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ZEOLITES AND MIXED OXIDES IN THE REMOVAL OF Cr (VI)

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A Thesis Submitted to the Department of Chemistry Presented in the Partial Fullfillment of the Requirements for the Degree of Master's of Science in Inorganic Chemistry.

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This is to certify that the thesis prepared by Girum Getachew Demissie, entitled: Zeolites and Mixed oxides in the removal of Cr (VI) and submitted in partial fullfillment of the requirment of the Degree of Master of Science in Inorganic Chemistry complies with regulation of the university and meets the accepted standards with respect to originality and quality.

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ABSTRACT

In this work, different natural zeolites, namely Clinoptilolite (Mexico) and Sample 7 (Ethiopia), mesoporous material SBA-15 calcined and uncalcined as well as mixed oxides Hydrotalcite and SBA-15 supported hydrotalcite were employed for removal of chromate from aqueous solution. This materials show adsorption capacity with different mechanisms and ion (cation and anion) exchange properties. UV-Vis spectroscopy was used for determining the concentration of Cr (VI) before and after the treatment.

Obtained data from chromate adsorption experiments over the mentioned materials were compared. It was shown that adsorption data for natural zeolite was very good having 66.5% and 74.5% adsorption capacity for Clinoptilolite and Sample 7, respectively. Maximum chromate adsorption was found over mixed oxides: 98.4% and 88.7% for SBA-15/HT and HT, respectively. It was much greater than that of the natural zeolites and mesoporous materials. For comparison purpose, pure silica mesoporous materials calcined and uncalcined SBA-15 were tested, showing retaining capacity of 13.6% and 39.89%, respectively. Finally, SBA-15/HT composite appears as a promising adsorbent for removal of chromate ion from waste waters.

Keywords: Adsorption, Retention, SBA-15, Hydrotalcite, SBA-15/HT composite, Clinoptilolite, Sample 7 and Chromate ion.

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LIST OF ABBREVIATION

CHT-Calcined hydrotalcite

CLI -Clinoptilolite

HT- Hydrotalcite

HTlcs-Hydrotalcite like compounds

MCM-41-Mobile Composition of Matter No.41

SBA-15 -Santa Barbara Amorphous No. 15

SBA-15/HT-SBA-15 supported Hydrotalcite

SEM-Scanning electron microscopy

TEM-Transmission electron microscopy

WHO-World Health Organization

UNAM-Universidad Nacional Autonoma de Mexico

1, 5-DPC-1, 5-Diphenylcarbazide

ICP-CSIC- Institute of Catalysis and Petroleochemistry

AAU- Addis Ababa University

WSU-Wolaita Sodo University

MOE-Ministry of Education

BACKGROUND

Environment is the totality of circumstances surrounding an organism or group of organisms especially, the combination of external physical conditions that affect and influence the growth, development and survival of organisms. It consists of the flora, fauna and the abiotic, and includes the aquatic, terrestrial and atmospheric habitats. A pollutant is any substance in the environment, which causes objectionable effects, impairing the welfare of the environment, reducing the quality of life and may eventually cause death. Such a substance has to be present in the environment beyond a set or tolerance limit, which could be either a desirable or acceptable limit. Hence, environmental pollution is the presence of a pollutant in the environment; air, water and soil, which may be poisonous or toxic and will cause harm to living things in the polluted environment. [1, 2]

1.1 Chromium occurrence in the environment

Chromium occurs in the environment under various forms chemically, physically and morphologically. Most surface water contains very low level of chromium, except the wastewater coming from industries. Industries dealing with paint, pigment, dyes, textile, leather, are an important source of discharge of chromium into the environment. Cr (III) and Cr (VI) oxidation states of chromium present in the environment are drastically different in charge, as well as chemical and biological activities. [3]

Chromium (III) is considered to be a trace element essential for the proper functioning of living organisms. It is also known as responsible for the control of glucose and lipid metabolism in mammals. Whereas chromium (VI) exerts toxic effects on biological systems and it was found that the occupational exposure to hexavalent chromium leads a variety of clinical problems. Inhalation and retention of Cr (VI) containing material can cause perforation of the nasal septum, bronchitis, inflammation of the larynx and liver and increased incidence of broncogenic carcinoma. Skin contact of chromium (VI) compound can induce skin allergies, dermatitis, dermal necrosis and dermal corrosion. [4]

The toxicological impact of chromium (VI) originates from the action of this form itself as an oxidizing agent, as well as from the formation of free radicals during the reduction of Cr (VI) to Cr (III) occurring inside the cell. [5]

1.2 Chemistry of chromium and chromium compounds

Chromium metal was discovered in 1797 by the French chemist, Louis Nicolas Vauquelin. It was named chromium because of many different characteristic colors of its compound (Greek word chroma meaning color). Chromium is a steel-gray, lustrous, hard metal. Like other transition metals, it exhibit variable oxidation states. The most common oxidation states of chromium are: 0, II, III, and VI, with III being the most stable one. But only three oxidation states are found in nature; these are: Cr (0) which occurs in metallic form, Cr (III) which occurs in soluble chromic compounds and Cr (VI) which occurs as soluble CrO_4^{2-} and $Cr_2O_7^{2-}$ compounds. [6] Other oxidation states of Cr are unstable and therefore, are not found in the natural environment. The oxidation state of the Cr has a significant effect on the transport and fate of Cr and on the type and cost of treatment required to reduce Cr concentrations less than regulatory health-based standards. Cr (VI) is far more mobile than Cr (III) and more difficult to remove from water. [7, 8] It is also the toxic form of Cr, approximately 10 to 100 times more toxic than Cr (III) by the acute oral route, presumably owing to the stronger oxidizing potential and membrane transport of Cr (VI). [9] The EPA classifies Cr (VI) as a known human carcinogen via inhalation, but classifies Cr (III) as not known to cause cancer. Cr (VI) compounds are anions. The most common Cr (VI) forms are chromate (CrO_4^{2-}), and hydrogen chromate ($HCrO_4^-$) also called bichromate. The relative amount of these two species depends on pH. Dichromate ($Cr_2O_7^{2-}$) can also occur. [10]

The equilibrium concentration of dissolved Cr (III) in natural waters is small compared to Cr (VI) concentration. In water, Cr (III) is mostly in the free-ion form Cr (III), although these ions associate with hydroxide OH^- ions in a pH-dependent manner, forming $Cr(OH)^{2+}$, $Cr(OH)_2^+$ $Cr(OH)_3$, and $Cr(OH)^{4-}$. The solid precipitate $Cr(OH)_3$ (s) will equilibrate with these dissolved species. Cr (III) will also form complexes with organic and inorganic ligand such as SO_4^{2-}, NH_4^+, and CN^-. [11]

Chromium compounds are widely used by industries, resulting in large quantities of this element being discharged into the environment. Some of the main uses for chromium compounds are as follows: (1) plastic coating of surfaces for water and oil resistance, (2) electroplating of metal for corrosion resistance, (3) leather tanning and finishing, and (4) in pigments and for wood preservative. Tannery effluent containing chromium is one of the most obvious problems in

leather industry. Chromium salts (particularly chromium sulphate) have been used widely in tanning due to the excellent properties that it renders to the leather along with simplicity of operation. However, only 60% of the total chromium salt reacts with the hides. In other words, about 40% of the chromium amount remains in the solid and liquid wastes. Therefore, the removal and reuse of the chromium content of these wastewaters is necessary for environmental protection and economic reasons. [12, 13]

1.3 Toxicity of Chromium

Chromium is one of the most abundant inorganic ground water contaminant at hazardous waste sites. Compared to its trivalent counterpart, Cr (VI) forms chromate (CrO_4^{2-}) or hydrogen chromate ($HCrO_4^-$) which is known to have 100-fold more toxicity than Cr (III) and more soluble at various pH range. It is due to its easy penetration into biological membranes resulting in health hazards such as skin disorders, respiratory track problems, lung carcinoma, acute tubular necrosis of kidney and even death in extreme cases. Humans are exposed to chromium through breathing, eating or drinking and through skin contact with chromium or chromium compounds. The level of chromium in air and water is generally low. [14] In drinking water the level of chromium is usually low as well, but contaminated well water may contain the dangerous chromium (VI). In human, Cr (VI) exposure caused marked irritation of the respiratory track and ulceration and perforation of the nasal septum in workers in the chromate producing and using industries. Ingestion of 1.0g to 5.0g of Cr (VI) as chromate results in severe acute gastrointestinal disorders and convulsions. [15] Death may occur following cardiovascular shock. The maximum levels permitted in drinking water are 5 mg/L for trivalent and 0.05mg/L for hexavalent chromium. But there is still uncertainty regarding what daily dose of Cr (VI) is considered toxic. The tolerance limit for Cr (VI) for discharge into inland surface waters is 0.1 mg/L and in potable water is 0.05mg/L. Therefore, among heavy metal ions, chromium requires considerable attention. [16, 17]

1.4 Wastewater and its treatment

The success of many different treatment technologies in remediating Cr (VI), contamination has been demonstrated. However, most of these technologies require knowledge of site-specific conditions, flexibility in remediation design and creativity in optimization strategies, not

adherence to a step-by-step recipe approach. Since the biogeochemical properties of Cr and the associated soil matrix can affect the removal efficiency of many treatment strategies, an understanding of these properties is essential for choosing an effective treatment method. Once the properties of Cr and the associated soil are understood and the behavior of Cr in the subsurface and treatment environments can be predicted, remedial alternatives for Cr (VI) can be addressed. [18] The form of the Cr determines toxicity, mobility, and treatment strategy applicability. Various treatment methods such as chemical precipitation, reverse osmosis, ion exchange, solvent extraction, coagulation and adsorption are utilized to remove metal ions from aqueous solutions. However, due to the economic constraints which the country is facing, a development of cost effective and clean processes is desired. Of all these methods, adsorption has proved to be the most effective. [19]

1.4.1 Adsorption method

Adsorption is a process, by which a substance in a gas or liquid becomes chemically attached to a solid surface, called an adsorbate. Adsorption is typically used in wastewater treatment to remove toxic or recalcitrant organic pollutants (especially halogenated but also non-halogenated), and to a lesser extent, inorganic contaminants, from the wastewater. It is commonly used in the treatment of industrial wastewaters containing organic compounds not easily biodegraded during secondary (biological) treatment or toxic. [20]

1.4.1.1 Chromium removal using Natural Zeolites

Many researchers have used natural zeolites for metal ion adsorption and several review works have been reported. For example, Panayotova *et al* (2001) conducted a series of experiments using a Bulgarian natural zeolite and modified forms for removal of several metal ions such as Ni^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+} and Pb^{2+}. In Ni^{2+} adsorption, natural and NaOH, NaCl, HCl, and CH_3COONa modified zeolites have been tested in a batch process. Zeolite modification with CH_3COONa and NaCl can increase Ni^{2+} adsorption by 25–30%. [21]

Turkman *et al*. (2004) studied removal of heavy metals (Pb^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+}) in synthetic and real wastewaters using activated and non-activated natural clinoptilolite. The clinoptilolite exhibited about 100, 98, and 96% removal efficiency for Pb^{2+}, Zn^{2+} and Cd^{2+}, respectively. [22]

In general, natural zeolites in wastewater treatment are quite effective in comparison with other methods mentioned above. Thus the possible regeneration of the zeolite, re-use of the zeolite and reuse of the obtained concentrate metal ions after regeneration of the zeolite, very positively impact on the environment without creating new waste. One of the heavy metal that has been a major focus in waste water treatment is chromium. [23]

Even though, it is possible to remove Cr (III) by using natural zeolites without modification, natural zeolite cannot remove Cr (VI) anion which is mainly found as oxyanions forms such as chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) in the solution. [24] Therefore modification of natural zeolite is required for such purpose. The modified zeolite can adsorb and remove Cr (VI) as well as Cr (III). Modification of natural zeolites can be performed by several methods, such as acid/base treatment, ion exchange, and surfactant functionalization. Surfactant functionalization is the commonly used method of modification of natural zeolite for the removal anions such as chromate anion. Commonly used surfactants are those positively charged organic cationic surfactant such as hexadecyltrimethyl-ammonium (HDTMA), cetylpyridinium bromide (CPB) and ethylhexadecyldimethylammonium (EHDDMA); when brought into contact with zeolite, the cationic surfactants those posses a permanent positive charge selectively exchange with the inorganic cations on the external surfaces of the zeolite crystals and form a surfactant modified zeolite with anion exchange properties. A general model of sorption of cationic surfactants on a zeolite surface is the formation of a monolayer or “hemimicelle” at the solid-aqueous interface via strong Coulombic (ionic) bonds at surfactant concentrations at or below its critical micelle concentration (CMC). If the surfactant concentration in solution exceeds the CMC, then the hydrophobic tails of the surfactant molecules associate to form a bilayer or “admicelle”. [25, 26] The mechanism of anion retention appeared to be the formation of a surfactant-anion precipitate on the zeolite surface for surfactant monolayer or the zeolite surface charge is reversed and anion exchange with the counter ion for surfactant bilayer. Several studies on application of surfactant-modified zeolites for chromate removal were published.

G. M. Haggerty and Robert S. Bowman (1994) performed batch sorption experiments that showed a significantly enhanced removal of chromate and other inorganic anions selenate and sulfate from aqueous solution by Clinoptilolite dominated zeolite modified by the quaternary amine hexadecyltrimethylammonium (HDTMA). While the natural zeolite had no affinity for the

oxyanions, the HDTMA-modified zeolite showed significant removal of chromate, selenate and sulphate (Figure 1). [27] The mechanism of anion retention appears to be the formation of an HDTMA-chromate precipitate on the zeolite surface. And the existence of the adsorbed chromium as in the form of Cr (VI) was well confirmed by the XANES spectrum which indicated that the chromium associated with the zeolite surface was 95% in the form of Cr (VI) and Fourier Transform Raman Spectroscopy which showed a strong signal attributable to chromate is seen for the HDTMA-chromate precipitate at 905 cm^{-1}. Sorption data for each anion were well-described by the Langmuir isotherm equation. [28]

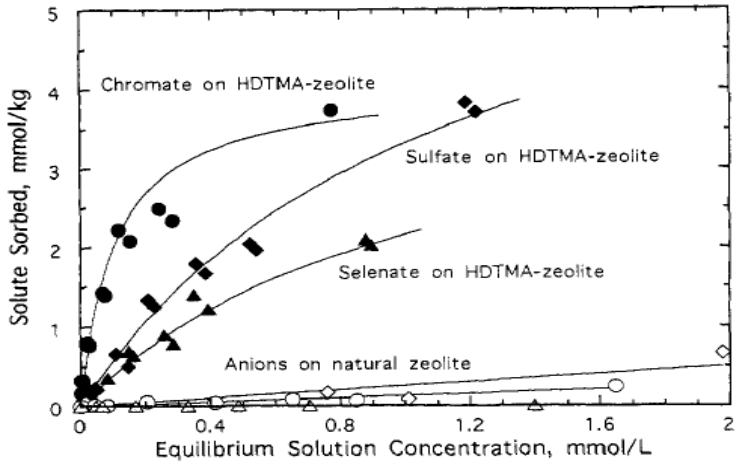


Figure 1: Sorption of oxyanions to natural zeolite and to HDTMA treated zeolite.

Batista *et al*. (2000) prepared an organo-zeolite by modification of the surface adsorptive properties of natural zeolites (Clinoptilolite) from Cuba, with a cationic surfactant, Br-HDTMA, and obtain an adsorbent with a maximum removal capability of Cr (VI) of 30 mg/g organo-zeolite. Ghiaci *et al*. (2004) compared the performance of natural zeolite modified by surfactant hexadecyltrimethylammonium (HDTMA) and cetylpyridinium bromide (CPB) for removal of chromate from aqueous solution. Their results showed that HDTMA and CPB modified Clinoptilolite exhibited higher chromate sorption than its natural form. [29] Campos *et al.* (2007) reported removal of hexavalent chromium by EHDDMA and HDTMA-HSO_4 cationic surfactants modified mordenite zeolite. A comparison with untreated phase indicates that surfactant-modified zeolite is more effective than the natural sample Mordenite. The data

indicated that the maximum percentage adsorption was 93% (HDTMA-HSO_4) and 67% (EHDDMA) for the initial chromium concentration of 2.5 mg L^{-1}. [30] Ramos *et al*. (2008) studied the adsorption of Cr (VI) form aqueous solution on Clinoptilolite and HDTMA modified Clinoptilolite. They stated that surfactant modified Clinoptilolite adsorbed 22 times more chromium than the non-modified. [31] Covarrubias *et al*. (2008) reported the CPB-modified FAU type zeolite presented the highest Cr (VI) retention capacity (37 mmol/kg) which is higher than the value found for HDTMA-modified Clinoptilolite (HDTMA-HSO_4^-, 28 mmol/kg) due to the higher Cr (VI) retention of its unmodified form (larger pore opening) which retained about 9.54 mmol/kg and its high CPB sorption capacity. In addition, the intrinsic Cr(III) exchange capacity of FAU zeolite increased with CPB loading (162– 527 mmol/kg), which appear to be due to an additional retention mechanism provided by the sorbed cetylpyridinium surfactant layer. CPB-modified FAU zeolite appears as a promising adsorbent for simultaneous removal of Cr (III) and Cr (VI) (Figure 2). [32]

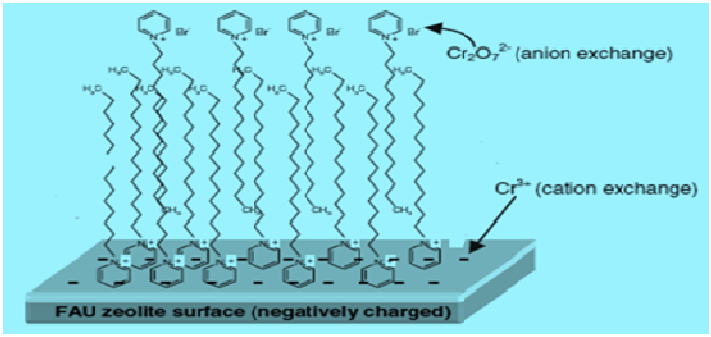


Figure 2: The retention of Cr (VI) on the CPB micelles and Cr (II) on the zeolite surface.

Zeng *et al*. (2010) studied the adsorption of Cr (VI) by hexadecylpyridinium bromide (HDPB) modified Clinoptilolite. Their results indicated that HDPB modified Clinoptilolite had higher affinities towards chromate than that of natural ones. [36] V. Swarnakar*et al*. (2011) reported sorption of Cr (VI) on HDTMA-modified zeolite (Erionite) in which the sorbed SMZ forms ad-micelle surfactant surface coverage which is responsible for chromate sorption. The isotherm data was analyzed and fitted to the Freundlich isotherm in which the sorption capacity of Chromate reached 21 mg/g. Zeolite modified with Fe could serve as medium to remove Cr (VI) from wastewater. [37] This is because, Fe-loaded zeolites showed electrochemical reduction ability, which was not observed in natural zeolites, while they maintained their original high

cation exchange capacity. Gaoxiang Du *et al*. (2012) reported that the added Fe (III) resulted in an enhanced Cr (VI) retention by the zeolite. The influence of present Fe (III) on Cr (VI) retention by and transport through zeolite was studied under batch and column experiments. The Cr (VI) adsorption on Fe (III)-zeolite followed a pseudo-second order kinetically and the Freundlich adsorption isotherm thermodynamically. The adsorption of Cr (VI) on the Fe (III)-zeolite increased as the equilibrium Cr (VI) concentration increased. [38] Natural zeolites modified with acid also showed better performance of Chromium from wastewater. Based on this: S. Kocaobaa and Y.Orhanb (2007) reported the chromium removal from wastewaters by natural and modified zeolites.Clinoptilolite-type Turkey natural zeolite will pretreated with HCl and HNO_3 to improve the adsorption capacity for heavy metals. The result showed that the modified Clinoptilolite showed removal efficiency of (70-80 %) and the natural Clinoptilolite showed an efficiency of about 70 % as shown in the figure bellow. [39] The very recent work by A. Nezamzadech and G. Kaja (2013) showed a novel chromate selective PVC membrane electrode constructed using a HDTMA-surfactant modified natural zeolite (Clinoptilolite). This membrane worked well over a wide range of concentration (5×10^{-6} to 1.0×10^{-2}mol/L) of CrO_4^{2-} with a better Nernstian behavior towards chromate ion in a wide pH range of 6.8-10.7. Hence, the modified nanoclinoptilolite with HDTMA was used as an ionophore for construction of a potentiometric sensor for this anion. [40]

For comparison of adsorption properties of natural and synthetic materials as well as micro-porous and mesoporous materials the work done by M. Ghiaci et al (2004) showed Synthetic (ZSM-5 zeolites) and natural (Clinoptilolite) zeolites, as well as MCM-41 molecular sieve were employed for removal of chromate from aqueous solution and the maximum chromate adsorption over as synthesized MCM-41 was much greater than that of the natural Clinoptilolite and ZSM-5 zeolites. The higher sorption of chromate by as-synthesized MCM-41 might be related to high surfactant aggregates on the inner surfaces of this mesoporous material. Hence, from the standpoint of industrial applications, this chromate sorption capacity of MCM-41 is very attractive. [41]

1.4.1.2 Chromium removal using Mixed oxides

Hydrotalcite consist of stacked layers of metal cations ($M^{2+}$and M^{3+}) similar to brucite-like structures. They are part of a common group of minerals known as layered double hydroxides

(LDHs). The brucite-type layers are stacked on top of each other and are held together by weak interactions through the H atoms. Substitution of divalent cations for trivalent cations with similar radii, where a maximum of one in three trivalent sites are substituted by a divalent cation, gives rise to positively charged layers. [42] The general formula for these structures is as follow $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}A_{x/m}^{m-}\cdot nH_2O$, where M^{2+} is a divalent cation, M^{3+} a trivalent cation, and A an interlamellar anion with charge m-. The resultant positive charge, caused by the substitution of aluminum, is neutralized through the intercalation and adsorption of anions. Charge neutrality is not confined to the interlayer region, but also to the external surfaces of the hydrotalcite structure. Because there is no overall charge, hydrotalcite are quite stable. The interlayer region of LDHs are complex, consisting of anions, water molecules, and other neutral or charged moieties. A large variety of anionic species can be positioned between the hydroxide layers, including halides, oxyanions, oxy and polyoxy-metallates, anionic complexes, and organic anion. [43, 44] The interlayer interactions of LDHs are mediated by Coulombic forces between the positively charged layers and the anions in the interlayer, and hydrogen bonding between the hydroxyl groups of the layer with the anions and the water molecules in the interlayer. Water molecules are connected through extensive hydrogen bonding to the hydroxyl ions of the metal hydroxide layers and interlayer anions. [45]

LDHs have a so-called “memory effect”, whereby a hydrotalcite material can be thermally treated to remove water, hydroxyl, and carbonate units from its matrix, then rehydrated in an aqueous solution to return to its original structure. This memory effect can be used effectively to remove harmful anions, both organic and inorganic, from wastewater solutions. The calcinations of hydrotalcite, at temperatures of 350-600°C, removes interlayer water, interlayer anions (Carbonate anions) and hydroxyls. The result is the collapse of the crystalline hydrotalcite to an amorphous magnesium oxide with dispersed Al^{3+} ions as a solid solution. The carbonate anions are decomposed to carbon dioxide (CO_2) and O^{2-}, leaving O^{2-} anions between the layers. [46]

Rehydrating the calcined product regenerates the LDH, where water is absorbed to reform the hydroxyl layers, as well as being absorbed into the interlayer, along with the anion in solution. The composition of hydrotalcite is dependent on the pH, where hydrotalcite formed at high pH (pH>13) had a Mg:Al ratio of 2:1 ($Mg_4Al_2(CO_3)(OH)_{12}\cdot xH_2O$), while those precipitated at pH=8 had a Mg:Al ratio of 4:1 ($Mg_8Al_2(CO_3)(OH)_{20}\cdot xH_2O$).

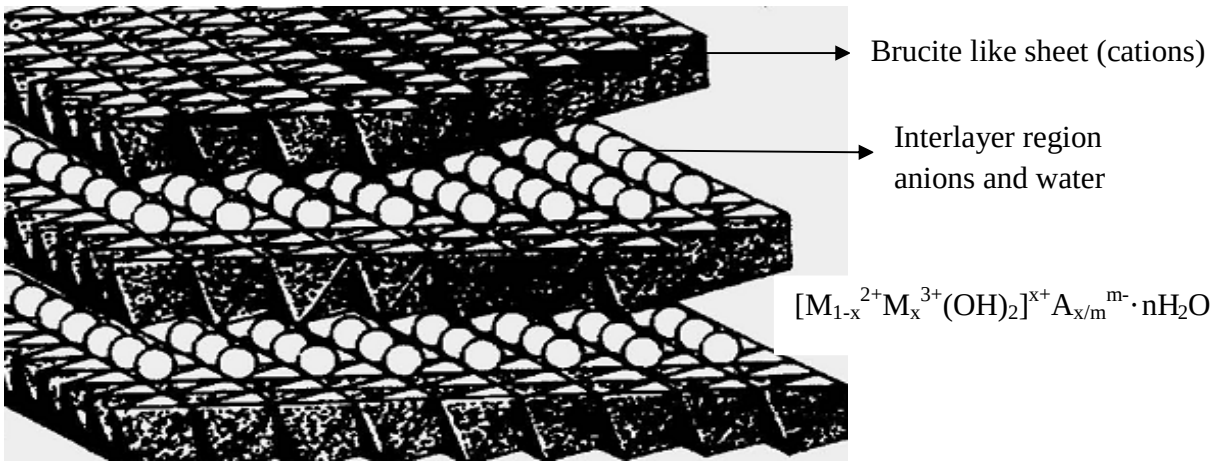


Figure 3: Schematic representation of the hydrotalcite-type an ionic clay structure.

At high pH, a more stable microcrystalline carbonate hydrotalcite forms, because of the readily adsorbed CO_2 from the atmosphere, producing a saturated carbonate solution. At lower pH (pH<9.5), a less well-defined crystal structure forms. Because of the decrease in the available carbonate in solution, the intercalation of other anions into the hydrotalcite structure is possible. The decrease in available carbonate is due to the rapid decrease in OH^- ions from solution resulting in a lower adsorption of CO_2, and therefore a decrease in available carbonate anions for intercalation. [48-52]

Many researchers have used Hydrotalcite for metal ion adsorption and several review works have appeared. However, these investigations focused on single metal ion and the affinity to mixed oxides. While for real wastewater systems, there are different types of contaminants and may contain a mixture of metal ions. In recent years, more investigations have concentrated in this area. For example, B. E. López Muñoz *et al* 2011, this study was all about sorption behavior of the chemical species of Cr(III) from aqueous solutions by hydrotalcite calcined products. The final pH of the chromium sulfate solutions in contact with the CHT in combination with the concentration that promote different chromium (III) chemical species play an important role for the chromium (III) sorption by the HT. The maximum sorption of CHT to exchange Cr (III) is 26.5 mmol/g and the SO_4^{2-} is incorporated into the lamellar crystalline structure of HT during the regeneration processes as a consequence of the memory effect. The removal of Cr(III) from wastewater using CHT is a good alternative because the oxidation of Cr (III) to Cr (VI). [53]

L. Cocheci *et al* 2010, in this paper, five hydrotalcite-like compounds containing Mg^{2+} and Zn^{2+} in different proportions as divalent cations were synthesized and characterized from a structural, textural and morphologic point of view, in order to be used as adsorbents for chromate anion removal. The calcined hydrotalcite like compound can be used as potential ion exchanger/adsorbent for the removal of toxic Chromium ion from wastewater. [54]

G N Manju *et al* 1999, show the sorbent power of hydrotalcite $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}A_{x/m}^{m-}\cdot nH_2O$ compound for Cr (VI) from water solution. The result show remarkable adsorption capacity compared to other adsorbent. The efficiency of Cr (VI) removal is enhanced by decreasing the pH of the solution. The maximum adsorption of Cr (VI) is observed at pH=2. This may be the fact that anion exchange mechanism is involved and CO_3^{2-} ions are exchanged by $HCrO^-_4$. Adsorption of Cr (VI) increased with increasing temperature. Desorption of Cr (VI) from spent adsorbent was 95.7% at 0.1M NaOH. 100% removal of Cr (VI) from synthetic wastewater could be achieved at pH=2. [55]

OBJECTIVE OF THE STUDY

2.1 General objective

The major attempt of this work is to study the adsorption capacity different natural zeolites from Mexico and Ethiopia, synthetic mesoporous materials (calcined and uncalcined SBA-15) and mixed oxides (Hydrotalcite and SBA-15 supported Hydrotalcite) for chromium metal ions from water solution.

2.2 Specific objective

- To investigate the efficiency of different porous material on chromium removal.
- Finding suitable adsorbent which is capable of removing or minimizing the risk of Cr (VI) which appear in the discharged waste water of tanneries.
- Introducing new, low cost, easily manageable and environmentally acceptable way of removing Cr (VI).

EXPERIMENTAL PART

3.1 Materials and Chemicals

3.1.1. Chemicals:

The raw material and chemicals used for this study include: two natural zeolites, Clinoptilolite ZEOCAT (from Mexico) and a natural zeolite from Gondar, Ethiopia named Sample 7; mesoporous materials (calcined and uncalcined SBA-15) synthesized at the Institute of Catalysis and Petroleochemistry (ICP-CSIC), Spain and mixed oxides (Hydrotalcite and SBA-15 supported Hydrotalcite) kindly donated by Prof. Pedro Bosch and Dr. Geolar Fetter from Universidad Nacional Autonoma de Mexico (UNAM). $K_2Cr_2O_7$, 1, 5-diphenyl carbazide, Ethanol and 0.2N H_2SO_4. All raw adsorbent obtained in powder form, were crushed and sieved to the particle size fraction 75-125 µm and prepared for the experiments. All other chemicals used were at least reagent grade.

3.1.2 Apparatus and Instruments used:

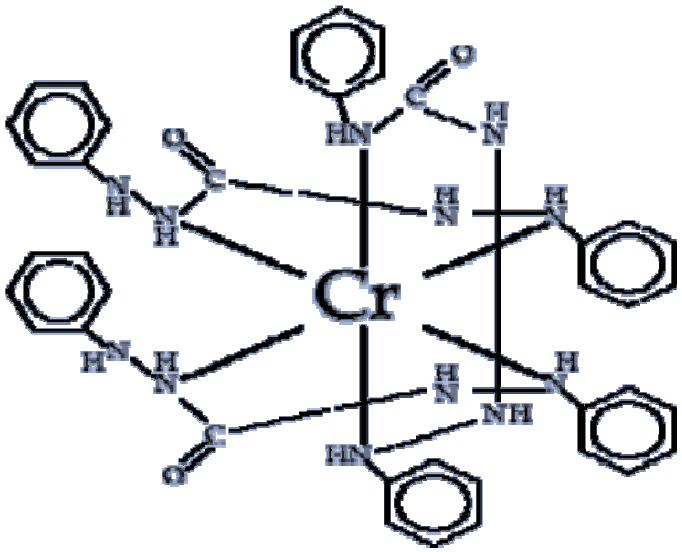
UV-VIS Spectrophotometer (PerkinElmer UV WinLab 6.0.3.0730 / 1.61.00 Lambda 900) has been used for the measurement of the concentration of chromium.

3.2 Experimental procedure

3.2.1 Preparation of standard solution for UV-Vis measurement

In order to improve the sensitivity of UV-Vis towards Cr (VI), a complexation agent, 1, 5-Diphenyl carbazide (DPC), (bidentate ligand) is used. The complexation must be done in acidic medium. The carbonyl oxygen and the nitrogens attached to the phenyl group on the 1, 5-DPC activate and the Cr (VI) will start to combine and form a complex with 1, 5-DPC having red violet color. The characteristics peak is due to the charge transfer from ligand to metal or metal to ligand.

0.25 g of of a common complexing agent of chromium (VI) for spectrophotometeric analysis was taken and dissolved with some amount of 95% ethanol. This solution was further diluted to 100 mL with distilled water.



Scheme 1: Schematic diagram for Cr (VI) complex with 1, 5-DPC.

0.360 g of $K_2Cr_2O_7$, analytical grade, was dissolved in distilled water and diluted to 1L. A series of eight standards were prepared by taking aliquots of 0.1, 0.2, 0.3, 0.4, 0.5, 0.7, 1 and 1.25 mL from the stock solution into 100 mL measuring flasks. (The mass of the aliquots was accurately determined by an analytical balance). They were acidified with 5 mL of 0.2 N sulfuric acid. Then 1 mL of freshly prepared 1, 5-DPC solution was added to each standard and a pink color was immediately developed. The solution was completed by adding water until the mark. The amount of complexing agent was increased for the last four series to make sure a total complex formation. The standard solutions were analyzed with UV-Visible spectrophotometer with 1cm quartz cell . the absorbance measurements were performed in the range of 400-700 nm. The absorption maxima were observed at 540 nm as shown.

A calibration curve is done by plotting the absorbance at the maximum vs the concentration of Cr (VI) in ppm.

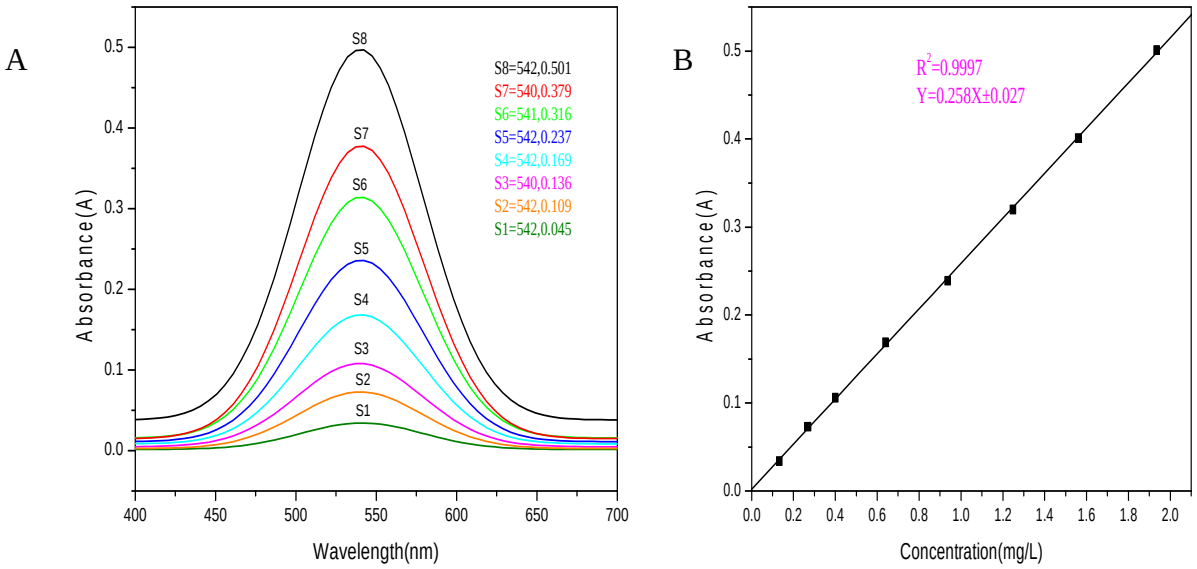


Figure 4: Spectral data of standard solution (A) and Calibration curve (B).

3.2.2 Procedure for Adsorption Experiment

For adsorption experiment, 4 ppm of Cr (VI) solution was prepared by weighing 11.3 mg and diluting then in 1000 ml volumetric flask. Then 2.5 ml of the solution was poured into each glass vials which had 25mg of the different adsorbent (Clinoptilolite, sample 7, calcined SBA-15, uncalcined SBA-15, Hydrotalcite and SBA-15/HT). Each vials containing the mixture and the solution was left for a contact time of 24h under vigorous stirring. After this, the solution was taken to centrifuge to separate the supernatant solution from the residue. Finally the supernatant solution was immediately analyzed in the UV-Vis measurement by adding small amount of 0.2N H_2SO_4 and 1.5-DPC to each solution. These amounts were accurately weighed in order to determine the dilution factor (correction). The absorbance was recorded at 540 nm and the concentration of each solution was calculated using the calibration curve.

Note: The absorbance of the initial solution must be measured every time to check the concentration.

RESULTS AND DISCUSSION

4.1 Cationic exchangers: Zeolites

Zeolites are crystalline aluminosilicates, compositionally similar to clay minerals, but differing in their well-defined three-dimensional nano- and micro-porous structure. Aluminum, silicon, and oxygen are arranged in a regular structure of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedral units that form a framework with small pores (also called tunnels, channels, or cavities) of about 0.1 nm-2 nm diameter running through the material. As a consequence of the framework being built from negatively charged units is that it possesses a net negative charge that must be balanced by the presence of positively charged cations. Most naturally occurring zeolites have the environmentally predominant sodium ion as a loosely bound counter ion. These can be readily displaced by other ions for which a particular framework has a much greater affinity, thus giving zeolites significant ion exchange properties. [33]

Clinoptilolite is the most abundant natural zeolite and has the chemical formula $Na_{0.1}K_{8.57}Ba_{0.04}(Al_{9.31}Si_{26.83}O_{72})\bullet 19.56H_2O$. [14] Its characteristic tabular morphology shows an open reticular structure of easy access, formed by open channels of 8-10-membered rings. Considerable research has been conducted to characterize the chemical, surface, and ion-exchange properties of Clinoptilolite. The ion-exchange capacity of natural zeolite for inorganic cations has been investigated by many authors. [34]

It should be noted that the ion exchange and the pore size properties of zeolites are partially linked. When the zeolite is in the sodium form (i.e., it has positively charged sodium ions balancing the net negative charge on the aluminosilicates framework), the sodium ions are associated with the tetrahedral aluminum or silicon atoms at the entrance to the pores and, because of their finite size, they effectively reduce the diameter of the pore opening slightly. If the sodium ions are replaced by potassium ions, which are larger than the sodium ions, then the opening of the pore is effectively reduced even further. This behavior permits a degree of control over the size of material that can enter the pores.

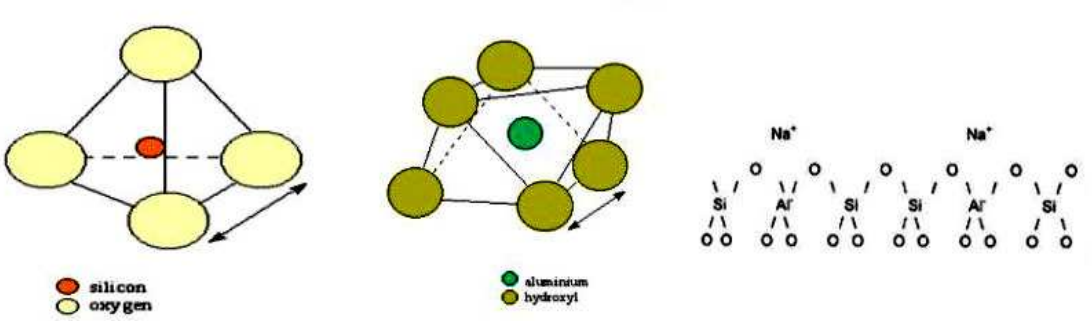
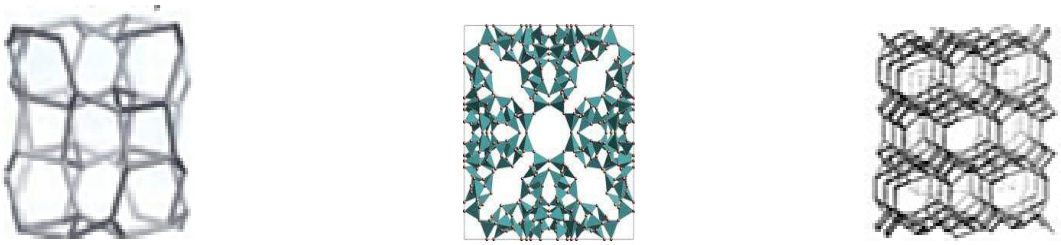


Figure 5: Aluminosilicates tetrahedral structure and exchangeable cations within the zeolite framework.

Zeolites are aluminosilicates, but other tetrahedral atoms such as phosphorus, gallium, germanium, boron, and beryllium can exist in the framework as well.

In our attempt to evaluate natural zeolites for chromium removal, we have tested a commercial natural zeolite, clinoptilolite ZEOCAT (from Mexico) and a natural zeolite from Ethiopia (Sample 7) collected in Gondar region which contains a lot of iron as extraframework cation. The X-ray diffraction pattern of this sample showed a mixture of two structures: Natrolite and Analcime (Figure 6A and B, respectively). Natrolite with a unit cell formula of $Na_2Al_2Si_3O_2(H_2O)_2$ shows to be the main product and Analcime ($Na(AlSi_2O_6)(H_2O)$) gives small intensities. The average chemical composition of Sample 7 provides a Si/Al of 1.88, and Fe/Ti of 11.14. The idea of using an Fe-containing zeolite was to survey the potential reducing behavior of the adsorbent. For comparison purposes, a clinoptilolite with Si/Al 4.5 and no Fe at all was evaluated and compared with the literature (Figure 6C).



(A) **(B)** **(C)**

Figure 6: Crystal's structure of Analcime(A), Natrolite (B) and Clinoptilolite (C).

Figure 7: Picture of Sample 7 from Gondar.

C. Covarrubias *et al*, 2008 showed that the natural mordenite adsorb only around 25-30% of hexavalent Chromium ion due to the narrow pore size. The data showed that modified zeolites having large surface area can easily absorb chromate ion whereas those with small pore volume will result in low affinity for chromate ion. Seunghak Lee *et al*, 2004 discussed the effect of Fe in zeolite structure for removal of chromium from wastewater. The paper shows the Fe-loaded zeolites have a great adsorption capacity. This is due to the role of the Fe^{3+} which is loaded in zeolite that would reduce the Cr (VI) (as chromate anion) to Cr (III) that could easily be exchanged by the negatively charged zeolite framework. The paper shows above 90% removal of a composition of 3 g adsorbent in 0.03 L of 0.5 mM Cr (VI) solution. [32]

In our experiments we chose solutions of 4 mg/L of Cr (VI) and at a solid to liquid dose of 10 g/L. The contact time between the Cr (VI) solution and the zeolite was not optimized, thus set at 24h where we assume that the saturation or equilibrium has been reached. As collected in Table 1, both samples show an unusually good adsorption capacity and it is worth noting that these zeolites are not modified nor doped, they are used as they are collected. These results indicate

that their pore volume is enough to retain the chromate ion from the solution. The UV-Vis spectra in Figure 8 show the solution treated by each natural zeolite show different absorption peak with different intensity.

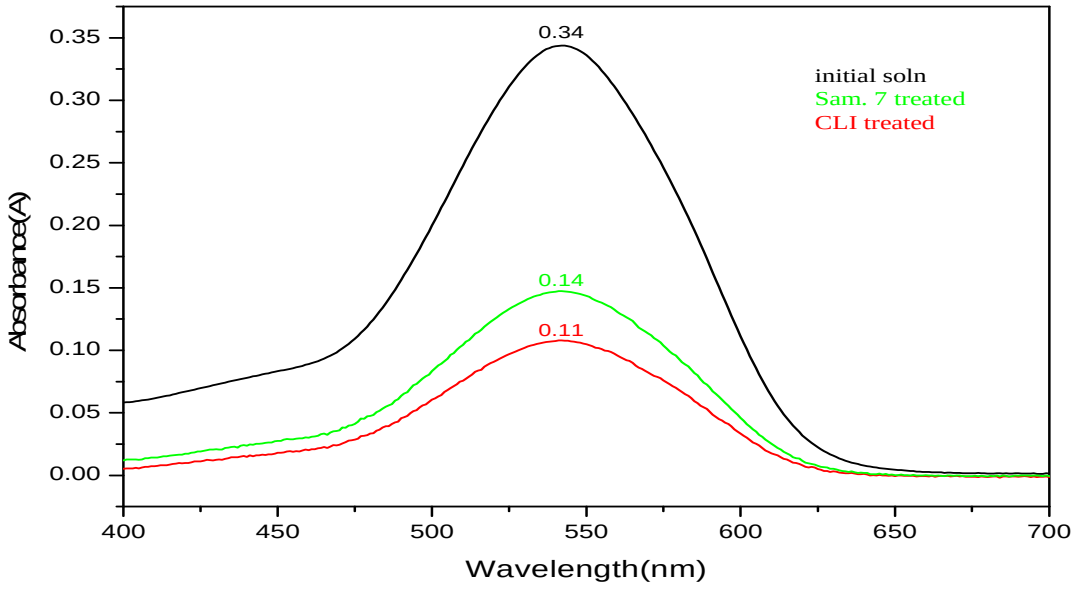


Figure 8: Spectral data of the initial solution (A=0.35) and the solution after treated by different natural zeolites, namely: Clinoptilolite (A=0.11) and Sample 7 (A=0.14).

Table 1: Adsorption capacity of natural zeolites with an initial concentration of Cr (VI) of 4mg/L.

Adsorbent type	**Amount of adsorbent/amount of Cr (VI) solution**	**%Removed**
Clinoptilolite	0.025g/0.0025L	74.43%
Sample 7	10g/L	67.65%

Zeolites are known to be cationic exchangers, thus they should not accept anions. From the table both natural zeolites show good (68 to75 %) adsorption results for chromate ion this may bring controversial idea with the expected ionic properties of zeolites. Then, what property of the natural zeolites help to remove such a high amount of chromate ions from the solution?

Three mechanisms may be proposed. 1) Most zeolites found in nature may contain impurities and they are not as neat as synthetic zeolites. The impurities are randomly located throughout the structure of the zeolite and they may retain the chromate ions from the solution. For instance, extra-framework alumina should interact with chromate ion improving the removal capacity.

2) Also the defects present in the structure of natural zeolites contribute to the removal of chromate ion. Defect structure is a fault or lack of some part of the zeolite framework. In other words positive charge centers may be present: the chromate ion from the solution can enter into the missing part of the zeolites and can be stacked into the pore.

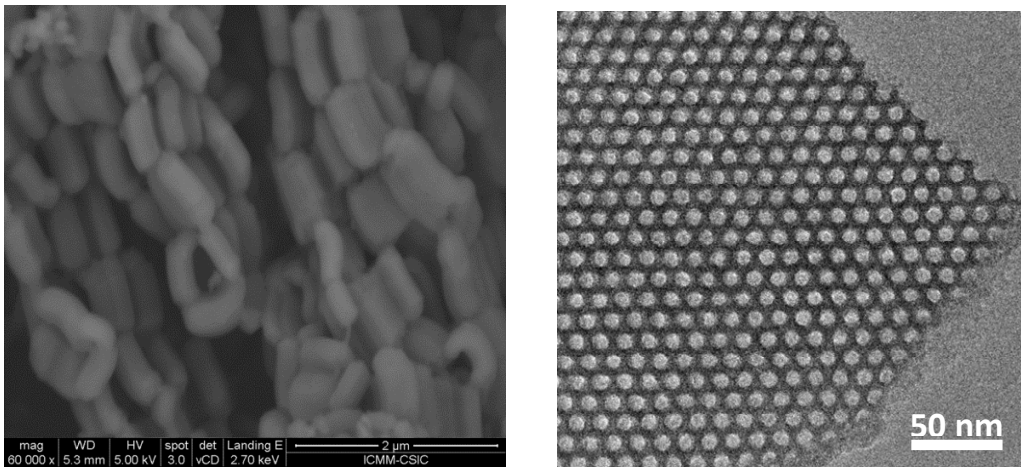
3) There is also the possibility of chromate ion (CrO_4^{2-}) to replace the hydroxyl anion (OH^-) from the extra framework alumina. This may increase the removal percentage of chromate ion. While in contact with the solution, this extra framework aluminum will have some interaction with chromate ions. So the removal capacity increases due to this reason.

In summary, despite the low adsorption capcity of raw natural zeolites, the two samples tested in this work show higher Cr removal than those reported in the literature.

4.2 Mesoporous Silicate SBA-15

SBA-15 (Santa Barbara Amorphous) is an interesting mesoporous silica material having highly ordered nanopores and a large surface area, which is widely employed as an adsorbent. Since it has a lack of functionality, heteroatoms and organic functional groups have been incorporated by direct or post-synthesis methods in order to modify their functionality. It exhibits interesting textural properties, such as large specific surface areas (above 1000 $m^2 \cdot g^{-1}$), uniform-sized pores (in the range 2 nm-30 nm), thick framework walls, small crystallite size of primary particles and complementary textural porosity. SBA-15 like MCM-41 is a mesoporous, hexagonally ordered material. Figure 9 shows the fiber like morphology of the SBA-15 sample employed in this work

(A), along with the TEM image of the projection along the pore channels where the honeycomb typical structure could be observed (B).

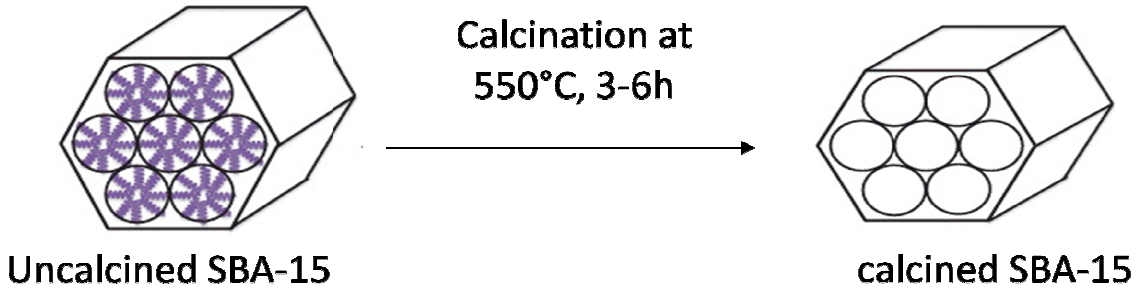


(A) (B)

Figure 9: SEM (a) and TEM (b) images of SBA-15

SBA-15 is commonly prepared using a non ionic surfactant (Pluronic P123) which forms micelles that provide the assembly in the mesopore range. After the hydrothermal synthesis of the silica around the micelles the resulting material (uncalcined SBA-15) has no porosity, furthermore, the surfactant is still located in the mesopore and the only room for adsorption would be the interface between the silica wall and the cationic head groups of the surfactant.

Some researchers have tested the material as described above (uncalcined MCM-41) for chromium removal [41] in an attempt to compare the resulting behavior with that of surfactant-modified zeolites. M. Ghiaci et al, 2001 show that the adsorption capacity of chromate onto the as-synthesized MCM-41 was higher than in surfactant-CLI (binaural Clinoptilolite). With a removal value of 73.6% from 62 ppm of Cr (VI) with a ratio of 0.15 g adsorbent in 0.025 L solution, in as-synthesized MCM-41. Any how, a final step to have the porosity of SBA-15 fully available requires calcinations at high temperatures (Scheme 2).



Scheme 2: Schematic representation of calcination of SBA-15.

From the UV-Vis data of Figure 10 we can see that calcined SBA-15 mesoporous material treated solution give absorption peak of A=0.284 which is almost near to the value of absorption peak of initial solution. This shows that calcined SBA-15 remove small amount of chromate ion from the solution most probably due to the large pore size of the channels that allow the chromium ions to pass through without retention. On the other hand uncalcined SBA-15 give an absorption peak at A=0.21 this shows us the uncalcined SBA-15 remove more amount of chromate ion than calcined one. This is due to the uncalcined SBA-15 has some functional group (the interface) which increase retention capacity of chromate ion in SBA-15 or in the micelles head groups which has positively charged ethylene oxide chains.

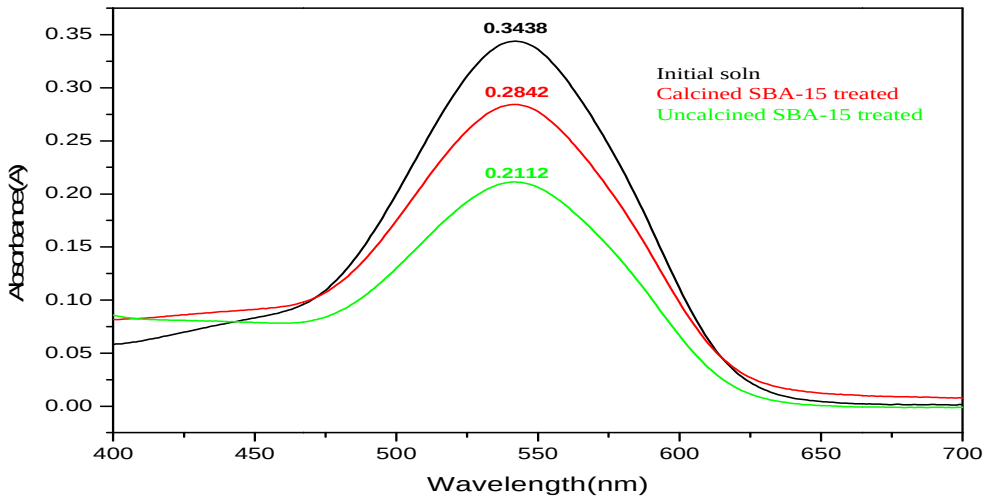


Figure 10: Spectral data of the intial solution (A=0.38), calcined SBA-15 (0.28) and uncalcined SBA-15 (0.21) treated solution.

Table 2 collects the removal efficiency of these materials. From the structural representation of SBA-15 and the large pore size (30 nm), the chromate ion in the solution will pass through the straight channels showing very low affinity with the silica wall. Thus, despite the promising properties of SBA-15 molecular sieve in separation, there is still a need to modify or functionalize the pore surface of SBA-15 for better removal behavior.

Table 2: Adsorption capacity of mesoporous materials with an initial concentration of Cr (VI) of 4mg/L.

Adsorbent type	**Amount of adsorbent/amount of Cr (VI) solution**	**%Removed**
Calcined SBA-15	0.025g/0.0025L	13.59%
Uncalcined SBA-15	10g/L	39.89%

4.3 Anionic exchangers: Mixed oxides (Hydrotalcite and SBA-15/Hydrotalcite)

Hydrotalcite is, in its natural form, a hydroxycarbonate of magnesium and aluminum, belonging to the class of anionic clays, with the formula $[Mg_6Al_2(OH)_{16}]^{2+}.CO_3^{2-}.4H_2O$, and a layered structure. Structurally, they are formed by brucite-like ($Mg(OH)_2$) sheets where isomorphous substitution of Mg^{2+} by a trivalent cation like Al^{3+} occurs. The positive charge of the layer is compensated by anions, which occupy the interlayer space along with water molecules. One of the most exploited property of double layered hydrotalcite is the so called ‘‘memory effect” which consists in the spontaneous structural reconstruction of the original layered structure after being calcinated and then put in water or aqueous solutions containing different anions. [45, 46] Anionic clays are the mirror images of cationic clays and contain positively charged layers and anions in the inter layers. Its name designates a whole class of natural or synthetic hydrotalcite-like compounds (HTlcs), with general formula $[(M^{II})_{1-x}(M^{III})_x(OH)_2]^{x+}[(A^{m-})_{x/m}nH_2O]^{x-}$

Where: M^{II} and M^{III}: divalent (Mg, Ni, Zn, Cu...) and trivalent cations (Al, Ga, Cr, Fe...)

A: Interlamellar anion with charge m (CO_3^{2-}, OH^-, Cl^-, SO_4^{2-} ...)

x: molar ratio $M^{III}/(M^{II}+ M^{III})$ and n: water molecule

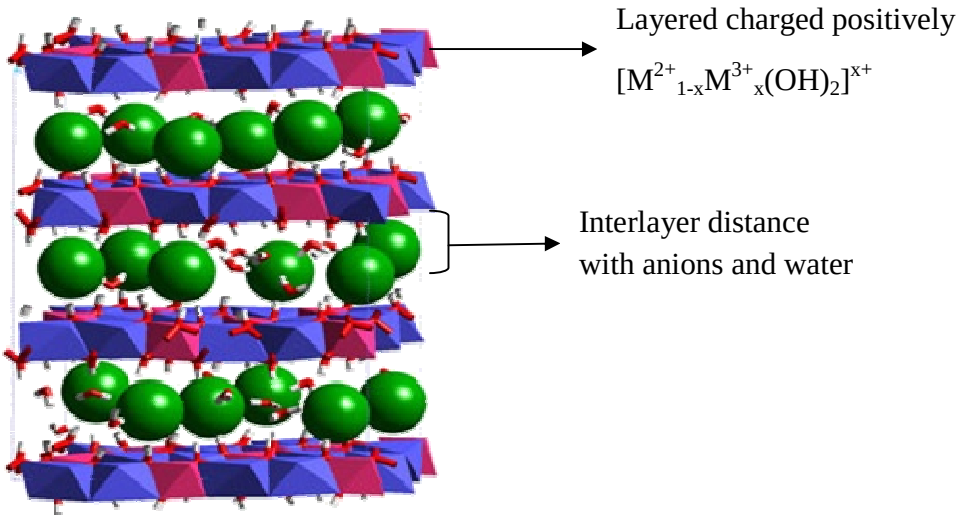
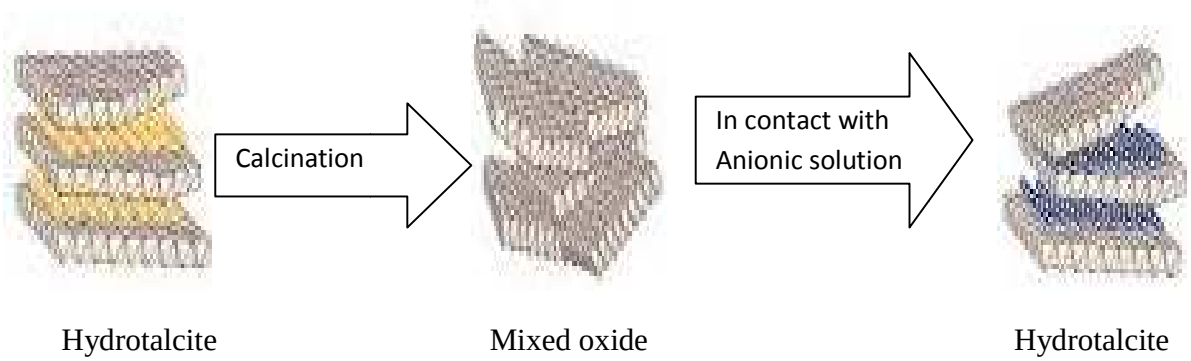


Figure 11: Layered structure of hydrotalcite

Memory effect of Hydrotalcite

The anion exchange capacity of hydrotalcite is due to the memory effect. The memory effect, which consists in the spontaneous structural reconstruction of the original layered structure after being calcinated and then put in water or aqueous solutions containing different anions.

When hydrotalcite are calcined, the layers become slept together by removing the interlayer distance. After in contact with anionic solution the mixed oxides will start to attain their former structure or reform again and they can start to retain anions (in our case CrO_4^{2-}) easily from the solution.



Scheme 3: Schematic diagram for memory effect.

In the aim to prepare nano-hydroxytalcite, a newly developed synthesis route has been explored in with the Hydrotalcite supported on a SBA-15. The final composite SBA-15/HT has the desired functionality in the pores surface, along with large pore size that will allow the Chromate ion to move through the channels.

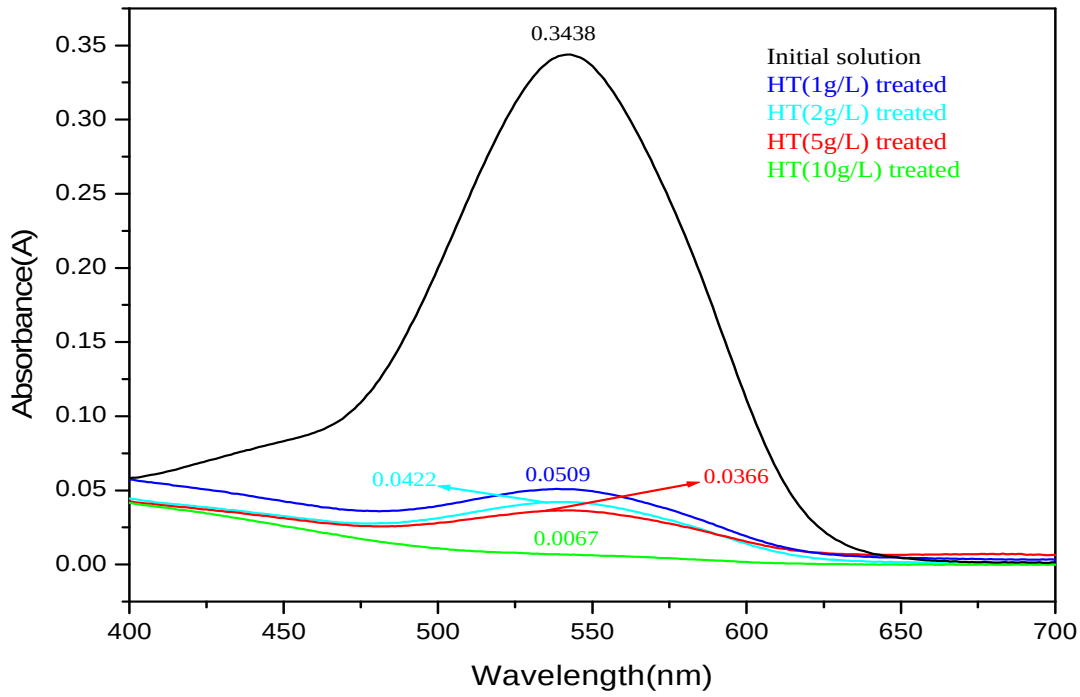


Figure 12: Spectral data of initial solution (A=0.35) and HT 5mg (A=0.042), HT 12.5mg (A=0.037) and HT 25mg (A=0.007) treated solution.

The UV-Vis spectra (Figure 12) show the absorbance peak for chromium in the prepared solution and after treating it with different dose of hydrotalcite. It's very easy to look and explain the absorbance peak intensity difference between treated and untreated one. The absorbance for HT 25 mg is A=0.006 which is almost zero.

The graph shown in Figure 13 tells us the absorbance of each solution treated by different adsorbent dose of the composite SBA-15/HT and the initial solution. As we can see from the

graph it shows great difference in absorption peak intensity. SBA-15/HT have A=0.004, which is insignificant for 25 mg adsorbent dose.

Also it has better adsorption ability for chromate ion even at lower dose amount. So SBA-15/HT is effective for adsorption of Chromate ion.

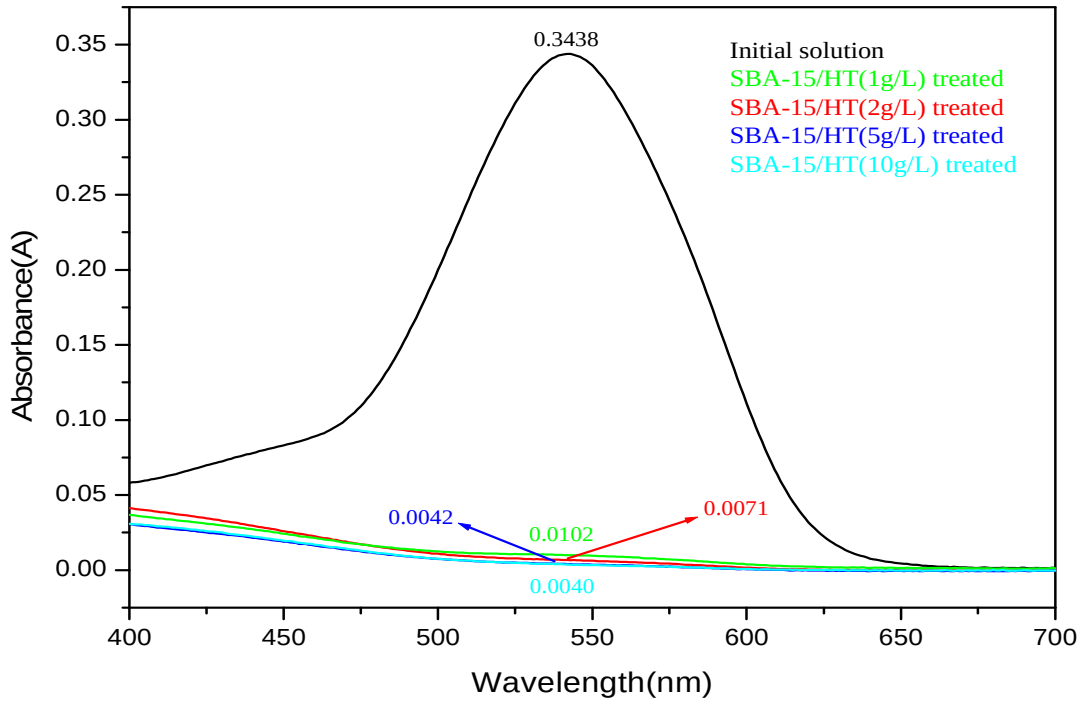


Figure 13: Spectral data of initial solution (A=0.35) and SBA-15/HT 5 mg (A=0.01), SBA-15/HT 12.5 mg (A=0.0042) and SBA-15/HT 25 mg (A=0.0040) treated solution.

Both mixed oxides HT and SBA-15/HT yield better adsorption capacity compared to other adsorbents used in this work. From the data collected in Table 3 it can be observed that SBA-15/HT has better adsorption capacity than Hydrotalcite. As decreasing the amount of adsorbent dose the percentage adsorption will decrease having a direct relationship. The result obtained by using SBA-15/HT (98.6% removal) is better than hydrotalcite (88.7% removal), the chromate ion effectively adsorbed by the composite.

SBA-15 supported hydrotalcite at 2g/L ratio remove 96.3 % which means retains higher capacity than hydrotalcite. This is because the hydrotalcite in the composite doesn't require calcination so it simply uses as anion exchanger. On the other hand the hydrotalcite crystals in the SBA-15/HT composite are very small due to the confinement effect. Because of those reasons the composite remove higher amount of chromate ion from the solution.

Table 3: Adsorption capacity of HT and SBA-15/HT from a solution of 4 mg/L of Cr (VI).

Adsorbent type	**Amount of adsorbent/Amount of Cr (VI) solution**	**% Removed**
Hydrotalcite	0.025g/0.0025L (10g/L)	100%
	0.0125g/0.0025L (5g/L)	88.7%
	0.005g/0.0025L (2g/L)	87.8%
	0.005g/0.005L (1g/L)	85.4%
SBA-15/HT	0.025g/0.0025L (10g/L)	100%
	0.0125g/0.0025L (5g/L)	98.6%
	0.005g/0.0025L (2g/L)	96.3%
	0.005g/0.005L (1g/L)	94.6%

Table 4 collects a summary of the data obtained in this work. The obtained results show us indirectly the chemical properties of each material, being these properties the determing factor for the adsorption capacity for a Chromate ion in the solution.

Hydrotalcite and SBA-15 supported hydrotalcite having anion exchange property show better adsorption capacity than the rest of adsorbent mentioned above. In contrast SBA-15 in the absence of functional group has lowest retaining capacity for chromate ion, lower even than Zeolites due to the large pore size. Natural zeolites show high removal percentages despite their cation exchange property, probably due to the various cations present in the channels of the zeolites which favour the adsorption of anions.

Table 4: Comparison of the adsorption behavior of the different materials.

Adsorbent type		**Amount of Adsorbent/Amount of Cr (VI) solution**	**% Removed**
Natural Zeolite	Clinoptilolite	10g/L	74.4%
	Sample 7		67.7%
SBA-15	Calcined		13.6%
	Uncalcined		39.9%
Hydrotalcite		10g/L	100%
		5g/L	88.7%
		2g/L	87.8%
		1g/L	85.4%
SBA-15/HT		10g/L	100%
		5g/L	98.6%
		2g/L	96.3%
		1g/L	94.6%

CONCLUSION

The adsorption capacity of different adsorbents for Chromate ion was studied using batch adsorption study. The absorption peak (from the UV-Vis spectra) difference between the initial solution and after treating it with different adsorbent show the amount of chromate ion removed from the solution with the respective adsorbent. The absorption peak on the UV-Vis spectra tells the amount or concentration of chromate ion that is still in the solution, not removed.

The two natural zeolites namely; Clinoptilolite and Sample 7 give an unusually good result. They removed above 60% of the Chromate ion from the solution. This is due to the size of the chromate ion in the solution have good probability to get in through the channel of zeolite structure. The defect structure of zeolite framework and extraframework aluminum species help the retaining capacity of natural zeolites.

We have also investigated Cr (VI) adsorption in SBA-15 porous material both in the absence and presence of surfactant. The Cr removal is not particularly high (less than 40%). The uncalcined SBA-15 show better adsorption capacity than calcined SBA-15 due to the presence of the functional group of the surfactants.

The best result was shown by mixed oxides such as Hydrotalcite and SBA-15 supported hydrotalcite. Each material removes almost all the chromate ion from the solution. The anion exchange property of hydrotalcite helps them to remove more chromate ion. The supported SBA-15 or the composite gave best result from each of the material tested in this work. The hydrotalcite having anion exchange property fixed in the SBA-15 material helps to retain more chromate ion. It shows excellent adsorption behavior.

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