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College of Science

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## **Bentonite; Economic view and scientific applications (Review)**

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## **Bentonite; Economic view and scientific applications (Review)**

### **Abstract:**

Water is one of our most important natural resources. Without it, there would be no life on earth. Water is a raw material which is available on Earth in unlimited quantities. Water is not consumed since, after use, it is fed back sooner or later into the Earth's water circulation. Water resources are one of the most essential issues due to climate change impacts and adaptation. A clean and reliable water supply is critical for domestic use, food and energy production, transportation, recreation, and maintenance of natural ecosystems. Water pollution is a major global problem which requires ongoing evaluation and revision of water resource policy at all levels. It has been suggested that it is the leading worldwide cause of diseases and deaths. Water pollution accounts for the deaths of more than 14,000 people daily. Pollutants have been categorized into organic, inorganic, and biological on the basis of their nature and origin. Heavy metal (inorganic pollutants) wastewater treatment techniques include chemical precipitation, Activated Carbon Adsorbents, Membrane filtration, Electrodialysis and Nanofiltration. Recent Researches aim to find high efficient and low cost pollutant removal. Some of these efforts were oriented to use bentonite in this trend. Types of bentonite are Sodium bentonite, Calcium bentonite, and Potassium bentonite. The main uses of bentonite are for drilling mud, binder, purifier, absorbent, groundwater barrier, absorb oils and grease, medically as bulk laxative and removal of heavy metal. Our case study is cobalt removal by bentonite which is an example of heavy metals, is a very toxic element affecting the environment

**Keywords:** water, water pollutants, water treatment, bentonite, cobalt removal.

## البنتونيت: نظرة اقتصادية وتطبيقات علمية (بحث نظري)

### الملخص العربي:

تعتبر المياه من أهم المصادر الطبيعية على وجه الأرض. فبدون المياه تنعدم الحياة، والمياه من المصادر الأساسية المتاحة بكميات غير محدودة على الأرض، كما أن كميات المياه ثابتة وغير مستنفذة حيث تستمر في دورات تعرف بدورة المياه في الطبيعة. ومصادر المياه هي احدى الموضوعات الهامة للتغيرات المناخية كما أن المياه النظيفة الصالحة للاستخدام هي احد الموضوعات الحرجة والهامة في الاستخدامات المنزلية ونتاج الطاقة والنقل والصناعة والحفاظ على البيئة المائية. والحفاظ على المياه من التلوث هو احد المجالات الهامة العالمية التي تحتاج الى تنظيمات وقوانين صارمة. حيث يؤدي تلوث المياه الى وفيات اكثر من ١٤٠٠٠ شخص يوميا. وتقسم ملوثات المياه الى ملوثات عضوية وغير عضوية وحيوية من ناحية مصدر التلوث . ويتم التخلص من تلوث العناصر الثقيلة (احدى الملوثات غير العضوية) باحدى الطرق والتقنيات الحديثة التي تشمل الترسيب الكيميائي والكربون النشط والترشيح بالأغشية والتحليل الكهربائي والترشيح بتقنية النانو. وتهدف الأبحاث الحديثة الى ايجاد طرق أكثر كفاءة واكثر اقتصادية لإزالة الملوثات ويتجه النظر في هذه الابحاث الى استخدام البنتونيت. ومن أنواع البنتونيت الصوديومي والبوتاسي والكالسيومي. ويستخدم البنتونيت اساسا في حفر الآبار وتنقية الألوان وامتصاص الغازات والزيوت والشحوم. وعلى سبيل المثال لازالة العناصر الثقيلة استخدام البنتونيت في ازالة الكوبلت من المياه.

### الكلمات الدالة:

المياه – تلوث المياه - معالجة المياه – البنتونيت – ازالة الكوبلت

## **1. Introduction:**

Water resources are defined as the sources which produce the water for our different types of uses and also those sources that give the huge benefit to the life of the humans. The water which is used in the production of different types of useful products are also included in the water resources. Basically, the function of the water resources is to overcome the desires or the requirement of the water for the agricultural or household purposes.

Water resources are one of the most essential issues due to climate change impacts and adaptation. A clean and reliable water supply is critical for domestic use, food and energy production, transportation, recreation, and maintenance of natural ecosystems [1].

Water (chemical formula:  $H_2O$ ) is a transparent fluid which forms the world's streams, lakes, oceans and rain, and is the major constituent of the fluids of organisms. As a chemical compound, a water molecule contains one oxygen and two hydrogen atoms that are connected by covalent bonds. Water is a liquid at standard ambient temperature and pressure, but it often co-exists on Earth with its solid state, ice; and gaseous state, steam(water vapor). It also exists as snow, fog, dew and cloud. Water covers 71% of the Earth's surface.[2] It is vital for all known forms of life. On Earth, 96.5% of the planet's crust water is found in seas and oceans, 1.7% in groundwater, 1.7% in glaciers and the ice caps of Antarctica and Greenland, a small fraction in other large water bodies, and 0.001% in the air as vapor, clouds (formed of ice and liquid water suspended in air), and precipitation.[3][4] Only 2.5% of this water is freshwater, and 98.8% of that water is in ice (excepting ice in clouds) and groundwater. Less than 0.3% of all freshwater is in rivers, lakes, and the atmosphere, and an even smaller amount of the Earth's freshwater (0.003%) is contained within biological bodies and manufactured products.[3] A greater quantity of water is found in the earth's interior.[5]

### **1.1 Water cycle:**

Water is continually moving around, through, and above the Earth as water vapor, liquid water, and ice. In fact, water is continually changing its form. The Earth is pretty much a "closed system," like a terrarium. That means that the Earth neither, as a whole, gains nor loses much matter, including water. The hydrological cycle moves water from the atmosphere to the Earth and back again in a process of perpetual motion powered by energy from the sun and by gravity. The cycle's processes provide the water that flows through rivers, lakes, reservoirs, and aquifers from which many people get their drinking water. Indeed, the water cycle makes life on Earth possible.[6]

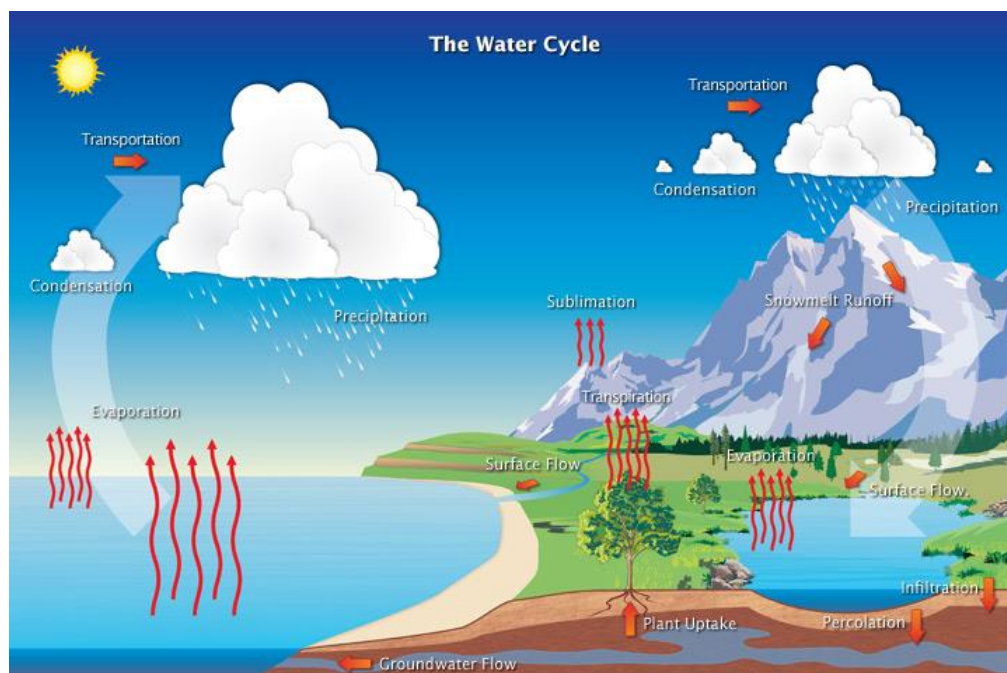


Fig. 1: The hydrological cycle moves water

## 1.2 Sources of water:

**1.2.1 Groundwater:** The water emerging from some deep ground water may have fallen as rain many tens, hundreds, or thousands of years ago. Soil and rock layers naturally filter the ground water to a high degree of clarity and often it does not require additional treatment other than adding chlorine as a preservative. Such water may emerge as springs, artesian springs, or may be extracted from boreholes and

wells. Deep ground water is generally of very high bacteriological quality (i.e., pathogenic bacteria or the pathogenic protozoa are typically absent), but the water may be rich in dissolved solids, especially carbonates and sulfates of calcium and magnesium

#### **1.2.2 Upland lakes and reservoirs:**

Typically located in the headwaters of river systems, upland reservoirs are usually sited above any human habitation and may be surrounded by a protective zone to restrict the opportunities for contamination. Bacteria and pathogen levels are usually low, but some bacteria, protozoa or algae will be present. Where uplands are forested or peaty, humic acids can colour the water. Many upland sources have low pH which require adjustment

#### **1.2.3 Rivers, canals and low land reservoirs:**

Low land surface waters will have a significant bacterial load and may also contain algae, suspended solids and a variety of dissolved constituents

**1.2.4 Atmospheric water generation:** is a new technology that can provide high quality drinking water by extracting water from the air by cooling the air and thus condensing water vapor.

#### **1.2.5 Rainwater harvesting or fog collection:**

which collects water from the atmosphere can be used especially in areas with significant dry seasons and in areas which experience fog even when there is little rain

### **1.3 Water pollution:**

Water pollution is a major global problem which requires ongoing evaluation and revision of water resource policy at all levels. It has been suggested that it is the leading worldwide cause of diseases and deaths [7]. Water pollution accounts for the deaths of more than 14,000 people daily [8]. In addition to the acute problems of water pollution in developing countries, developed countries continue to struggle with



pollution problems, bioaccumulation in human and animal tissue and biomagnifying in food chains and to have potential significant impacts on human health and the environment. Many POPs are currently used as pesticides. Others are used in industrial processes and in the production of a range of goods such as solvents, polyvinyl chloride, and pharmaceuticals. There are a few natural sources of POPs but most POPs are created by humans in industrial processes, either intentionally or as by-products [9].

#### **1.4 Types of Pollutants:**

Pollutants have been categorized into organic, inorganic, and biological on the basis of their nature and origin. A classification of pollutants is shown in Figure 2. Besides, a list of industries discharging various contaminants is given in Table 1-1. A brief summary of the types of pollutants is discussed below.

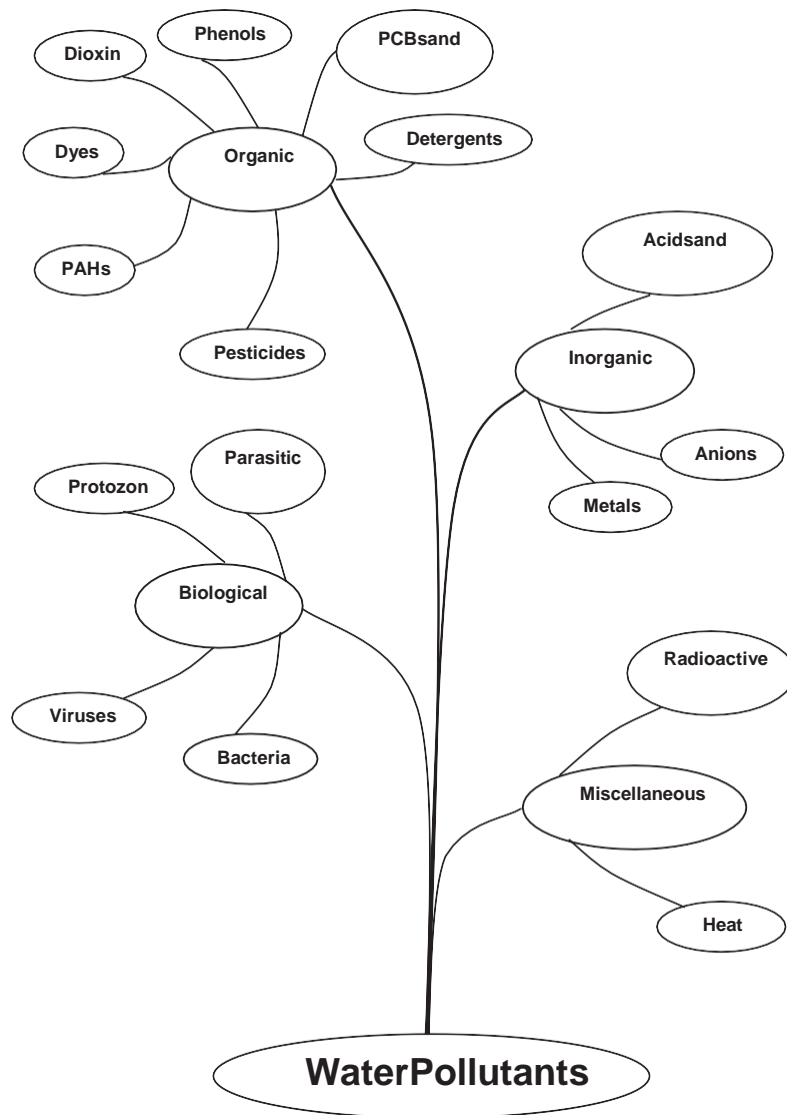


Figure 2: A classification of pollutants is shown

### 1.4.1 Organic Pollutants

Agents that degrade water quality and are organic in nature form big threats to healthy human existence and aquatic life. Organic water pollutants mainly include

1. Food processing waste, which can include oxygen-demanding substances, fats, and grease.
2. Petroleum hydrocarbons, including fuels (gasoline, diesel fuel, jet fuels, and fuel oil), lubricants (motor oil), and fuel combustion by-products [10].
3. Disinfection by-products (DBPs) found in chemically disinfected drinking water, such as chloroform.

4. Volatile organic compounds (VOCs), such as industrial solvents, from improper storage.
5. Insecticides and herbicides, a huge range of organohalides and other chemical compounds.
6. Tree and bush debris from logging operations.
7. Chlorinated solvents, which are dense nonaqueous phase liquids, may fall to the bottom of reservoirs, since they do not mix well with water and are denser.
8. Perchlorate.
9. Polychlorinated biphenyl (PCB).
10. Trichloroethylene.

Persistent organic pollutants (POPs) are a class of organic pollutants, resistant to environmental degradation. These are quite stable organic compounds and therefore, easily resist degradation to different environmental stresses. Because of this, they have been observed to persist in the environment, to be capable of long-range transport.

	Industries	Inorganic Pollutants	Organic Pollutants
22	Food processing	Alkali metals.	Amino acids
23	Pesticide industry		Dichlorophenol
24	Tannery industry	Chromium sulphides	Phenols, tartaric acid
25	Explosive industry	Data not available	Nitro-compounds
26	Laundry industry	Alkalies, free chlorine	Oils, grease
27	Wood processing	Zinc, sulphides, and	Not available

Table 1 List of Industries Discharging Various Contaminants

#### 1.4.2 Inorganic Pollutants

Inorganic chemical pollutants are naturally found in the environment but due to human development, these pollutants are often concentrated and released into the environment in urban storm water. The primary inorganic pollutants of concern in urban storm water are cadmium, copper, lead, zinc, nitrogen, nitrate, nitrite, ammonia, phosphorous, and phosphate. These chemicals are used in every aspect of human activity and are often highly toxic to humans and the environment. Some common trace metal ions such as cadmium (Cd), copper (Cu), lead (Pb), zinc (Zn), nitrogen (N), phosphorous (P), nitrate, nitrite, ammonia, and phosphate are present in the

environment as a inorganic pollut- ants. Some of the events that lead to the increased accumulation of inorganic pollutants into the environment include

1. Acidity caused by industrial discharges (especially sulfur dioxide from power plants).
2. Fertilizers containing nutrients—nitrates and phosphates—which are found in storm water runoff from agriculture, as well as commercial and residential use.
3. Chemical waste as industrial by-products.
4. Ammonia from food processing waste.
5. Silt (sediment) in runoff from construction sites, logging, slash. and burn practices or land clearing sites.
6. Heavy metals from motor vehicles (via urban storm water runoff) and acid mine drainage.

#### **1.4.3 Biological Pollutants**

Biological contaminants include bacteria, molds, mildew, cat saliva, viruses, animal dander, house dust, mites, cockroaches, and pollen. Such pollutants originate from different sources. Pollens originate from plants; viruses are transmitted by people and animals; bacteria are carried by people, animals, and soil and plant debris; and household pets are sources of saliva and animal dander. The protein in urine from rats and mice is a potent allergen. When it dries, it can become airborne. Contaminated central air handling systems can become breeding grounds for mold, mildew, and other sources of biological contaminants and can then distribute these contaminants through the home [11]. Molds, mildew, fungi, bacteria, and dust mites are some of the main biological pollutants inside the house. Some, such as pollen, are generated outside the home. Mold and mildew are generated in the home and release spores into the air. Mold, mildew, fungi, and bacteria are often found in areas of the home that have high humidity levels, such as bathrooms, kitchens, laundry rooms, or basements. Dust mites and animal dander are problematic when they become airborne during vacuuming, making beds, or when textiles are disturbed [12,13]. Outdoor air pollution in cities is a major health problem. Much efforts and money continue to be spent cleaning up pollution in the outdoor air. Many ordinary activities such as cooking, heating, cooling, cleaning, and redecorating can cause the release and spread of indoor pollutants at home and thereby,

## **1.5 Heavy metal wastewater treatment techniques:**

### **1.5.1 Chemical precipitation :**

Chemical precipitation is effective and by far the most widely used process in industry [14] because it is relatively simple and inexpensive to operate. In precipitation processes, chemicals react with heavy metal ions to form insoluble precipitates. The forming precipitates can be separated from the water by sedimentation or filtration. And the treated water is then decanted and appropriately discharged or reused. The conventional chemical precipitation processes include hydroxide precipitation and sulfide precipitation.

### **1.5.2 Activated Carbon Adsorbents:**

In 1940's, activated carbon was introduced for the first time as the main water industry's standard adsorbent for the reclamation of municipal and industrial wastewater to a potable water quality [15,16]. The use of carbon adsorption for the direct treatment of liquid industrial waste streams is a relatively recent practice but has been successfully utilized for the reclamation of metals from electroplating wastewater [17]. It has been found as a good adsorbent due to its high capacity of adsorption because of small particle sizes and active free valences. In spite of this, activated carbon could not be used as the adsorbent for water treatment at large scale due to its high cost of production. Moreover, the regeneration of activated carbon is difficult due to the use of costly chemicals and, hence, its regeneration is not easily possible at commercial scale.

### **1.5.3 Membrane filtration:**

Membrane filtration technologies with different types of membranes show great promise for heavy metal removal for their high efficiency, easy operation and space saving. The membrane processes used to remove metals from the wastewater are ultrafiltration, reverse osmosis, nanofiltration and electrodialysis

### **1.5.4 Electrodialysis:**

Electrodialysis (ED) is another membrane process for the separation of ions across charged membranes from one solution to another using an electric field as the driving

force. In most ED processes, ion-exchange membranes are used. The membranes are actually of two basic types: cation-exchange and anion-exchange membranes. This process has been widely used for the production of drinking and process water from brackish water and seawater, treatment of industrial effluents, recovery of useful materials from effluents and salt production [18] ED has also proven a promising method in heavy metal wastewater treatment. [19] performed a new working system to investigate the removal of hexavalent chromium ions using a built ED pilot plant comprising a set of ion-exchange membranes. Results were satisfactory in meeting the maximum contamination level of 0.1 mg/L for chromium. The effectiveness of ED for the separation of Cu and Fe and water recovery from solutions in copper electrowinning operations was studied by [20] They found that ED proved very effective in the removal of Cu and Fe from the working solution. [21] studied the separation of Cr(III) from sodium ion by ED using modified cation-exchange membranes. [22] investigated the effect of operating parameters on Pb<sup>2+</sup> separation from wastewater using ED. The results showed that increasing voltage and temperature improved cell performance; however, the separation percentage decreased with an increasing flow rate. At concentrations of more than 500 mg/L, dependence of separation percentage on concentration diminished.

### **1.5.5 Nanofiltration:**

Nanofiltration (NF) is the intermediate process between UF and RO. NF is a promising technology for the rejection of heavy metal ions such as nickel [23] chromium [24] copper [25] and arsenic [26] from wastewater. NF process benefits from ease of operation, reliability and comparatively low energy consumption as well as high efficiency of pollutant removal [27,28] studied the removal of pentavalent arsenic from synthetic water by two commercial NF membrane (NF90 and N30F). They found that an increase of pH and a decrease of operating temperature and As feed concentration led to higher As removal for both membranes. Among the parameters affecting the As rejection, feed concentration plays a key role for the production of a permeate stream. In recent years, Murthy and Chaudhari devoted a lot in the removal of heavy metal ions using NF membrane. They reported the application of a thin-film composite polyamide NF membrane for the rejection of nickel ions from aqueous wastewater [29] The maximum observed rejection of nickel is found to be 98% and 92% for an initial feed concentration of 5 and 250 mg/L, respectively. And

they investigated the binary heavy metals (cadmium and nickel) separation capability of a commercial NF membrane from aqueous solutions [30]. The maximum observed solute rejection of nickel and cadmium ions is 98.94% and 82.69%, respectively, for an initial feed concentration of 5 mg/L. There are many reports on the removal of heavy metal by NF and RO membrane. [31] used NF and RO to recover copper from process wastes. [32] studied the performance of different NF and RO membranes in treating the toxic metal effluent from metallurgical industry. They reported that the product water by both NF and RO desalination satisfied the State Reutilization Qualification, but NF would be more suitable for large-scale industrial practice. [33] investigated the recovery of silver from mining wastewaters using NF or RO after the silver is taken into solution as  $\text{AgCN}$  employing re-cyanidation and subsequent sedimentation and/or pre-filtration of wastewaters. Silver recoveries achieved by hybrid cyanidation and membrane separation were 29.59% and 54.62% for NF and RO membranes, respectively.

**Recent Researches aim to find high efficient and low cost pollutant removal. Some of these efforts were oriented to use bentonite in this trend.**

Bentonite is an absorbent aluminum phyllosilicate clay consisting mostly of montmorillonite, which is a very soft phyllosilicate group of minerals that typically form as microscopic crystals, known as clay. It is named after Montmorillon in France. Montmorillonite, a member of the smectite group, is a 2:1 clay, meaning that it has two tetrahedral sheets of silica sandwiching a central octahedral sheet of alumina. The particles are plate-shaped with an average diameter around 1  $\mu\text{m}$  and a thickness of  $9.6 \times 10^{-9}$  m. Members of this group include saponite.

### **1.6 Bentonite in x-ray**

For centuries, bentonite clay has been used by natives and indigenous people to cure many diseases and promote internal healing. An XRD pattern of the clay, shown in Figure 1, was collected on Rigaku's Ultima IV multipurpose diffraction system. Figure 2 shows the major clay phase present is beidellite. Such phases can easily absorb water, and the toxins in it, working like a sponge. The simultaneous presence of hydroxyl anions and alkali metal cations in the other phases present in the

bentonite sample promote ion migration out of the body and into the clay promoting health and internal healing.

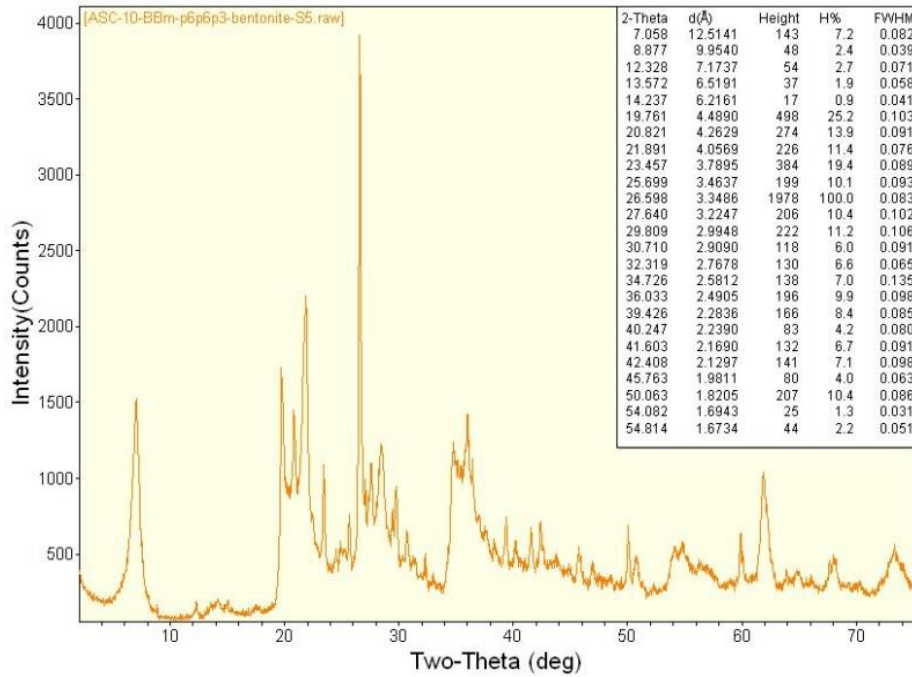


Figure 3<sup>[3]</sup> An XRD pattern of the clay

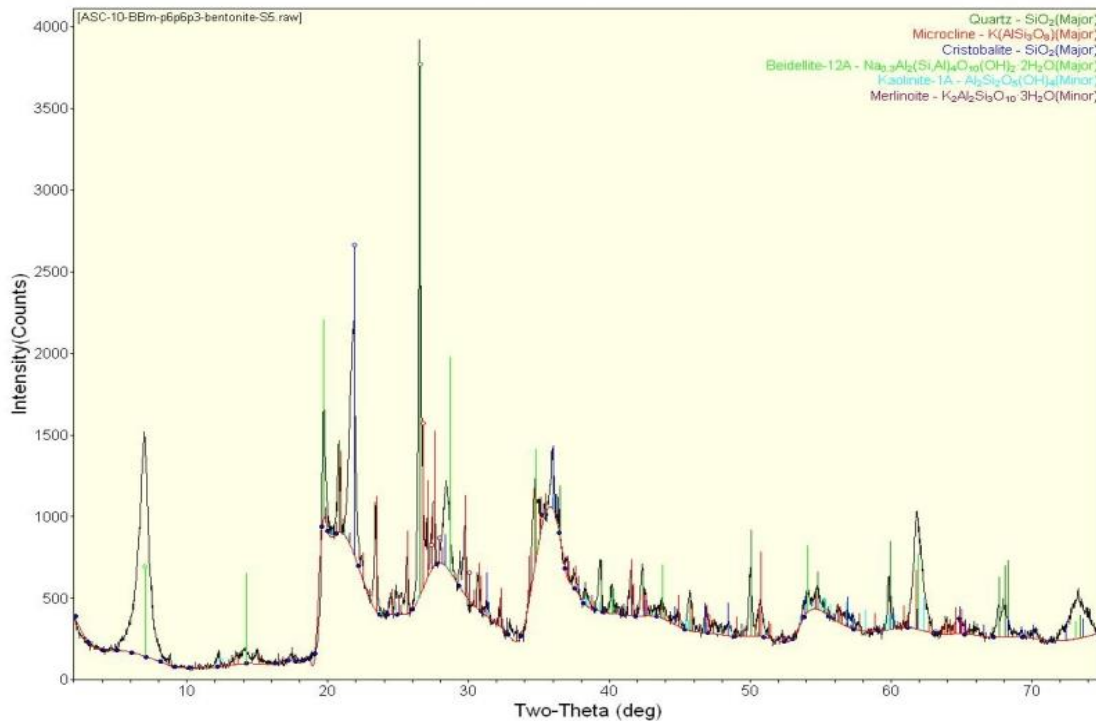


Figure 4<sup>[3]</sup> the major clay phase present is beidellite



## 1.7 Types of bentonite:

**1.7.1 Sodium bentonite** expands when wet, absorbing as much as several times its dry mass in water. Because of its excellent colloidal properties,[34] it is often used in drilling mud for oil and gas wells and boreholes for geotechnical and environmental investigations[35] The property of swelling also makes sodium bentonite useful as a sealant, since it provides a self-sealing, low permeability barrier. It is used to line the base of landfills, for example. Various surface modifications to sodium bentonite improve some rheological or sealing performance in geoenvironmental applications, for example, the addition of polymers.[36]

**1.7.2 Calcium bentonite** is a useful adsorbent of ions in solution,[37] as well as fats and oils. It is the main active ingredient of fuller's earth, probably one of the earliest industrial cleaning agents.[38] Calcium bentonite may be converted to sodium bentonite (termed sodium beneficiation or sodium activation) to exhibit many of sodium bentonite's properties by an ion exchange process. In common usage, this means adding 5–10% of a soluble sodium salt such as sodium carbonate to wet bentonite, mixing well, and allowing time for the ion exchange to take place and water to remove the exchanged calcium.<sup>[citation needed]</sup> Some properties, such as viscosity and fluid loss of suspensions, of sodium-beneficiated calcium bentonite (or sodium-activated bentonite) may not be fully equivalent to those of natural sodium bentonite.[39] For example, residual calcium carbonates (formed if exchanged cations are insufficiently removed) may result in inferior performance of the bentonite in geosynthetic liners.[40]

**1.7.3 Potassium bentonite** is also known as potash bentonite or K-bentonite, which is a potassium-rich illitic clay formed from alteration of volcanic ash.[41]

**1.8 General Formula :**  $(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10})$  and Exists in huge reserves in economic quantities in the province of Jeddah Khulais.

**1.9 Uses of bentonite:**The main uses of bentonite are for drilling mud, binder (e.g. foundry-sand bond, iron ore pelletizer), purifier, absorbent (e.g. pet litter), and as a groundwater barrier.[42] As of around 1990, almost half of the US production of bentonite was used for drilling mud.[42]

**1.9.1 Drilling mud:** Bentonite is used in drilling fluids to lubricate and cool the cutting tools, to remove cuttings, and to help prevent blowouts.[35] Much of bentonite's usefulness in the drilling and geotechnical engineering industry comes from its unique rheological properties. Relatively small quantities of bentonite suspended in water form a viscous, shear-thinning material. Most often, bentonite suspensions are also thixotropic, although rare cases of rheopectic behavior have also been reported. At high enough concentrations (about 60 grams of bentonite per litre of suspension), bentonite suspensions begin to take on the characteristics of a gel (a fluid with a minimum yield strength required to make it move). So, it is a common component of drilling mud used to curtail drilling fluid invasion by its propensity for aiding in the formation of mud cake.



Fig. 5: Bentonite is used in drilling fluids

[44]CETCO bentonite products are used to contain contaminated groundwater, dewater excavations and stabilize dams, levees, and other similar structures. Bentonite slurry has a slightly higher specific gravity than water, creating a positive hydrostatic head that stabilizes the sides of the trench to hold soil particles together and prevent collapse. The backfill material, some of which may contain soil, bentonite and cement, provides an impervious barrier and over time will set to final form.

Binder Bentonite has been widely used as a foundry-sand bond in iron and steel foundries. Sodium bentonite is most commonly used for large castings that use dry molds, while calcium bentonite is more commonly used for smaller castings that use "green" or wet molds.[35] Bentonite is also used as a binding agent in the manufacture of iron ore (taconite) pellets as used in the steelmaking industry. Bentonite, in small percentages, is used as an ingredient in commercially designed clay bodies and ceramic glazes. Bentonite clay is also used in pyrotechnics to make end plugs and rocket engine nozzles.

**1.9.2 Purification** Bentonites are used for decolorizing various mineral, vegetable, and animal oils. They are also used for clarifying wine, liquor, cider, beer, and vinegar.[35]Bentonite has the property of adsorbing relatively large amounts of protein molecules from aqueous solutions. Consequently, bentonite is uniquely useful in the process of winemaking, where it is used to remove excessive amounts of protein from white wines.

**1.9.3 Absorbent:** Bentonite is used in a variety of pet care items such as cat litter to absorb the odour and surround the feces. It is also used to absorb oils and grease.

**1.9.4 Groundwater barrier** [42]: The property of swelling on contact with water makes sodium bentonite useful as a sealant, since it provides a self-sealing, low-permeability barrier. It is used to line the base of landfills to prevent migration of leachate, for quarantining metal pollutants of groundwater, and for the sealing of subsurface disposal systems for spent nuclear fuel.<sup>[9]</sup> Similar uses include making slurry walls, waterproofing of below-grade walls, and forming other impermeable barriers, e.g., to seal off the annulus of a water well, to plug old wells.

Bentonite can also be "sandwiched" between synthetic materials to create geosynthetic clay liners (GCLs) for the aforementioned purposes. This technique allows for more convenient transport and installation, and it greatly reduces the volume of bentonite required. It is also used to form a barrier around newly planted trees to constrain root growth so as to prevent damage to nearby pipes, footpaths and other infrastructure. Farmers use bentonite to seal retention ponds.

**1.9.5 Medical:** Bentonite has been prescribed as a bulk laxative, and it is also used as a base for many dermatologic formulas.<sup>[45]</sup> Granular bentonite is being studied for use in battlefield wound dressings.<sup>[46]</sup> Bentonite is also sold online and in retail outlets for a variety of indications.<sup>[47]</sup>

Bentoquatam is a bentonate-based topical medication intended to act as a shield against exposure to urushiol, the oil found in plants such as poison ivy or poison oak.<sup>[48]</sup> Bentonite can also be used as a desiccant due to its adsorption properties. Bentonite desiccants have been successfully used to protect pharmaceutical, nutraceutical, and diagnostic products from moisture degradation and extend shelf life. In fact, in the most common package environments, bentonite desiccants offer a higher adsorption capacity than silica geldesiccants. Bentonite complies with the FDA for contact with food and drugs. <sup>[49]</sup>

**1.9.6 In Thai farming** The application of clay technology by farmers in northeast Thailand, using bentonite clay, has dramatically reversed soil degradation and resulted in greater economic returns, with higher yields and higher output prices. Studies carried out by The International Water Management Institute and partners in 2002–2003 focused on the application of locally sourced bentonite clays to degraded soils in the region. These applications were carried out in structured field trials. Applying bentonite clays effectively improved yields of forage sorghum grown under rain-fed conditions.[50][51]

Bentonite application also influenced the prices that farmers received for their crops. Production costs are higher, but due to more production and the quality of the food, clay farmers could afford to invest and grow more and better food, compared to nonclay-using farmers.[52][53]

**1.9.7 Bentonite slurry walls** in modern construction[47][54]: Bentonite slurry walls (also known as diaphragm walls [55] ) are used in construction, where the slurry wall is a trench filled with a thick colloidal mixture of bentonite and water.[56] A trench that would collapse due to the hydraulic pressure in the surrounding soil does not collapse as the slurry balances the hydraulic pressure. Forms for concrete, and rebar, can be assembled in a slurry-filled trench, and then have concrete poured into the form. The liquid concrete being denser displaces the less-dense bentonite slurry and causes the latter to overflow from the trench. This displaced bentonite slurry is then channelled to a recycling unit from which it can subsequently be reused in a new trench elsewhere on the construction site.

In addition, because the colloid is relatively impervious to water, a slurry wall can prevent the seepage of groundwater, which is useful in preventing the further spread of groundwater that has been contaminated by toxic material such as industrial waste.[55]

### **1.10 Removal of heavy metal from water by using bentonite**

Recent studies aim to investigate the feasibility of using Saudi activated clay (bentonite) in removing cobalt and heavy metals from wastewater. Wastewaters from metal industries contain various toxic heavy metals. These heavy metals present a high health risk when they enter the human food chain [57,58].

### **1.11 Example Study**

Cobalt as example of heavy metals is a very toxic element affecting the environment. Cobalt is present in the wastewater of nuclear power plants and many other industries such as mining, metallurgical, electroplating, paints, pigments and electronic industries. High levels of cobalt may affect several health problems such as paralysis, diarrhea, low blood pressure, lung irritation and bone defects [59,60]The standard level of cobalt in drinking water is 2 lg/L [61]. Adsorption of cobalt ions by different types of clay has been the subject of several studies [61,62]. These studies investigate the effect of different factors which affect the adsorption process such as sorbent amount, initial metal-ion concentration, contact time and solution pH.

The khulays bentonite (Saudi bentonite) which is located 95 km north of Jeddah is calcium montmorillonite equivalent to a “Texas bentonite” in the USA or Fuller’s earth in the UK. It has reserves ranging from 420 thousand tons (proven) to 28.9 million tons (indicated) and 38.9 million tons (possible) [63]. Saudi activated bentonite was used for the removal of lead from aqueous solutions. The results showed that sorption of lead ions on Saudi activated clay was affected by shaking time, initial lead concentration, and mixture pH. Saudi activated bentonite can be considered as a promising adsorbent for the removal of other heavy metals from aqueous solutions [64]. Therefore, the main objective of this example study is to investigate the feasibility of using Saudi activated clay (bentonite) in removing cobalt from wastewater. The choice of this material is based on its low cost, considering its abundance in Khulays bentonite deposit.

The effect of solution pH on the removal of cobalt ions using Saudiactivated bentonite was investigated in the solution pH range 1–10 with a constant clay amount of 0.5 g/50 mL of cobalt solution, a shaking time of 30 min and cobalt concentration of 50 mg/L. pH adjustments were carried out using 1 N HCl and 1 N NaOH, 200 rpm stirring rate and  $25 \pm 2$  °C temperature was applied to the shaker. The results presented in Fig. 3 shows cobalt removal percentage at different solution pH. The lowest cobalt removal was found at pH 1. As the solution pH increased, cobalt removal percentage gradually increased up to pH 8. This may be attributed to the surface of Saudi bentonite which contains large number of active sites. Consequently, it may become positively charged at low pH, leading to increase the competition between  $H^+$  and cobalt ions for available adsorption sites. However, as pH increases, this competition decreases as these surface active sites become more negatively charged, which enhances the adsorption of the positively charged metal ions through electrostatic force of attraction [65]. Increasing solution pH, cobalt removal percentage stays constant in the solution pH range 8–10, where the removal percentage was about 100%. This was due to the precipitation of  $Co(OH)_2$  as reported before [66].

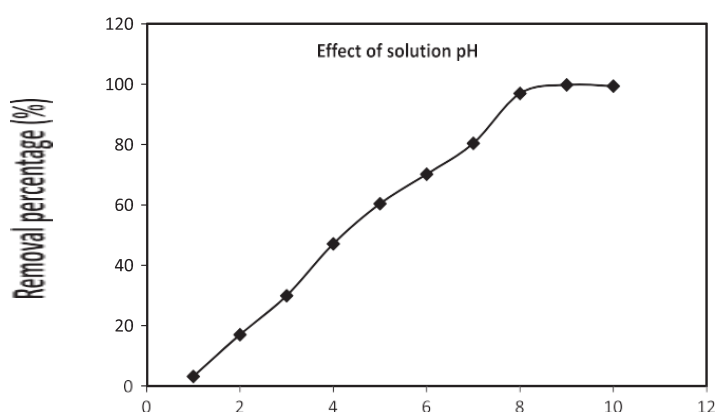


Fig. 6 cobalt removal percentage at different solution pH

Fig.4 shows the effect of initial cobalt concentration on cobalt removal when cobalt concentration varies from 25 to 200 mg/L under operating conditions of 30 min

shaking time, 0.5 g of clay/50 mL for adsorbate and solution pH was kept constant at 7. The results showed a gradual decrease in cobalt removal. Effect of cobalt concentration on the removal of cobalt by Saudi activated bentonite. Clay dosage: 0.5 g/50 mL. pH=7, contact time: 30 min when the cobalt concentration increased in the solution. The results also showed that about 90% of cobalt was removed when cobalt concentration was about 25 mg/L. Cobalt removal percentage decreases with increasing cobalt concentration to about 37% when cobalt concentration was 200 mg/L. This decrease was due to the fact that an increase in cobalt concentration makes a high ratio of the number of cobalt ions present in solution to the number of available adsorption sites [59]

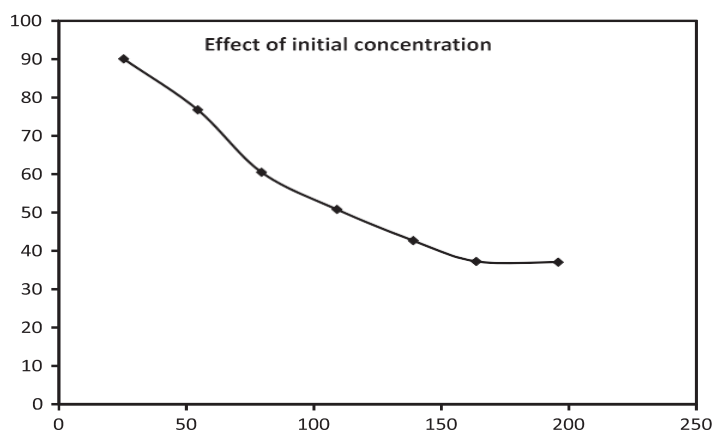


Fig.7 The effect of initial cobalt concentration on cobalt removal

Finally, in this example study, the interaction of cobalt ions with Saudi activated bentonite from Khulays bentonite deposit: 95 km north of Jeddah was investigated under various conditions. The results obtained from this study are summarized below. Cobalt removal percentage gradually increased with increasing solution pH up to pH 8. This may be attributed to the surface of Saudi bentonite which contains large number of active sites. Further, increase in solution pH cobalt removal was kept constant in the solution pH range 8–10, where the removal percentage was about 100%. Cobalt removal decreased with increasing cobalt concentration when cobalt concentration increased from 20 to 100 mg/L. The removal of cobalt increased as the dose of Saudi activated bentonite increased. This was due to increase in the number of adsorbent sites.



Fuller's earth is being used industrially for its decolorizing properties globally as it is an inexpensive and naturally abundant material. There are many kinds of clays but montmorillonite may be expected to have the highest sorptive capacity in comparison to other. El-Guendi [67] reported the adsorption of BB 69 and BR 22 from aqueous solutions on natural clay. El-Guendi et al. [68] reported the adsorption of cationic dyestuffs (BB 69 and BR 22) from aqueous solutions by natural and activated clays. The maximum adsorption capacities ( $q_{max}$ ) of BB 69 and BR 22 on natural clay were 390 and 365 mg/g, respectively. The natural clay was treated with H<sub>2</sub>O<sub>2</sub> and HCl to enhance its adsorption capacity for dyestuffs. The efficiency of activation with H<sub>2</sub>O<sub>2</sub> was greater by 23% and 13% in the case of BB 69 and BR 22, respectively, in comparison to natural clay.

The efficiency of activation with HCl was greater by 30% and 16% in the case of BB 69 and BR 22, respectively, relative to natural clay. Gupta and Shukla [69] reported adsorption techniques for the treatment of carpet effluents containing mainly Metomega Chrome Orange GL using various low-cost materials, i.e. coal, flyash, china clay, and wollastonite. Low initial dye concentration, temperature, and pH favored the removal process. McKay et al. [70] described the adsorption capacity of Fuller's earth for basic and AB to be 220 and 120 mg/g, respectively. Thus, they proposed the adsorbent for the treatment of textile effluents. The adsorption capabilities of clay were due to negative charge on the structure of fine grain silicate minerals. This negative charge was neutralized by the adsorption of positively charged cations such as dyes etc. Besides, the clays showed a large surface area up to 800 m<sup>2</sup>/g, which contributes to its high adsorption capacity [71]. Lee et al. [72] modified montmorillonite and reported the removal of 2-chlorophenol, cyanophenol and 4-nitrophenol from water.

This resulted in the change in surface property of montmorillonite from hydrophilic to organophilic. Polubesova et al. [73] also reported interactions of phenolic acids (ferulic, p-coumaric, syringic, and vanillic) with Fe(III)-montmorillonite. Adsorption of the various phenolic acids on Fe(III) enriched montmorillonite was accompanied by their oxidative transformation and formation of Fe(II). Similar findings were reported by Kim et al. [74]. Sorption of phenol and 2-, 3-, and 4-chlorophenol from water by tetramethylammonium (TMA<sup>+</sup>)-smectite and tetramethylphosphonium (TMP<sup>+</sup>)-smectite was reported by Lawrence et al. [75]. TMP-

smectite seems to be a good sorbent. Besides, TMP-smectite possessed selective sorption within the group of chlorinated phenols examined. Phenol and 4-chlorophenols were effectively sorbed by TMP-smectite.

Contrarily, 2- and 3-chlorophenols could not be sorbed. The adsorption-desorption of 2,4,6-trichlorophenol (TCP) on calcium montmorillonite (pure clay), prepared montmorillonite humic complexes, and natural soils were investigated by Sabbah and Rebhun [76]. Daneis et al. [77] determined the adsorption properties of alumina pillared montmorillonite (PMt) and mesoporous alumina aluminum phosphates for the removal of 2,4-dichlorophenol, 2,4,6-trichlorophenol, and pentachlorophenol. Malusis et al. [78] reported the adsorption of phenol on soil-bentonite (SB) vertical barriers amended with AC. SB backfills were amended with 0–10 wt% granular AC (GAC) or PAC. The AC amended backfills exhibited enhanced phenol adsorption than unamended backfill due to hydrophobic partitioning to the AC. Adsorption capacity increased with increasing AC content but does not change for the GAC and PAC. Gil et al. [79] studied the removal of orange II and MB by two-pillared clay formed by the intercalation of two pillared of aluminum (Al-PILC) and zirconium (Zr-PILC).

For orange II, both the pillared clays have same adsorption capacity while for the MB the adsorption capacity of Zr-PILC was higher than that of Al-PILC. It was found that the pore size distribution had affected the efficiency and selectivity of adsorption of two dyes. Clay could be modified to enhance its efficiency for the removal of pollutants from water and wastewaters. Cadena et al. [80] modified bentonite by replacing the natural exchangeable cations present in the clay by the organophilic cations, TMA ion. Results revealed that the adsorption capacity of natural bentonite were improved by heat treatment while the acid treatment decreased the same.

The adsorption of four types of amino acids (lysine, glycine, glutamic acid, and alanine) on sodium and calcium bentonite has been reported [80]. [Boyd et al. [81] reported the mechanisms of the adsorption of substituted nitrobenzenes onto smectite clays. Cheknane et al. [82] reported the adsorption of two basic dyes, i.e. CI Basic Yellow 28 (BY 28) and CI Basic Green 4 (BG 4) in single and binary solute systems

using two classes of inorganic–organic pillared clay granules as sorbents prepared by granulation from an Al cetyltrimethylammonium bromide intercalated clay powder.

Adsorption rate data indicated that BY 28 adsorbs more rapidly than BG 4 but the adsorption of BG 4 was greater than that of BY 28 in single solute and binary dye systems. Errais et al. [83] reported the textile dye removal by Fouchana Tunisian clay in leaching textile and dye industry. The adsorbent contains 60% smectites, 30% kaolinite, and 10% illite, having the cation-exchange capacity of about 50 meq/100 g of clay. Ho et al. [84] reported the kinetics of BR 18 and AB 9 sorption onto activated clay. Activation energy of sorption was also determined based on the pseudosecond-order rate constants. Wu et al. [85] reported the adsorption of phenol by both inorganic and organic PMts. The adsorbing capacity of modified clays depended not only surface area but mainly on micropore structure and surface components. The modified PMt with surfactant was found to improve adsorbing capacity greatly. The PMt can be recycled, and it is a potential substance for adsorption of environmental pollutants.

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TO REALIZE MY WISHES”**

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ETERNAL GAURDIAN OF ALL HEAVENS AND EARTHS,  
WITHOUT WHOSE GRACE AND GENEROUSITY THIS WORK  
WOULD HAVE NOT BEEN COMPLETED**