. It was concluded, that montmorillonite can be regarded a low-cost alternative for removal of toxic metal ions from aqueous solutions[60].

Comprehensive study was carried out by He et al to investigate the interaction between minerals and heavy metals [61]. Through the selective adsorption experiment of Ca-montmorillonite, illite and kaolinite to $Cu^{2+,}$ Pb^{2+}, Zn^{2+}, Cd^{2+} and Cr^{3+} ions at certain conditions. It was reported that Cr^{3+} is most effectively sorbed by all the three minerals. Also, it can be found that Pb^{2+} shows a strong affinity for illite and kaolinite while Cu^{2+} for montmorillonite. Based on the adsorption experiment at varying pH of solution, it can be found that the amount of heavy metals sorbed by minerals increases with increasing pH of the solution.

Mercury is one of most important environmental containments. Many methods were used for assessing the influence of mercury on montmorillonite and vermiculite layers. Brigatti et all reported the adsorbed Hg amount by montmorillonite (Hg=37.7 meq/100 g) [62].

Acid activation of montmorillonite enhances the adsorption capacity of Pb and Cd, which is explained because the increasing of surface area and pore volume [63].

The batch adsorption technique for the removal of Malachite green and Fast green dyes using montmorillonite clay as adsorbent showed maximum adsorption at concentrations $3x10^{-4}$ and $6.3x10^{-4}$ M of Malachite green and Fast green dyes, respectively. 1 g adsorbent system showed optimum adsorption over varied amounts of adsorbent of 0.1–1.2 g using dye concentration of $3x10^{-5}$ M. Adsorptions of the dyes increased with increasing time and reached maximum removal at the adsorption equilibrium. Maximum adsorption capacities were obtained at 10 and 30 min for Fast green -montmorillonite and Malachite green -montmorillonite clay systems respectively [64].

The effects of adsorbent dose, initial pH, dye concentrations and temperature on Basic Blue 16 (BB16) adsorption by montmorillonitic clay was investigated by Günay et al [65]. According to the study results, the adsorption rates of the dye were very fast at the initial stages for all the four parameters tested, while it slowed gradually as the equilibrium was approached due to the reduction of available active sites on montmorillonitic clay. The adsorption capacity of the adsorbent was maximum at pH 3.6 and further increase in pH resulted in a negative effect on BB16 adsorption due to the changes in swelling properties and surface chemistry of clay with pH.

It was reported that about 40 min of contact time are sufficient for the adsorption of methyl orange (MO) on Algerian montmorillonite to reach equilibrium. In a study for the investigation of the adsorption activity of methyl orange by the Algerian montmorillonite, the influences of several parameters such as contact time, adsorbent dose, pH and temperature on the adsorption of methyl orange have been tested. Adsorption kinetics was best described by the pseudo-second order model [66].

For the removal of oxytetracycline from water by adsorption on Iraqi montmorillonite and optimisation of operation conditions, the most favourable operating conditions for oxytetracycline was found in montmorillonite content, 6.85 g/L^{-1}; oxytetracycline concentration, 1.0 mmol L^{-1}; and pH 5.5. However, it was reported that that introduction of iron in montmorillonite structure improves its performance as an adsorbent of oxytetracycline [67].

In the same direction, montmorillonite exhibits an increase in the fluoride adsorption rate at higher temperatures and this confirms the endothermic nature of the process. The adsorption process follows both Langmuir and Freundlich models. The adsorption mechanism also follows the intraparticle diffusion pattern and surface adsorption. XRD studies show changes in the crystalline nature of montmorillonite due to adsorption of fluoride on its surface [68].

3.5. Zeolite:

Natural zeolites are hydrated aluminosilicate minerals of a porous structure with valuable physicochemical properties, such as cation exchange, molecular sieving, catalysis and sorption.

The general chemical formula of zeolites is $Mx/n[AlxSiyO_2(x+y)]\cdot pH_2O$ where M is (Na, K, Li) and/or (Ca, Mg, Ba, Sr), n is cation charge; $y/x = 1$–6, $p/x = 1 - 4$. The primary building block of zeolite framework is the tetrahedron, the center of which is occupied by a silicon or aluminum atom, with four atoms of oxygen at the vertices. Substitution of Si^{4+} by Al^{3+} defines the negative charge of the framework, which is compensated by monovalent or divalent cations located together with water.

The ion-exchange behaviour of natural zeolite depends on several factors, including the framework structure, ion size and shape, charge density of the anionic framework, ionic charge and concentration of the external electrolyte solution [69, 70].

In the past decades, utilization of natural zeolites has been focused on ammonium and heavy metal removal due to the nature of ion exchange and some review papers have been appeared [71, 72, 73].

Tarek et al were studied the optimum conditions for removal of heavy metals using zeolites A and X prepared from local Egyptian kaolin and zeolite (Table 1). Metal removal was investigated using synthetic solutions at initial concentrations of 20 mg/L of individual metals (Cd, Cu, Pb, Zn and Ni) and mixture of the pre-mentioned metals with concentration of 20 mg/L for each at constant temperature and pH (25±0.1 °C and 7.5±0.2) respectively. The removal efficiency was determined at different contact time and different zeolite doses. It was reported that, the prepared two zeolite types were highly efficient in heavy metal removal due to the presence of 8 faces including nanometer pores. Optimum contact time for Cd, Cu, Pb and Zn was 30 min with both zeolite types. On the other hand, optimum contact time for Ni was 60 min for both zeolite types. Optimum dose was 0.8 g with all metals in case of zeolite X. The same trend was obtained in case of zeolite A except for Pb which has an optimum dose of 0.4 g. Tarek et al concluded, Zeolites can transfer a heavy metal contamination problem of many thousands of liters to a few kilos of easily handled solid which can be effective exchanger regeneration or can be cement stabilized or vitrified [74].

Table 1. The preparation percent for zeolite A and zeolite X.

Zeolite	Reaction composition (moles/Al_2O_3)		
	Na_2O	SiO_2	H_2O
Zeolite A	3.5	2.2	140
Zeolite X	7.8	8	200

Malamis and Katsou carried a comparative study of zinc and nickel from water and wastewater adsorption on natural and modified zeolite, bentonite and vermiculite [75]. The analysis has shown that the adsorbate type, solution pH, metal concentration and ionic strength as well as the adsorbent type and concentration are usually the most influential parameters. Solution temperature, mineral grain size and agitation speed also seem to affect the process. The presence of other ions in the solution and/or certain wastewater compounds adversely impact on the process. The chemical and/or thermal modification of natural minerals can increase its adsorption capacity. However, mineral modification is not always associated with increased metal uptake since some cases have been reported where modified minerals exhibited an inferior performance compared to natural ones. The influence of a wide pool of parameters on adsorption is also reflected by the variability in the mineral adsorption capacities for zinc and nickel uptake in the summarized scientific works.

Nurul Widiastuti reported that the natural zeolite has good performance for ammonium removal with up to 97% removal efficiency depending on the contact time, the amount of zeolite loading, initial ammonium concentration, and pH. Ammonium removal by the zeolite was fast in the initial 15 min and at least 100 min is necessary for attaining exchange equilibrium. The percent of ammonium removal increased with increase of amount of zeolite loading. Ammonium removal capacity of zeolite increases with increase of initial ammonium concentration. The ammonium removal efficiency of natural zeolite was found to be high at pH 4 to 6 when the ammonium ion was a predominant species. The adsorption kinetics is best approximated by the pseudo second order model. The adsorption isotherm results indicated that Freundlich model provided the best fit for the equilibrium data. The negative value of ($\Delta G°$) indicates the spontaneous nature of the adsorption process. The adsorption process was found to be endothermic as confirmed by the positive sign of the enthalpy ($\Delta H°$). The entropy change ($\Delta S°$) is positive indicating increasing randomness at the solid-solution interface during adsorption [76].

The adsorption capacity of tetracycline onto zeolite was reported to be increased when pH was increased from 2.0 to 5.0, and then decreased significantly. Therefor; it can be said, the effect of pH was associated with the pH-dependent speciation of tetracycline and surface charge property of zeolite. Also; it was reported that 90% of adsorption of tetracycline onto the zeolite occurred rapidly in the first 45 minutes and the adsorption equilibrium was reached about 3 hr. Moreover, Freundlich and Langmuir equations were well used to describe the adsorption isotherm, and thermodynamic analyses showed that the adsorption process was spontaneous and endothermic, and increasing temperature facilitated the adsorption. Analysis of fourier transform infrared spectroscopy showed that surface complexation between tetracycline and the aluminum atoms in zeolite was responsible for the adsorption of tetracycline on the zeolite. It seems that tetracycline adsorption kinetics onto the zeolite is the similar to Langmuir [77].

Valičková et al carried a study on the removal of Five chlorinated pesticides, i.e. hexachlorobenzene (HCHB), hexachlorobutadiene (HCHBD), lindane (LIN), pentachlorobenzene (PCHB) and heptachlor (HCH) by adsorption on granular activated carbon (GAC), zeolite (Zeo) and activated sludge (AS) [78]. The effect of contact time on the removal efficiency of studied substances was investigated. In the case of zeolite, maximum removal efficiency of 93.8 % was measured after adsorption time 0.5 h for HCHB. The next highest efficiency, viz. 92.1 % was achieved for HCH, followed by HCHBD with removal efficiency of 83.7 %, PCHB with 72.9 % removal efficiency and LIN with 25.8 % removal efficiency.

3.6. Calcite:

Calcite ($CaCO_3$) is one of the most common minerals in the environment. It is predominant in the sedimentary environment and is primarily formed at relatively shallow depth and forms rocks in both shallow and deep water settings. It is an important mineral in the aquatic environment due to its important role in regulating the pH and alkalinity.

Three different polymorphs of $CaCO_3$ are found in sediments and organisms: calcite, aragonite and vaterite. As they are polymorphs, they have different crystal structures and symmetry.

Calcite is used for a wide range of industrial purposes, e.g. paper production, building materials, agriculture, paints, plastics, ceramics, glasses, pharmaceuticals and cosmetics [79, 80].

Calcite is considered a potentially important sink for both anions and cations due to the reactive nature of calcite and its ubiquity in groundwater aquifers. A great deal of information has been gathered about the sorption properties of calcite, especially its propensity to uptake divalent cations [81, 82]

Foremost, Zachara et al in 1991, studied the sorption behaviour of seven different divalent metal cations (Ba, Sr, Cd, Mn, Co and Ni) in calcite-saturated solutions under ambient conditions (~ 25ºC and atmospheric $pCO_{2(g)}=10^{-3.5}$). They present metal adsorption as an ion exchange reaction with Ca ions exposed on a calcite surface ($>Ca^+$) or by the metal complexation to carbonate groups ($>CO_3^-$) on a hydrated surface layer [83].

Dilekoglu reported adsorption of methylene blue onto White Urfa Rock(its contain %99 calcite) has a good capability, he observed no significant adsorption of methylene blue onto calcite in batch experiments [84]. Nevertheless, it is important to note that the efficiency of sorption is contingent upon the physical (e.g. temperature, sorbent particle loading) and chemical properties (e.g. pH, ionic strength)

of the system, when altered, can either reduce or promote metal sorption [85]. The adsorption of divalent metals on calcite is considered to be strongly pH-dependent [83, 85]. For instance, free metal cations compete directly with Ca^{2+} for the adsorption surface sites [83].

In similar aspects, Van der Weijden and Comans demonstrated that the presence of phosphate (PO_4) and sulfate (SO_4) in solution reduced the cadmium (Cd^{2+}) fractional sorption on calcite [86]. Dilekoglu was studied Zn^{2+} and Cd^{2+} heavy metals adsorption on calcite based White Urfa Rock[85].

Multi-component isotherm models have been applied to predict the equilibrium behaviour of Methylene Blue and Safrabine T onto calcite in single and binary component systems [87]. The study results show that calcite mineral can be successfully used for removal of Methylene Blue and Safrabine T from single and binary dye solutions. The H shaped isotherms exhibit that both dyes are completely removed from their individual solutions by calcite in the concentration range of 0.02–0.4 mM at 20 g^{-1} adsorbent dosage. The adsorption capacity of calcite for Safrabine T is lower than that of Methylene Blue because of steric effects. The site distribution function calculated assuming competitive adsorption show that the number of adsorption sites having higher affinity for Methylene Blue is slightly greater than for Safrabine T.

Aiming to improve the de-fluoridation of groundwater, Ben Nasr A et al 2013 investigated the removal of fluoride from model solutions and a Tunisian groundwater sample using calcite particles in the presence of acetic acid [88]. It was reported, At 5 mg L^{-1} fluoride concentration, removal efficiency increased from 17.4% without acid to 30.4% with 0.1 M acetic acid. The increase in fluoride removal with acetic acid was mainly attributed to the renewal of the area available for adsorption on the calcite particles. At the fluoride concentration of 50 mg L^{-1}, the removal efficiency was equal to 9.5% without acid and 94.3% with the addition of 0.1 M acetic acid. Optimum parameters were selected for the defluoridation of a Tunisian groundwater sample with initial fluoride concentration around 2.7 mg L^{-1}. The final F concentration after treatment with calcite in the presence of 0.1 M acetic acid was found equal to 1.2 mg L^{-1}, which was below the standard of the World Health Organisation.

Phosphorus is often present in low concentrations in wastewater, almost solely in the form of organic and inorganic phosphates (ortho- and poly-phosphates). The removal of phosphates from surface waters is generally necessary to avoid problems, such as eutrophication and its concomitant effects on living organisms and environment. Kostantinos Karageorgiou studied the orthophosphate species uptake from aqueous solutions using calcite [89]. Electrokinetic measurements indicate that phosphate species are specifically adsorbed onto calcite surface. Also, significant amount of orthophosphates can be adsorbed onto relatively low mass of calcite. It was reported that the adsorption process is more effective in the highly basic pH region, resulting to complete removal of the various orthophosphate species. The authors mentioned, besides, the calcite adsorbed-phosphate product is friendly to the environment, as it does not require further treatment for the phosphate species desorption because of its potential application to acid soils fertilization.

4.   CONCLUSION

According to the previous provided information, it is clear that natural geologic materials and its composites are capable of removing contaminants ranging from heavy metals, dyes, antibiotics etc, from contaminated environment and life sources.

Results from the recent advances in using natural geologic materials and its modified composites show their flexible nature, and its ecofriendly nature. They are capable of removing contaminants with very high removal ratios of toxic trace metals, nutrients, and organic matter. In most of the cases, they proved to be better or comparable with the existing commercial materials, adsorbents, and conventional methods used now.

Further research should be focused on the optimization of the surface modification procedures to raise their efficiency and to enhance the capability of regeneration. Furthermore, detailed characterization of natural and modified clay materials, Calcite and zeolites is needed to better understand the structure-property relationship, in order to open up new possibilities for their application.

Being natural and their abundance presence makes them a low-cost green, nontoxic adsorbent which can be used for removal of different contaminants.

REFERENCES

[1]   Wang, S., and Peng, Y., "Natural zeolites as effective adsorbents in water and wastewater treatment," Chemical Engineering Journal, 156, 11–24, 2010.

[2]   Lin, S.H., and Juang, R.S., "Heavy metal removal from water by sorption using surfactantmodified montmorillonite", J. Hazard. Mater, B 92, 315–326, 2002.

[3]   Abd El-Latif, MM., El-Kady, MF., Ibrahim, AM., and Ossman ME., "Alginate/polyvinyl alcohol-kaolin composite for removal of methylene blue from aqueous solution in a batch stirred tank reactor", J Am Sci 6:280–292, 2012.

[4]   Eriksson, E., Auffarth, K., Henze, M., and Ledin A.," Characteristics of grey wastewater", Urban Water, 4, 1, 85–104, 2002.

[5]   Du, Q., Liu, S., Cao, Z., and Wang, Y., "Ammonia removal from aqueous solution using natural Chinese clinoptilolite", Separation and Purification Technology, 44 ,3, 229–234, 2005.

[6]   Masel, R. I., Principles of Adsorption and Reaction on Solid Surfaces Wiley, New York, NY, 1996:

[7]   Slejko, E.L., and Dekker, M., 'Adsorption Technology: a step by step approach to process evaluation and application, Ed M.DKKER, New York, 1985.

[8]   Do, D.D., "Adsorption Analysis: Equilibria and Kinetics, Imperial College Press, Singapore", 1998.

[9]   Robinson, T., Chandran, B., and Nigam, P., "Removal of dyes from a synthetic textile dye effluent by biosorption on apple pomace and wheat straw," Water Res 36, 2824–2830, 2002.

[10]   Chen, Y-M., Tsao T-M., and Wang M-K., "Removal of crystal violet and methylene blue from aqueous solution using soil nano-clays", International conference on environment science and engineering, IPCBEE, vol 8. IACSIT Press, Singapore, pp 252–254, 2011.

[11]   Purkait, MK., Maiti, A., DasGupta, S., and De, S.,"Removal of Congo red using activated carbon and its regeneration", J Hazard Mater, 145, 287–295, 2007.

[12]   Joo, JB., Park, B., and Yi, J., "Preparation of polyelectrolyte-functionalized mesoporous silicas for the selective adsorption of anionic dye in an aqueous solution", J Hazard Mater, 168, 102–107, 2009.

[13]   Babel, S., and Kurniawan, T.A, "Journal of Hazardous Materials", B97, 219–243, 2003.

[14]   El-Said, GF., "A Future Overview of the Usage of Minerals as an Eco-friendly Adsorbent for the Removal of Pollutants", J Geol Geophys, 6, 3, 2017.

[15]   Ong, L.K., Soetaredjo, F.E., Kurniawan, A., Ayucitra, A., Liu, J.C., and Ismadji, S., "Investigation on the montmorillonite adsorption of biocidal compounds incorporating thermodynamicalbased multicomponent adsorption isotherm," Chem, Eng, J, 241, 9–18 ,2014.

[16]   Mohan, D., and Singh, K.P., "Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse--an agricultural waste", Water Res, 36, 2304–2318, 2002.

[17]   Bhattacharya, A.K., Mandal, S., and Das, S., "Adsorption of Zn(II) from aqueous solution by using different adsorbents", Chem, Eng, J., 123, 43–51, 2006

[18]   Arivoli, S., and Thenkuzhali, M., Kinetic, "mechanistic, thermodynamic and equilibrium studies on the adsorption of Rhodamine B by acid activated low cost carbon", Electron J Chem 5, 187–200, 2008.

[19]   Ucar, D. "Adsorption of remazol black Rl and reactive yellow 145 from aqueous solutions by pine needles", Iranian Journal of Science and Technology. Transactions of Civil Engineering, 38:C1, 147, 2014.

[20]   Anggraini, M., Kurniawan, A., Ong, L.K., Martin, M.A., Liu, J.C., Soetaredjo, F.E., Indraswati, N., and Ismadji, S, "Antibiotics detoxification from synthetic and real effluents using a novel MTAB surfactant—montmorillonite (organoclay) sorbent", RSC Adv. 4, 16298–16311, 2014.

[21]   Putra, E.K., Pranowo, R., Sunarso, J., Indraswati, N., and Ismadji, S., "Performance of activated carbon and bentonite for adsorption of amoxicillin from wastewater: mechanisms, isotherms and kinetics", Water Res, 43, 2419–2430, 2009.

[22]   Chaturvedi, A. K., Yadava, K. P., Pathak, K. C, and. Singh, V. N., "Defluoridation of water by adsorption on fly ash," Water, Air, and Soil Pollution, vol. 49, no. 1-2, pp. 41–69, 1990.

[23]   Sujana, M. G., Thakur, R. S., and. Rao, S. B., "Removal of fluoride from aqueous solution by using alum sludge," Journal of Colloid and Interface Science, vol. 206, no. 1, pp. 94–101, 1998.

[24]   Toyoda, A., and Taira, T., "A new method for treating fluorine wastewater to reduce sludge and running costs," IEEE Transactions on Semiconductor Manufacturing, vol. 13, no. 3, pp. 305–309, 2000.

[25]   WHO (World Health Organization), Fluorine and Fluorides, Environmental Health Criteria, Geneva, Switzerland, World Health Organization, 1984.

[26]   Watson, R., "Climate change. Synthesis Report", Cambridge University Press. UK, 2001.

[27]   Jeong, J.Y., Kim, H.K., Kim, J.H. and Park, J.Y., "Electrochemical Removal of Nitrate Using ZVI Packed Bed Bipolar Electrolytic Cell", Chemosphere, 89, 172-178, 2012.

[28]   Zhou, M., Fu, W., Gu, H. and Lei, L., "Nitrate Removal from Groundwater by a Novel Three-Dimensional Electrode Biofilm Reactor," Electrochimica Acta, 52, 6052-6059, 2007.

[29]   Rytwo, G., Tropp, D., and Serban, C, "Adsorption of diquat, paraquat and methyl green on sepiolite: experimental results and model calculations", Applied Clay Science, 20, 273–282, 2002.

[30]   Roulia, M., and Vassiliadis, A.A.,"Sorption characterization of a cationic dye retained by clays and perlite", Microporous and Mesoporous Materials, 116, (1–3), 732–740, 2008.

[31]   Sandhya, B., and Tonni, A.K., "Low-cost adsorbents for heavy metals uptake from contaminated water: a review", Journal of Hazardous Materials, B97, 219–243, 2003.

[32]   Guggenheim, S., and Martin RT., "Definition of clay and clay mineral: joint report of the AIPEA nomenclature and CMS nomenclature committees", Clay, Clay Miner, 43,255–256, 1995.

[33]   Chen, C.C., and Hayes, KF., "X-ray absorption spectroscopy investigation of aqueous Co(II) and Sr(II) sorption at clay-water interfaces", Geochim Cosmochim Acta, 63, 3205–3215, 1999.

[34]   Murray, H," Industrial clays case study", Int Inst Environ Dev (IIED), 64, 1–9, 2002.

[35]   Odom, IE., "Smectite clay minerals: properties and uses," Philos Trans R Soc, A, 311, 391, 1984.

[36]   Lagaly, G., "Surface and interlayer reactions: bentonites as adsorbents", In, Churchman GJ, Fitzpatrick RW, Eggleton RA (eds) Clays controlling the environment. Proceedings of the 10th international clay conference, Adelaide, Australia. CSIRO Publishing, Melbourne, pp 137–144, 1995.

[37]   Robertson, RHS., Fuller's Earth: A History of calcium montmorillonite, Volturna Press, U.K, 1986.

[38]   Hajjaji, M., and El Arfaoui, H., "Adsorption of methylene blue and zinc ions on raw and acid-activated bentonite from Morocco", Applied Clay Science, 46, 418–421, 2009.

[39]   Rafiei, H.R., Shirvani, M., Ogunseitan, O.A., "Removal of lead from aqueous solutions by a poly (acrylic acid)/ bentonite nanocomposite", Appl Water Sci 6, 331–338, 2016.

[40]   Saad, A. A., and Fares, D. A., "Adsorption of Cu & Ni on Bentonite Clay from Waste Water", Athens Journal of Natural & Formal Sciences, vol.1, No.1, 2014.

[41]   Mahfoud, B., Salah, C., Abdelhamid, M., Belgacem, B., Djamel N., and Makhlouf, B., "Application of Algerian Bentonite in the Removal of Cadmium (II) and Chromium (VI) from Aqueous Solutions", Journal of Surface Engineered Materials and Advanced Technology, 4, 210-226, 2014.

[42]   Bellir, K., Bencheikh-Lehocine, M., and Meniai, A-H., "Removal of methylene blue from aqueous solutions using an acid activated Algerian bentonite: equilibrium and kinetic studies", Int Renew Energy Congr , 360–367, 2010.

[43]   Raymond, K., Rhesa, P.U., Yi-Hsu, J., Aning, A., Felycia E.S., Jaka, S., Suryadi, I., "Acid Green 25 removal from wastewater by organo-bentonite from Pacitan", Applied Clay Science, 48, 81–86, 2010.

[44]   Tabak, A., Baltas, N., Afsin, B., Emirik, M., Caglar, B., and Eren, E, "Adsorption of reactive red 120 from aqueous solutions by cetylpyridinium-bentonite," J. Chem. Technol. Biotechnol, 85, 1199–1207,2010.

[45]   Yesi, Sisnandy, F.P., Ju, Y.H., Soetaredjo, F.E., and Smadji, S.," Adsorption of acid blue 129 from aqueous solutions onto raw and surfactant modified bentonite: application of temperaturedependent forms of adsorption isotherms. Adsorpt. Sci. Technol," 28, 847–868, 2010.

[46]   Nevim, G., Esra, C., "Adsorption kinetics of the antibiotic ciprofloxacin on bentonite, activated carbon, zeolite, and pumice", Desalination and Water Treatment, 53, 785–793,2015.

[47]   Fernanda, M., Lidiane, C., and Nilce O., "The Use of Converter Slag (Magnetite) and Bentonite Clay for Amoxicillin Adsorption from Polluted Water", Electron. J. Chem, 5, 3, 213-217, 2013.

[48]   Mohamed, El Miz., Samira, S., Ikrame, C., Ali, El Bachiri., Marie-Laure, F., and Abdesselam T., "Characterization and Adsorption Study of Thymol on Pillared Bentonite", Open Journal of Physical Chemistry, 4, 98-116, 2014.

[49]   Yan, Z., De-yue, Q ., and Yue-jun, Q,. L. M.,. "Research on Absorption Treatment of Waste Water of Pirimiphos Methyl by Bentonite," Fine Chem Intermed,2011(4), 2011.

[50]   Moore, D., and Reynolds, R., X-ray diffraction and the identification and analysis of clay minerals, Oxford University Press, New York, 1997.

[51]   Adebowale, K.O., Unuabonah, I.E,. and Olu-Owolabi B.I., "Adsorption of some heavy metal ions on sulfate- and phosphate-modified kaolin", Applied Clay Science 29, 145– 148, 2005.

[52]   Kamel, M.M., Ibrahm, M.A., Ismael, A.M., and.El-Motaleeb, M.A., "Adsorption of some heavy metal ions from aqueous solutions by using kaolinite clay", Ass, Univ, Bull, Environ, Res, Vol, 7, No 1, 2004.

[53]   Qingfeng, W., Hanlie, H., and Xiaoling, Z., "Studies on the Adsorption of p-Aminoazobenzene onto Kaolinite", The Open Surface Science Journal, 4, 14-18, 2012.

[54]   Kayode, O., Adebowale., Bamidele, I., Olu-Owolabi., Emmanuel, C., and Chigbundu., "Removal of Safranin-O from Aqueous Solution by Adsorption onto Kaolinite Clay", Journal of Encapsulation and Adsorption Sciences, 4, 89-104, 2014.

[55]   Soumia, Z., Fatima Zohra, El B., "Adsorption of tannery anionic dyes by modified kaolin from aqueous solution", Desalination and Water Treatment, ISSN, 1944-3994, 2014.

[56]   Sadiq, J.B., Ahmed, F. H., and Zahraa., H.A., "Removal Reactive Blue Dye from Wastewater by Adsorption on White Iraqi Kaolin clay", Journal of Babylon University, Pure and Applied Sciences, No.,7, Vol.,22, 2014.

[57]   Muhammad, S., Makshoof, A., Umer ,S., Rabia, R., Sadia, A., Sana, Z., and Muhammad, A., "Removal of formaldehyde from aqueous solution by adsorption on kaolin and bentonite: a comparative study", Turkish J. Eng. Env. Sci,.36 , 263 – 270, 2012.

[58]   Morteza, M., Shamsuddin, S., and Kumars E., "Nitrate Adsorption on Clay Kaolin: Batch Tests", Journal of Chemistry Volume, Article ID 397069, 7 pages,2015.

[59]   Jaafar S., "Adsorption study—dye removal using clay" A B. Chem. Eng, Thesis, Faculty of Chemical Engineering and Natural Resources, University College of Engineering & Technology, 2006.

[60]   Nurdan, G., and Okan O., "Study of Montmorillonite Clay for the Removal of Copper (II) by Adsorption", Full Factorial Design Approach and Cascade Forward Neural Network, Hindawi Publishing

Corporation The Scientific World Journal Volume, Article ID 342628, 11 pages, 2013.

[61]   He, H., Guo, J., Xie, X., and Peng, J., "Experimental study of the selective adsorption of heavy metals onto clay minerals", Chinese Journal of Geochemistry, https://link.springer.com/article/10.1007/BF03166865, 2000.

[62]   Brigatti, M.F., Colonna, S., Malferraria, D., Medici, L., and Poppi L., "Mercury adsorption by montmorillonite and vermiculite: a combined XRD, TG-MS, and EXAFS study", Applied Clay Science, 28, 1– 8, 2005.

[63]   Susmita, S. G., and Krishna, G. B., "Treatment of water contaminated with Pb(II) and Cd(II) by adsorption on kaolinite, montmorillonite and their acid-activated forms", Indian Journal of chemical technology, Vol. 16, pp,457-470, November 2009.

[64]   Tahir, H., Hammed, U., Sultan, M., and Jahanze, Q., "Batch adsorption technique for the removal of malachite green and fast green dyes by using montmorillonite clay as adsorbent," Afr J Biotechnol, 9, 8206–8214, 2010.

[65]   Günay, A., Bahri, E., Sedef, D., and Atilla E., "Investigation of equilibrium, kinetic, thermodynamic and mechanism of Basic Blue 16, adsorption by Montmorillonitic Clay, Adsorption", v 19, Issue 2-4, 757-768, DOI 10.1007, s10450-013-9509-4, April 2013.

[66]   Djelloul, B., Tabet Ainad, D., and Djillali, B., "Removal of Anionic Dye by Natural Algerian Montmorillonite", J Environ Anal Chem, an open access journal, Volume 2, Issue 2, 2015.

[67]   Barbooti, M., M, Su H., Punamiya, P., and Sarkar, D., "Oxytetracycline sorption onto Iraqi montmorillonite", Int. J. Environ. Sci. Technol, 11:69–76, 2014.

[68]   Karthikeyan, G., Anitha, P., and Alagumuthu, G., "Fluoride adsorption studies of montmorillonite clay", Indian Journal of Chemical Technology, Vol. 12, pp. 263-272, 2005.

[69]   Bish, D.L., and Ming, D.W., "Applications of natural zeolites in water and wastewater treatment, Natural Zeolites: Occurrence, Properties", Applications, 45, 2001.

[70]   Kallo, D., "Applications of natural zeolites in water and wastewater treatment, in: D.L. Bish, D.W.Ming (Eds.)", Natural Zeolites, Occurrence, Properties, Applications, 519–550, 2001.

[71]   Hedstrom, A., "Ion exchange of ammonium in zeolites: a literature review", Journal of Environmental Engineering, ASCE, 127, 673–681, 2001.

[72]   Kesraouiouki, S., Cheeseman, C.R., and Perry R., "Natural zeolite utilization in pollution-control—a review of applications to metals effluents", Journal of Chemical Technology and Biotechnology, 59, 121–126, 1994.

[73]   Caputo, D., and Pepe, F., "Experiments and data processing of ion exchange equilibria involving Italian natural zeolites", a review, Microporous and Mesoporous Materials, 105, 222–231, 2007.

[74]   Tarek, S., Jamil, H.S., Ibrahim, I.H., Abd El-Maksoud, S.T., and El-Wakeel, "Application of zeolite prepared from Egyptian kaolin for removal of heavy metals: Optimum conditions", Desalination 258, 34–40, 2010.

[75]   Malamis, S., and. Katsou, E., "A review on zinc and nickel adsorption on natural and modified zeolite, bentonite and vermiculite", Examination of process parameters, kinetics and isotherms, Journal of Hazardous Materials, 252– 253, 428– 461, 2013.

[76]   Nurul, W., Hongwei, W., Ha, M.A., Dongke, Z., "Removal of ammonium from greywater using natural zeolite", Desalination 277, 15–23, 2011.

[77]   Mohsen, H., "Adsorption and removal of tetracyclin antibiotic from water by zeolite adsorbent", International Journal of Geology, Earth & Environmental Sciences, ISSN, 2277-2081, Vol. 7, (1), pp. 55-64, January-April, 2017.

[78]   Mária, V., Ján, D., Katarína, Š., "Removal of selected pesticides by adsorption", Acta Chimica Slovaca, Vol. 6, No. 1, pp. 25—28, 2013.

[79] Baltrusaitis, J., and Grassian, V. H., "Calcite surface in humid environments", *Surf. Sci,* 603, L99-L104, 2009.

[80] Villegas-Jiménez, A., Mucci, A., and Whitehead, M. A., "Theoretical insights into the hydrated (10.4) calcite surface: structure, energetics, and bonding relationships," Langmuir 25, 6813-24, 2009.

[81] Green-Pedersen, H., and Jensen, B. T., "Nickel adsorption on MnO2, Fe(OH)3, montmorillonite, humic acid and calcite: A comparative study", Environmental Technology, 18, 807-815,1997.

[82] Lakshtanov, L. Z., and Stipp, S. L. S., "Experimental study of nickel(II) interaction with calcite" Adsorption and coprecipitation. Geochimica et Cosmochimica Acta, 71, 15, 3686-3697, 2007.

[83] Zachara J.M., Cowan, C. E., and Resch, C.T," Sorption of divalent metals on calcite," Geochim, Cosmochim, Acta 55, 1549-1562,1991.

[84] Dilekoğlu, Mehmet Fatih. "Adsorption of methylene blue dye on Urfa stone obtained around at agriculture land in Harran plain", Türkiye Tarımsal Araştırmalar Dergisi, 5.1:19-30 2018.

[85] Dilekoğlu, M. Fatih, "Investigation of Adsorption Kinetics of Cd^{2+} and Zn^{2+} heavy metals in Aqueous Solutions onto White Urfa Stone", pHd Thesis, Yildiz Technical University Graduate Institute of Natural and Applied Sciences, 2003.

[86] Van der Weijden, R. D., and Comans, R. N. J., Sorption and sorption reversibility of cadmium on calcite in the presence of phosphate and sulfate," Mar. Chem,. 57, 119-132, 1997.

[87] Gülten, A., and Elif T., "Competitive Adsorption of Basic Dyes onto Calcite in Single and Binary Component Systems", Separation Science and Technology, 45, 1471–1481, 2010.

[88] Ben Nasr, A., Walha, K,. Puel, F,. Mangin, D,. Ben Amar, R. and Charcosset, C., "Precipitation and adsorption during fluoride removal from water by calcite in presence of acid, Desalin. Water Treat", doi: 10.1080/19443994.2013.799441, 2013

[89] Kostantinos, K., Maximos, P., and Georgios, N., "Removal of phosphate species from solution by adsorption onto calcite used as natural adsorbent", Journal of Hazardous Materials, A, 139, 447 –452, 2007.