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A Review on Cr(VI) Adsorption Using Inorganic Materials

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ABSTRACT

Chromium compounds are widely used in electroplating, metal finishing, magnetic tapes, pigments, leather tanning, wood protection and electronic and electrical equipment. Hexavalent chromium is a highly toxic metal and produces health damages. The most soluble, mobile and toxic forms of hexavalent chromium in soils are chromate and dichromate and the chromium distribution is also controlled by redox processes, its adsorption decreases with increasing pH and when competing dissolved anions are present. Several techniques have been developed to remove Cr(VI) from wastewater but these techniques have disadvantages such as high cost, non-selective, pH dependence, etc. The use of low cost sorbents has been investigated as a replacement for current costly methods; natural materials with a high adsorption capacity for heavy metals can be obtained. Modification of the sorbents can improve adsorption capacity. This paper includes some techniques for remove Cr(VI) with clays, silica and zeolites from aqueous solutions, some of the treated adsorbents show good adsorption capacities.

Keywords: Sorption; Hexavalent Chromium; Clay; Silica; Zeolites

1. Introduction

Hexavalent chromium is a strong oxidizing agent that is water-soluble in its anionic form. Due to its solubility, it is highly mobile in soil and aquatic environments and readily penetrates plant and animal epidermis where it irritates the tissues [1,2]. To meet strict environmental regulations, Cr(VI) in wastewater is typically removed by either adsorption or a reduction + precipitation method, both of which have problems. Adsorption of Cr(VI) anions by cellulose-based sorbents is relatively ineffective, while carbon is expensive. Therefore, Cr(VI) anions must be first reduced to Cr(III) cations for effective sorption. Likewise, to precipitate Cr(VI), it must first be reduced to Cr(III). The reduction of Cr(VI) is advantageous in itself because the trivalent form is a thousand times less toxic [3] and can be effectively adsorbed or precipitated.

The reduction of Cr(VI) in wastewater is typically done with a reducing agent like iron or iron(II) ions under acidic conditions. The process usually involves lowering the pH to 1 or 2, adding reducing agent, then raising the pH to the level for adsorption or precipitation [4].

All of these steps require large amounts of reagents, which affect the cost, the sustainability, the overall quality and ionic properties, and the amount of sludge generated. Thus, new ways to remove Cr(VI) from wastewater in a single step would be advantageous.

In this review, we focus attention on new ways to remove Cr(VI) from aqueous solutions using inorganic materials. In this sense we center our study on the use of natural and modified clays, silica and zeolites.

Figure 1 shows a classification of thenatural inorganic materials that have been recently studied for Cr(VI) sorption.
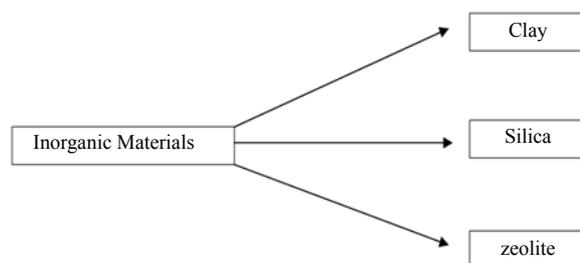
Figure 1. Inorganic materials currently used as Cr(VI) sorbent materials.

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2. Clay

Clay is mineral composed of alumina and silica that usually includes bound water. A mineral is a naturally occurring crystalline material that has a specific or limited range of chemical compositions. Clays have a sheet-like structure and are composed mainly of tetrahedrally arranged silicates and octahedrally arranged aluminates. Kaolinite is the principal mineral in kaolin clays. It is a 1:1 clay mineral with the basic unit being a 2-dimensional (2D) layer of silicate groups tightly bonded to a 2D layer of aluminate groups [5].

Clay occurs in all types of sediments and sedimentary rocks and is a common constituent of hydrothermal deposits. It is the most abundant mineral in sedimentary rocks perhaps comprising as much as 40% of these rocks. Half or more of the clay minerals in the earth's crust are illites, followed, in order of relative abundance, by montmorillonite and mixed-layer illite-montmorillonite, chlorite and mixed-layer chlorite-montmorillote, kaolinite and septachlorite, attapulgite, and sepiolite. The clay minerals are fine-grained: they are built up of tetrahedrally and octahedrally coordinated cations organized to form either sheets or chains. All are hydrous [6].

Clays exhibit large surface areas and are capable of adsorbing cationic, anionic, and neutral metal species. These materials are also able to participate in cationic and anionic exchange processes. Their sorption capacities, cation and anion exchange properties and binding energies vary widely [8]. Clays are extremely fine particles exhibiting chemical properties of colloids [9]. The high specific surface areas, chemical and mechanical stability, layered structure, high cation exchange capacity (CEC), have made clays excellent adsorbent materials [10]. The classification of clays is shown in **Table 1**.

Clays intercalated with metal oxides are of enormous importance because of their high thermal stability, high surface area, and intrinsic catalytic activity. These materials are usually prepared by ion-exchange cations in the interlayer region of swelling clays with bulky alkylammonium ions, polynuclear complex ions bearing inorganic ligands (hydroxyl, chloro, etc.), large metal complex ions bearing organic ligands, etc. The intercalated species are capable of preventing the collapse of the interlayer spaces, propping open the layers as pillars, and forming an interlayer space. On heating, the intercalated inorganic species are converted to metal oxide clusters, generating a stable microporous structure with a high surface area [10].

Clays have the property of adsorbing certain ions and retaining them in an exchangeable state. Exchangeable ions are held on external surfaces of the mineral. The CEC is confined primarily to the surface, in contrast to smectites and illites where a large part of the CEC belongs to interior sites. Therefore, to study purely surface

Table 1. Classification of clays.

Group name	Minerals	Chemical composition
Kandites	Nacrite	$Al_2Si_2O_5(OH)_4$
	Dickite	$Al_2Si_2O_5(OH)_4$
	Kaolinite-Tc	$Al_2Si_2O_5(OH)_4$
	Kaolinite-M	$Al_2Si_2O_5(OH)_4$
	Metahaloisite	$Al_2Si_2O_5(OH)_4$
	Haloisite	$Al_2Si_2O_5(OH)_4 \cdot 2H_2O$
	Anauxite	$Al_2Si_2O_5(OH)_4$
Septeclorites	Antigorite	$Mg_6Si_4O_{10}(OH)_8$
	Crisolite	$Mg_6Si_4O_{10}(OH)_8$
	Amesite	$(Mg,Fe)_4Al_4Si_2O_{10}(OH)_8$
	Cronstedite	$Fe_6(Si_2Fe_2)O_{10}(OH)_8$
	Berthierine	$(Fe,Mg,Al)_6(Si_3Al)O_{10}(OH)_8$
Clorites	Clorites	Variable
Mikas	Illite	$(K,H_3O)Al_2(Si,Al)_4O_{10}(OH)_2$
	Glauconite	$(K,H_3O)Al_2(Al,Fe)_2O_{10}(OH)_2$
	Ledikite	$(K,H_3O)Mg_3(Si,Al)_4O_{10}(OH)_2$
Esmectites	Montmorilonite	$0.33M+(Al_{1.67}Mg_{0.33})Si_4O_{10}(OH)_2$
	Baidellite	$0.33M+Al_2(Si_{3.67}Al_{0.33})O_{10}(OH)_2$
	Nontronite	$0.33M+Fe_2(Si_{3.67}Al_{0.33})O_{10}(OH)_2$
	Volkonskite	$0.33M+(Fe,Cr,Al)_2(Si,Al)_4O_{10}(OH)_2$
	Saponite	$0.33M+Mg_3(Si_{3.67}Al0.33)O_{10}(OH)_2$
	Sauconite	$0.33M+(Mg,Zn)_3(Si_{3.67}Al_{0.33})O_{10}(OH)_2$
	Hectorite	$0.33M+(Mg, Li)_3(Si, Al)_4O_{10}(OH)_2$
Vermiculites	Vermiculite	$0.67M+(Mg,Fe,etc.)_2(Si,Al)_4O_{10}(OH)_2$
	Vermicilite dioctahedrical	$0.67M+(Al,Fe,etc.)_2(Si,Al)_4O_{10}(OH)_2$
Hormitas	Sepiolite	$H_6Mg_3Si_{12}O_{30}(OH)_{10} \cdot 6H_2O$
	Paligorskite	$H_4Mg_5Si_8O_{20}(OH)_6 \cdot 6H_2O$

Source: [7].

processes, kaolinite may be an ideal material. Acid treatment of clay minerals is an important control over mineral weathering and genesis [10]. Such treatments can often replace exchangeable cations with H^+ ions and release Al^{3+} and other cations out of both tetrahedral and octahedral sites, but leaving the SiO_4 groups largely intact [11]. It was reported that acid activation followed by thermal treatment increases the adsorbent capacity to a good extent. **Table 2** shows the chemical composition of red clay.
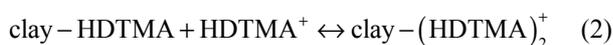
Table 2. Mineralogical and chemical composition of red clay.

Mineralogical Composition		Chemical Composition	
Illite	23% - 37%	SiO_2	64.79%
Kaolinite	6% - 12%	Al_2O_3	16.26%
Chlorite	3% -5%	Fe_2O_3	7.22%
Quartz	30% - 45%	MgO	2.38%
Hematite	3% - 6%	K_2O	2.68%
		CaO	0.4%
		TiO_2	0.91%
		MnO	0.09%

Source: [12].

Surface Modification of Clay

Clays modified by cationic surfactants, used in chromate removal from water, include bentonite (smectite), stevensite, kaolinite, illite, palygorskite, and sepiolite. The isotherm HDTMA adsorption on clay shows at least two adsorption sites, differing in the energy of interaction with HDTMA$^+$ cations, as well as in capacity. It should be noted that the composition of the clay, containing illite, kaolinite and quartz as main components, is the key feature responsible for the characteristics of this isotherm. The first part of the isotherm probably represents HDTMA adsorption on hydrophilic sites, *i.e.* illite and kaolinite. The dominant interaction in these places is electrostatic attraction of the positively charged surfactant cations by the negatively charged network of illite and kaolinite. There is, however, a difference in the structure of these two minerals, *i.e.* illite is a 2:1 type, whereas kaolinite is a 1:1 type clay. Potassium-exchanged kaolinite and illite interact with surfactant cations in the following manner:

$$\text{clay} - \text{K} + \text{HDTMA}^+ \leftrightarrow \text{clay} - \text{HDTMA} + \text{K}^+ \qquad (1)$$

$$\text{clay} - \text{HDTMA} + \text{HDTMA}^+ \leftrightarrow \text{clay} - \left(\text{HDTMA}\right)_2^+ \qquad (2)$$

where the first equation refers to ion exchange and the second one relates to a Van der Waals interaction between the alkyl chains of surfactant cations with the consequent formation of a so-called bilayer. Contrary to kaolinite, where the adsorption of surfactant takes place on the mineral surface, in the case of illite, there is also penetration into the interlamellar space and reactions (1) and (2) are more advanced, *i.e.* surfactant cations are more strongly held by the clay matrix.

The second part of the isotherm is probably a result of Van der Waals and electrostatic interactions between surfactant and the quartz surface. The HDTMA adsorption on non-charged and charged sites on quartz surfaces,

resulting from silanols Si-OH dissociation. HDTMA-bromide and HDTMA$^+$ cations are more easily adsorbed on the hydrophobic surface of quartz than on the hydrophilic surfaces of illite and kaolinite. The presence of HDTMA$^+$ cation micelles on the quartz surface was probably responsible for the strong affinity of Cr(VI) anions to the surface of red clay. The occurrence of surfactant micelles, apart from the bilayer of surfactant cations, is rather unquestionable taking into account the ratio of surfactant concentration in adsorbent to the maximum Cr(VI) concentration [12].

Metal adsorption onto hydrous solids such as metal oxides and clay minerals is a surface coordination process that can be modeled thermodynamically as a complex reaction between surface sites and adsorbate. The developed surface sites for a hydrated adsorbate are formulated as following expressions:
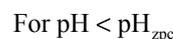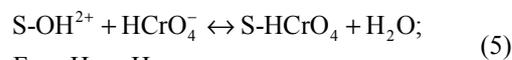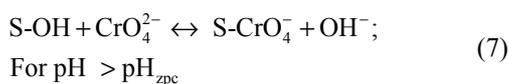
$$\text{S-OH}_2^+ \leftrightarrow \text{S-OH} + \text{H}^+ \qquad (3)$$

$$\text{S-OH} \leftrightarrow \text{S-O}^- + \text{H}^+ \qquad (4)$$
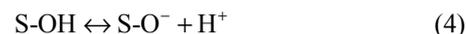
where S represents the spent activated clay surface sites accounting for both Si- and Al- surfaces, and $\text{S}-\text{OH}_2^+$, S-OH and S-O$^-$ refer to protonated, neutral and deprotonated surface hydroxyl functional groups, respectively. It is well known that pH$_{zpc}$ is a master variable to characterize the deprotonation of the amphoteric surface functional groups. In this work, at pH value below pH$_{zpc}$, the positively charged SAC surface (S-OH_2^+) would be favorable for the anionic hydrochromate, HCrO_4^-, adsorption whereupon the coulombic interaction forces can readily take place. Note that the hydro-chromate, HCrO_4^-, ion is the dominant species involved in the formation of surface complexes below pH$_{zpc}$.

Hence, the adsorption capacity of HCrO_4^- will decrease due to the decrease of attractive surface charge of spent active clay. A small amount of Cr(VI) was removed between pH 3.8 and 7.0 whereupon pH is greater than pH$_{zpc}$. At this region, the neutral surface hydroxyl functional group, S-OH, may be the sole active site providing for both HCrO_4^- and CrO_4^{2-} adsorption.

As the solution pH increases, not only is less functional group (S-OH) deprotonated but also more OH$^-$ is now competing with the coexistence of HCrO_4^- and CrO_4^{2-} ions for the active surface sites. Consequently, it is difficult for them to form complexes and the adsorbed amount will decrease. In **Table 3** the interaction between Cr(VI) and some adsorbents are presented.

Thus, the possible mechanisms for the pH-dependent Cr(VI) adsorption onto spent active clay are proposed as follows:

$$\text{S-OH}^{2+} + \text{HCrO}_4^- \leftrightarrow \text{S-HCrO}_4 + \text{H}_2\text{O};$$
$$\text{For pH} < \text{pH}_{zpc} \qquad (5)$$

$$S\text{-OH} + HCrO_4^- \leftrightarrow S\text{-HCrO}_4 + OH^-;$$
$$\text{For } pH < pH_{zpc} \tag{6}$$

$$S\text{-OH} + CrO_4^{2-} \leftrightarrow S\text{-CrO}_4^- + OH^-;$$
$$\text{For } pH > pH_{zpc} \tag{7}$$

where $S\text{-HCrO}_4$ and $S\text{-CrO}_4^-$ are the formation of the bonding complexes [13].

3. Silica

Silica (SiO_2) is a very common mineral due to the abundance of silicon and oxygen in nature, some silica properties are described in **Table 4** [14]. Free silica occurs in many crystalline forms with compositions very close to that of pure silicon dioxide: 46.75 wt% silicon and 53.25 wt% oxygen. Quartz is by far the most common form. Tridymite, cristobalite, and the hydrous silica mineral

opal are rare, as are vitreous (glassy) silica, coesite and stishovite. Several other forms have been produced in the laboratory but have not been found in nature [5].

Silica produced in the laboratory is a polymer of silicic acid, consisting of inter-linked tetrahedral SiO_4, which has the stoichiometry SiO_2. Silica gel is a porous, granular form of silica tetrachloride or substituted chlorosilane/orthisilicate. The sol-gel route is a versatile method for silica synthesis. In a sol-gel process hydrolysis of sodium silicate or alkoxysilane in presence of acid or base produces $Si\text{-(OH)}_4$ entities, which on controlled condensation result in a sol. the active silica surface with large specific surface area is of great importance in adsorption and ion exchange. These properties are well studied, even though the shape of the silica surface is basically unknown. The method involving direct measurement (imaging) of the outer surface of silica or modified silica is atomic force microscopy (AFM), which is

Table 3. Results of Chromium(VI) removal with natural and modified clays.

Adsorbent	pH	Experimental conditions	Adsorption capacity (mg·g^{-1})	Reference
Kaolinite	4.6	2 g sorbent 1000 mL solution [Cr(VI)] = 0.1 mmol·L^{-1}	6.1 mg·g^{-1}	[10]
Acid-activated kaolinite	4.6	2 g sorbent 1000 mL solution [Cr(VI)] = 0.1 mmol·L^{-1}	8.0 mg·g^{-1}	[10]
Poly(oxozirconium) kaolinite	4.6	2 g sorbent 1000 mL solution [Cr(VI)] = 0.1 mmol·L^{-1}	5.6 mg·g^{-1}	[10]
Tetrabutylammonium kaolinite	4.6	2 g sorbent 1000 mL solution [Cr(VI)] = 0.1 mmol·L^{-1}	5.4 mg·g^{-1}	[10]
Red clay	4 - 6.5	0.4 g sorbent 100 mL solution [Cr(VI)] = 0.1 - 10 mmol·L^{-1}	1.3 mg·g^{-1}	[12]
Red clay—modified with HDTMA	4 - 6.5	0.4 g sorbent 100 mL solution [Cr(VI)] = 0.1 - 10 mmol·L^{-1}	4.3 mg·g^{-1}	[12]
Spent activated clay	2	0.1 g sorbent 30 mL solution [Cr(VI)] = 0.13 mmol·L^{-1}	1.422 mg·g^{-1}	[13]

Table 4. Properties of silica minerals.

Name	Crystal system	Remarks
Low quartz (alpha-quartz)	Hexagonal	Common form of silica
High quartz (beta-quartz)	Hexagonal	Metastable above 870°C
Low tridymite	Orthorhombic	Exists metastably up to 117°C
Middle tridymite	Hexagonal	Exists metastably between to 117°C and 163°C
High tridymite	Hexagonal	Exists metastably from 163°C to 870°C; unstable over 1470°C; melts at 1670°C
Low cristobalite	Tetragonal	Exists metastably up to 200°C - 250°C
High cristobalite	Isometric	Exists metastably from 200°C - 250°C to 1470°C; melts at 1713°C
Keatite	Tetragonal	Not yet found in nature; high-pressure phase
Coesite	Monoclinic	Characteristic mineral of meteorictic shock; high-pressure phase
Stishovite	Tetragonal	
Vitreous silica	Amorphous	Unstable glass below 1713°C
Opal	Poorly crystalline or amorphous	

Source: [5].

based on scanning of the surface with a special probe. At the surface, the structure terminates in either siloxane group ($\equiv$Si–O–Si$\equiv$) with the oxygen atom on the surface, or one of the several forms of silanol groups ($\equiv$Si–OH). The silanol groups can be isolated (free silanol groups), where the surface silicon atom has three bonds into the bulk structure and the fourth to OH group and the vicinal or bridged silanols, where two isolated silanol groups attached to two different silicon atoms are bridged by H-bond. A third type of silanols called geminal silanols consists of two hydroxyl groups attached to one silicon atom. The geminal silanols are close enough to have H-bond whereas free silanols are too far separated as indicated in **Figure 2** [15].

Surface Modification of Silica Gel

Modification of the silica surface relates to all the processes that lead to change in chemical composition of the surface. Surfaces can be modified either by *physical treatment* (thermal or hydrothermal) that leads to a change in ratio of silanol and siloxane or by *chemical treatment* that leads to change in chemical characteristics of silica surface. Modifications significantly affect the adsorption properties of the material. Chemisorption of chelating molecules on a silica surface provides immobility, mechanical stability and water insolubility, thereby increasing the efficiency, sensitivity and selectivity of the analytical application. A silica gel surface can be modified by two distinct processes: organofunctionalization, where the modifying agent is an organic group, and inorganofunctionalization, in which the group anchored on the surface can be an organometallic composite or a metallic oxide. The most convenient way to develop a chemically modified surface is achieved by simple immobilization (or fixing) of the group on the surface by adsorption or electrostatic interaction or hydrogen bond formation or other type of interaction [15].

Heavy metals are effectively removed by silica compounds functionalized with carboxylic acids, sulfonic acids and quaternary ammonium groups. The support for these groups is often silica-based, because silica provides chemical resistance and is mechanically robust. Silica-based support structures are widely used in the field of selective separations because of their well-known acid and solvent stability, as well as their excellent mechani-

cal properties and do not have the shrink/swell characteristics. Chromium removal by a LaSiCS composite was mainly governed by adsorption mechanism. The positively charged La^{3+} surface in the hybrid composite attracts the negatively charged chromium ions by means of electrostatic attraction. The chromium removal by Si is mainly due to its porous nature which entraps chromium by means of electrostatic attraction. The strong electrostatic adsorption and complexation between La^{3+} and $HCrO_4^-$ ion are mainly responsible for the significant enhanced adsorption capacities of the La(III) incorporated hybrid composite. The reactive -OH and -NH$_2$ electron donor groups present in the LaSiCS composite reduce the Cr(VI) to less toxic Cr(III) in an adsorption coupled reduction.

The effect of pH on the sorption of Cr(VI) onto the sorbents is higher at low pH and decreases with increasing pH. The reason could be that at lower pH, the sorbents acquire a positive charge due to the protonation of amino groups and that the predominant species of chromium is $HCrO_4^-$. There is a gradual decrease in the adsorption capacities of the sorbents as the pH of the solution increases, which may be due to the competition of OH$^-$ ion for the sorption sites of the sorbent surface [16]. The adsorption capacity of the natural and modified silica is shown in **Table 5**.

4. Zeolites

A zeolite is a crystalline mineral with a structure characterized by a framework of linked tetrahedrals, each consisting of four oxygen atoms surrounding a cation. This framework contains open cavities in the form of channels and cages. They are usually occupied by water molecules and extra-framework cations that are commonly exchangeable and are large enough to allow the passage of guest species. In hydrated phases, dehydration occurs at temperatures mostly below about 400°C and is largely reversible. The framework may be interrupted by hydroxyl
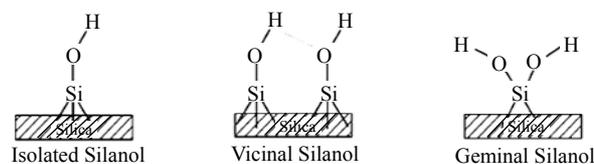

Figure 2. Silanol groups. Source: [15].

Table 5. Results of chromium(VI) removal with silica.

Adsorbent	pH	Experimental Conditions	Adsorption capacity (mg·g^{-1})	Reference
Silica	2 - 4	0.1 g sorbent 50 mL solution [Cr(VI)] = 10 mg·L^{-1}	1.5 mg·g^{-1}	[16]
Silica-Chitosan	2 - 4	0.1 g sorbent 50 mL solution [Cr(VI)] = 10 mg·L^{-1}	4.0 mg·g^{-1}	[16]
La(III) Silica-Chitosan	2 - 4	0.1 g sorbent 50 mL solution [Cr(VI)] = 10 mg·L^{-1}	5.5 mg·g^{-1}	[16]

or flour groups which occupy a tetrahedron apex that is not shared with the adjacent tetrahedral [17]. Natural zeolites are hydrated crystalline aluminosilicate minerals with uniform pore size that are based on three dimensional network of AlO_4 and SiO_4 tetrahedrally linked to each other by sharing oxygens [2,18].

Zeolites to be elevated to series status and the conesquential new species to be recognized on the basis of the most abundant extra-framework cation are set out in **Table 6**.

Zeolites are structures containing an interrupted framework of silica and alumina tetrahedrals, but can include substitution by elements other than Si and Al. Separate species are recognized in topologically distinctive compositional series in which different extra-framework cations are the most abundant in atomic proportions. Zeolite species are not to be distinguished solely on the ratio Si:Al except for heulandite (Si:Al < 4.0) and clinoptilolite (Si:Al > 4.0). Dehydration, partial hydration, and overhydration are not sufficient grounds for the recognition of separate species of zeolites. Use of the term "ideal formula" should be avoided in referring to a simplified or averaged formula of a zeolite. Newly recognized species in compositional series are as follows: brewsterite-Sr, -Ba, chabazite-Ca, -Na, -K, clinoptilolite-K, -Na, -Ca, dachiardite-Ca, -Na, erionite-Na, -K, -Ca, faujasite-Na, -Ca, -Mg, ferrierite-Mg, -K, -Na, gmelinite-Na, -Ca, -K, heulandite-Ca, -Na, -K, -Sr, levyne-Ca, -Na, paulingite-K, -Ca, phillipsite-Na, -Ca, -K, and stilbite-Ca, -Na (see **Table 7**) [17].

There are more than 30 natural zeolites known, but only seven (mordenite, clinoptilolite, chabazite, erionite, ferrierite, phillipsite, and analcime) occur in sufficient quantity and purity to be considered exploitable [8].

The most important properties of zeolites are uniform pore size, reversible hydration and ion exchange [2,21]. Zeolites, modified by ion exchange, can be used for adsorption of different metal ions [8]. Zeolites possess a net negative structural charge, resulting from isomorphic substitution of cations in the crystal lattice. This permanent negative charge results in the favorable ion exchange selectivity of zeolites for certain cations [4].

Most of the naturally occurring zeolites have negative charges on their external surfaces, which prevents sorption and retention of anions, but efforts have been made to convert the surface charges from negative to positive by surface modification. Cationic surfactants have been used extensively for modification of clay minerals and zeolites [9].

Clinoptilolite is the most abundant natural zeolite of the Heulandite group [21]. Its characteristic tabular morphology shows an open reticular structure formed by open channels of 8 - 10 membered rings. It includes exchangeable ions such as Na(I), K(I), Ca(II) and Mg(II) [22]. The reported composition is indicated in **Table 8**.
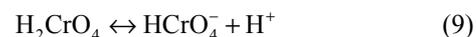
Table 6. Classification of zeolites.

Name	Chemical composition
Group 1 (S4R)	
Analcime	$Na_{16}[(AlO_2)_{16}(SiO_2)_{32}] \cdot 16H_2O$
Harmotome	$Ba_2[(AlO_2)_4(SiO_2)_{12}] \cdot 12H_2O$
Phillipsite	$(K,Na)_{10}[(AlO_2)_{10}(SiO_2)_{22}] \cdot 20H_2O$
Gismondine	$Ca_4[(AlO_2)_8(SiO_2)_8] \cdot 16H_2O$
P	$Na_6[(AlO_2)_6(SiO_2)_{10}] \cdot 15H_2O$
Paulingite	$K_2,Na,Ca,Ba)_{76}[AlO_2)_{152}(SiO_2)_{520}] \cdot 700H_2O$
Laumontite	$Ca_4[(AlO_2)_8(SiO_2)_{46}] \cdot 16H_2O$
Yugawaralie	$(K,Na)_{10}[(AlO_2)_{10}(SiO_2)_{22}] \cdot 20H_2O$
Group 2 (S6R)	
Erionite	$(Ca,Mg,K_2,Na_2)_{4.3}[(AlO_2)_9(SiO_2)_{27}] \cdot 27H_2O$
Offretite	$(K_2,Ca)_{2.7}[(AlO_2)_{5.4}(SiO_2)_{12.6}] \cdot 15H_2O$
T	$(Na_{1.2},K_{2.8})[(AlO_2)_4(SiO_2)_{14}] \cdot 14H_2O$
Levynite	$Ca_3[(AlO_2)_6(SiO_2)_{12}] \cdot 18H_2O$
Omega	
Hydrated Sodalite	$(Na_{6.8}TMA_{1.6})[(AlO_2)_8(SiO_2)_{28}] \cdot 21H_2O$
	$Na_6[(AlO_2)_6(SiO_2)_6] \cdot 7.5H_2O$
	$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot 19H_2O$
Group 3 (D4R)	
A	$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot 27H_2O$
N-a	$(Na_4TMA_3)[(AlO_2)_7(SiO_2)_{17}] \cdot 21H_2O$
ZK-4	$(Na_8TMA_{1.6})[(AlO_2)_8(SiO_2)_{15}] \cdot 28H_2O$
Group 4 (D6R)	
Faujasite	$(Na_2,K_2,Ca,Mg)_{29.5}[(AlO_2)_{59}(SiO_2)_{133}] \cdot 235H_2O$
X	$Na_{86}[(AlO_2)_{86}(SiO_2)_{105}] \cdot 264H_2O$
Y	$Na_{56}[(AlO_2)_{56}(SiO_2)_{136}] \cdot 250H_2O$
Chabazite	$Ca_2[(AlO_2)_4(SiO_2)_8] \cdot 13H_2O$
Gmelinite	$Na_8[(AlO_2)_8(SiO_2)_{16}] \cdot 24H_2O$
ZK-5	$(R,Na_2)_{15}[(AlO_2)_{30}(SiO_2)_{66}] \cdot 98H_2O$
L^R	$K_9[(AlO_2)_9(SiO_2)_{27}] \cdot 22H_2O$
Group 5 (T_5O_{10})	
Natrolite	$Na_{16}[(AlO_2)_{16}(SiO_2)_{24}] \cdot 16H_2O$
Scolecite	$Ca_8[(AlO_2)_{16}(SiO_2)_{24}] \cdot 16H_2O$
Mesolite	$(Na_{16}Ca_{16})[(AlO_2)_{48}(SiO_2)_{72}] \cdot 64H_2O$
Thomsonite	$(Na_4Ca_8)[(AlO_2)_{20}(SiO_2)_{20}] \cdot 24H_2O$
Gonnardite	$(Na_4Ca_2)[(AlO_2)_8(SiO_2)_{12}] \cdot 14H_2O$
Edingtonite	$Ba_2[(AlO_2)_4(SiO_2)_6] \cdot 8H_2O$
Group 6 (T_8O_{16})	
Mordenite	$Na_8[(AlO_2)_8(SiO_2)_{40}] \cdot 24H_2O$
Dachiardite	$Na_5[(AlO_2)_5(SiO_2)_{19}] \cdot 12H_2O$
Ferrierite	$(Na_{1.5},Mg_2)[(AlO_2)_{5.5}(SiO_2)_{30.5}] \cdot 18H_2O$
Epistilbite	$Ca_3[(AlO_2)_6(SiO_2)_{18}] \cdot 18H_2O$
Bikitaite	$Li_2[(AlO_2)_2(SiO_2)_4] \cdot 2H_2O$
Group 7 ($T_{10}O_{20}$)	
Heulandita	$Ca_4[(AlO_2)_8(SiO_2)_{28}] \cdot 24H_2O$
Clinoptilolita	$Na_6[(AlO_2)_6(SiO_2)_{30}] \cdot 24H_2O$
Stilbita	$Ca_4[(AlO_2)_8(SiO_2)_{28}] \cdot 28H_2O$
Brewsterita	$(Sr,Ba,Ca)_2[(AlO_2)_4(SiO_2)_{12}] \cdot 10H_2O$

Source: [19].

Table 7. Composition of zeolites.

Component	Percent
SiO_2	35.58%
Al_2O_3	28.07%
Na_2O	17.21%
SO_3	1.08%
LOI	17.53%

Source: [20].

Modification of Zeolites with Cationic Surfactants

The negative charge on their external surfaces results in the favorable ion exchange selectivity of zeolites for certain cations, but causes them to have little or no affinity for anions [4]. Some heavy metals like chromium are present as cations, anions, or non-ionized species. Hence, development of materials with the capability to adsorb anions, cations, and neutral molecules is very important. Zeolites can be treated with cationic surfactants in order to do this. Through treatment, an organic layer is created on the external surfaces and the charge is reversed to positive [20]. These cationic surfactants increase the fractional organic carbon content in order to enhance the sorption of non-polar hydrophobic organic contaminants. It was observed that the longer the tail group of the cationic surfactant, the more stable the surfactant retained on the surface [3].

Chromium(VI) sorption was performed at different pH values. At neutral pH chromium is present in the form of CrO_4^{2-} which is a stable form of Cr(VI). However, at lower pH dichromate ions are formed which have a larger particle size than chromate ions. The pore size of zeolite is more suitable for the sorption of CrO_4^{2-} ions than the $Cr_2O_7^{2-}$ ions [24].

$$HCrO_4^- \leftrightarrow CrO_4^{2-} + H^+ \qquad (8)$$

$$H_2CrO_4 \leftrightarrow HCrO_4^- + H^+ \qquad (9)$$

$$Cr_2O_7 + H_2O \leftrightarrow HCrO_4^- \qquad (10)$$

Quaternary amines such as hexadecyltrimetylammonium (HDTMA) are tetrasubtituted ammonium salts with a permanently charged pentavalent nitrogen and at least one alkyl chain. HDTMA is strongly surface active and contains a long straight alkyl chain (C16) which imparts a high degree of hydrophobicity. A general model of sorption of cationic surfactants on a solid surface can be explained by formation of a monolayer or hemimicela in the solid-liquid interface via ionic bonding, in concentrations of surfactant equal to or below its critical micelle concentration (CMC). At higher concentrations of the solution, the surfactant molecules can be absorbed by interactions with the alkyl chain, forming a bilayer or admicel [25]. The Cr(VI) interaction with natural and modified zeolites are presented in **Table 9**.

Table 8. Composition of clinoptilolite.

Mineralogical Composition	Percent	Chemical Composition	Percent
Clinoptilolite	80%	SiO_2	55.80%
Mordenite	5%	Al_2O_3	13.32%
Quartz, Feldspart, Montmorillonie and Illite	15%	CaO	5.75%

Sources: [4,23].

Table 9. Results of chromium(VI) removal with natural and modified zeolites.

Adsorbent	pH	Experimental Conditions	Adsorption capacity (mg·g^{-1})	Reference
Zeolite HDTM	6	0.5 g sorbent 25 mL solution [Cr(VI)] = 15 mmol·mL^{-1}	39.47 mg·g^{-1}	[2]
Zeolite TBA	6	0.5 g sorbent 25 mL solution [Cr(VI)] = 15 mg·mL^{-1}	29.5 mg·g^{-1}	[2]
Clinoptilolite exchanged various metal cations	4.5 7.5 7.2 6.3 6.5 7.2 4.5	2 g 50 mL solution [Cr(VI)] = 10 - 100 mmol·L^{-1}	Pb = 0.560 mg·g^{-1} Ag = 410 mg·g^{-1} Ba = 0.340 mg·g^{-1} Hg = 0.360 mg·g^{-1} Sr = 0.210 mg·g^{-1} Ca = 0.210 mg·g^{-1} Clip = 0.006 mg·g^{-1}	[4]
Modified Nanozeolite A HDTMA-Br	3.0	0.25 g sorbent 50 mL solution [Cr(VI)] = 1.0 mg·L^{-1}	14.16 mg·g^{-1}	[20]
Clinoptilolite modified with BrHDTMA	2	0.1 g sorbent 30 mL solution [Cr(VI)] = 0.4 mmol·L^{-1}	3.83 mg·g^{-1}	[23]
HDTMA-Modified Zeolites (Erionite)	7.0	0.1 g sorbent 50 mL solution [Cr(VI)] = 2.0 mmol·L^{-1}	0.103 mg·g^{-1}	[24]
HDTMA-Modified Zeolites Cowlesite	7.0	0.1 g sorbent 50 mL solution [Cr(VI)] = 2.0 mmol·L^{-1}	0.763 mg·g^{-1}	[26]
HDTMA-Modified Zeolites Willhendersonite	7.0	0.1 g sorbent 50 mL solution [Cr(VI)] = 2.0 mmol·L^{-1}	0.719 mg·g^{-1}	[26]
Clinoptilolite modified with hexadecyltrimethylammonium (C16)	2.6 - 3.1	20 mg sorbent 10 mL solution [Cr(VI)] = 0.2 - 6.24 mmol·L^{-1}	0.124 mg·g^{-1}	[27]
Clinoptilolite modified with dioctadecyldimethylammonium (2C18)	2.6 - 3.1	20 mg sorbent 10 mL solution [Cr(VI)] = 0.2 - 6.24 mmol·L^{-1}	0.103 mg·g^{-1}	[27]
Clinoptilolite	3.0	0.5 g sorbent 50 mL solution [Cr(VI)] = 10 mmol·L^{-1}	19.9 mg·g^{-1}	[28]
Clinoptilolite-ODA	3.0	0.5 g sorbent 50 mL solution [Cr(VI)] = 10 mmol·L^{-1}	54 mg·g^{-1}	[28]
Clinoptilolite HDTMA	7	1 g sorbent 25 mL solution [Cr(VI)] = 4 mmol·L^{-1}	0.844 mg·g^{-1}	[29]

5. Conclusions

Today there exists a problem of water pollution with heavy metals, this problem has led to the search of techniques and materials that are environmentally friendly and that can be used to remove heavy metals. Chromium Hexavalent is one the most important pollutants. There are a number of available technologies for the remediation of chromium, but none of them is applicable to all situations.

The adsorption has proven a useful tool to control the degree of contamination of chromium in the water. Low cost materials have an adsorption capacity. Some studies have been shown the applicability of inorganic materials such as clay minerals, silica and zeolites as sorbents heavy metal ions and the chemical modification of these material surfaces by using chemical ligating groups providing increased capacity for trapping metal ions specifically and selectively even at trace level. Such studies have been limited to evaluate the capacity of adsorption solution but it is necessary to continue studies at pilot plant scale for knowing their true scope.

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