

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

Heavy metals are often found in the environment as a result of their wide industrial use (Pehlivan and Cetin, 2009). Chromium is one of the most dangerous of heavy metals and is a major pollutant in wastewater. The interest in chromium originates from the widespread use of this metal in various industries such as metallurgical, refractories and chemical. Chromium exists in two stable oxidation states, Cr(III) and Cr(VI). Both of them have drastically different charge, physicochemical properties as well as chemical and biochemical reactivities (Kotaś and Stasicka, 2000). Cr(III) is considered to be a trace element essential for the proper functioning of living organisms. On the other hand, Cr(VI) exerts toxic effects on biological systems. When Cr(VI) ingestion is higher than its permissible level, it causes health disorders, such as vomiting and hemorrhage (Selvaraj *et al.*, 2003) because it can easily cross the cell wall and exert its toxic influence on the cell. The toxicological impact of Cr(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 (Selvaraj *et al.*, 2003). Since the compounds of chromium, especially the Cr(VI) species, are known to be detrimental to human health, the maximum level permitted in wastewater is 5 ppm for Cr(III) and 0.05 ppm for Cr(VI) (Acar and Malkoc, 2004; Pehlivan and Cetin, 2009). Due to the extreme toxicity of Cr(VI), its selective determination and removal from wastewater is of particular concern.

Various methods have been developed for removal of Cr(VI) from aqueous solution such as chemical precipitation, chemical oxidation or reduction, filtration, ion exchange,

electrochemical treatment, application of membrane technology and evaporation recovery (Malkoc and Nuhoglu, 2007) (a & b). However, these technology processes have considerable disadvantages including incomplete metal removal, necessity for expensive equipment and monitoring system, high reagent or energy requirement or generation of toxic sludge or other waste products that require disposal (Bengulla and Benaissa, 2002). In the light of these disadvantages, adsorption is the most effective and widely used technique (Wan Ngah *et al.*, 2002). It is a physiochemical wastewater treatment process, which is gaining prominence as a mean of producing high quality effluents, which are low in metal ion concentrations. The development of inexpensive adsorbent for the treatment of wastewater is an important area in environmental sciences (Barrera *et al.*, 2006). Adsorption has been found to be superior to other techniques for water treatment in terms of flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants (Crini, 2008). In addition it does not result in the formation of harmful substances (Crini, 2006) and has high efficiency at a relatively lower cost (Yasar and Aksoy, 2009).

Many different types of adsorbents were used for selective determination and removal of chromium species from water samples. Some of the reported adsorbents include activated carbon (Schneider *et al.*, 2007), industrial by-products (Raji and Anirudhan, 1998) and biomass (Tewari *et al.*, 2005). Much attention has recently been focused on biopolymers and natural molecules (Zhou *et al.*, 2004 and Zhu *et al.*, 2009) such as chitosan, starch or β -cyclodextrin (β -CD) as adsorbents.

β -CD is a torus-shaped cyclic oligosaccharide made up of seven α -1,4-linked-D-glucopyranose units. It has low toxicity, excellent biocompatibility and biodegradability (Prabaharan and Mano, 2006). The unusual properties of cyclodextrins (CDs) originate in

their unique structure. Despite a hydrophilic surface, CDs contain a hydrophobic cavity. It is well known that this structure gives rise to a remarkable capacity to form inclusion complexes in a solution with various molecules through host-guest interactions. However, its solubility in water makes it inconvenient to use as adsorbent (Chin *et al.*, 2010). There are several reported procedures to synthesize CD as an adsorbent and the methods can be generally classified in two ways. First, CD molecules can be polymerized with a coupling agent to form insoluble crosslinked polymers. The second relies on the covalent bonding of CD molecules to a pre-existing insoluble matrix (Mocanu, *et al.*, 2001; Crini and Morcelet, 2002). In this study, both methods were used to synthesize the adsorbent. The first method, two adsorbents have been synthesized, which are β -cyclodextrin crosslinked 1,6-hexamethylene diisocyanate (β -CDP-HMDI) and β -cyclodextrin crosslinked toluene-2,4-diisocyanate (β -CDP-TDI). For second method, the adsorbent has been synthesized using silica as a solid support and TDI as a spacer arm (Si-TDI- β -CD).

So far, only a few research studies have reported on the use of crosslinked CD polymers as an adsorbent for metals. To the best of our knowledge, studies on the removal of Cr(VI) ion from aqueous solution using β -CD as an adsorbent have not yet been reported. In this paper, we proposed the use of CD-containing adsorbent for the sorption of Cr(VI). The method is based on the complex reaction of 1,5-diphenylcarbazide (DPC) with Cr(VI) in acidic condition. DPC is a complexing reagent that gives sensitive and specific color reaction with Cr(VI) (Rajesh et al, 2008). The adsorption isotherm and kinetics of Cr-complex with DPC onto CD-containing adsorbent were studied.

1.2 OBJECTIVES OF STUDY

The main objectives of the present study are:-

- i) To synthesize poly-cyclodextrin (β -CDP-HMDI, β -CDP-TDI) and immobilization of cyclodextrin on silica (Si-TDI- β -CD) using bifunctional isocyanate as a linker.
- ii) To characterize poly-cyclodextrin and cyclodextrin immobilized on silica.
- iii) To apply poly-cyclodextrin and cyclodextrin immobilized on silica as an adsorbent for sorption of Cr-complex with DPC.
- iv) To compare the adsorption isotherm, adsorption kinetic and thermodynamic of poly-cyclodextrin and cyclodextrin immobilized on silica.

CHAPTER 2

LITERATURE REVIEW

2.1 CHROMIUM SPECIES IN ENVIRONMENT

Chromium is an element which has several roles in our daily lives. At low concentration it is an essential micronutrient in human and animal nutrition and at high concentration it is a known carcinogen when present as chromate.

Cr(VI) as hexavalent chromium can be found as CrO_4^{2-} , HCrO_4^- , or $\text{Cr}_2\text{O}_7^{2-}$ depending on pH of the medium. However, Cr(VI) oxyanions are readily reduced to trivalent forms by electron donors such as organic matter or reduced inorganic species, which are ubiquitous in soil, water and atmospheric system. Cr(VI) exerts toxic effects on biological systems. It was found that occupational exposure to hexavalent Cr compounds leads to variety of clinical problem. Inhalation and retention of Cr(VI) containing materials can cause perforation of the nasal septum, asthma and bronchitis. It is known to be carcinogenic and mutagenic and it induces dermatitis. It occurs in a range of compounds used in industrial processes, such as chrome plating, metallurgical, and refractories. The toxic properties of chromates arise from the possibility of free diffusion across cell membranes and strong oxidative potential. The toxicological impact of Cr(VI) originates from the action of this form itself as an oxidizing agents, as well as from the formation of free radicals during the reduction of Cr(VI) to Cr(III) occurring inside the cell (Kotas and Stasicka, 2000; Gomez and Callao, 2006).

Because of the toxicity of Cr(VI), it is very important to remove the Cr(VI) from aqueous solution. Several methods are available for the determination and separation of Cr(VI) ion for aqueous solution such as, ion-exchange, reduction process, ion-pairing, co-precipitation, membrane separation, adsorption and chemical precipitation.

The application of membrane system for the wastewater treatment has major problems like membrane scaling, fouling and blocking. The drawback of the ion exchange process is the high cost of the resin. Among these methods, adsorption is one of the most economically favorable and a technically easy method.

2.2 ADSORPTION

Adsorption using sorbents is one of the popular methods since proper design of the adsorption process will produce high-quality treated effluents. Adsorption is a well-known equilibrium separation process. It is now recognized as an effective, efficient and economic method for water decontamination applications and separation analytical purposes (Crini, 2005). Adsorption process is a multi-step process involving transport of the solute molecules from the aqueous phase to the surface of the solid particles followed by diffusion of the solute molecules into the pore interiors (Crini *et al.*, 2007). Besides, the advantages of adsorption techniques are in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Adsorption also does not result to harmful substances (Crini, 2006). Trace elements are usually adsorbed on solid phase through Van Der Waals forces or hydrophobic interaction. Hydrophobic interaction occurs when the solid materials is highly non-polar. Table 2.1 shows various type of adsorbents for adsorption of Cr(VI) ion in wastewater.

Table 2.1: Various type of adsorbents for adsorption of Cr(VI) ion in the wastewater.

No	Adsorbent	Reference
1.	Activated cow dung carbon	Das <i>et al.</i> , 2000.
2.	<i>Hevea Braslinsis</i> sawdust activated carbon	Karthikeyan <i>et al.</i> , 2005.
3.	<i>Thuja orientalis</i>	Oguz, 2005.
4.	<i>Ectodermis</i> of <i>Opuntia</i>	Barrera and Gupta, 2006.
5.	Clays	Bhattacharyya <i>et al.</i> , 2006.
6.	waste acorn of <i>Qeucus ithaburensis</i>	Malkoc and Nuhoglu, 2007 (a)
7.	treated pine sawdust	Uysal, and Ar, 2007.
8.	treated oil palm fibre	Isa <i>et al.</i> , 2008.
9.	modified coconut coir pith	Namasivayam and Sureshkumar, 2008.
10.	chitosan flakes	Aydin and Aksoy, 2009

2.3 ADSORBENT

Adsorbent, in particular natural or synthetic solid sorbent which are able to remove pollutants from contaminated water solution. The nature and properties of the sorbent are of prime importance for effective retention of metallic species. In practice, the main requirements for a solid sorbent are:

- i) The possibility to extract a large number of trace elements over a wide pH range (along with selectivity towards major ions);
- ii) Fast and quantitative sorption;
- iii) High capacity;
- iv) Regenerability;

In particular, sorbents that allow fast reaction rates are preferred to achieve faster extraction as well as higher loading capacities. Sorbents can be mainly characterized as inorganic based (silica gel SiO_2 , alumina Al_2O_3 , magnesia MgO and other oxide species) as well as organic based (natural polymers and synthetic polymers). Immobilization of organic compounds on the surface of the solid support is usually aimed at modifying the surface with certain target functional groups for a higher selectivity of the extraction.

i) Inorganic based sorbents

Inorganic based sorbents are mainly made of silica gel even though other inorganic oxides may be used (Figure 2.1). Silica gel can be used as adsorbing agents, as it does not swell or strain, has good mechanical strength and can undergo heat treatment (Parida *et al.*, 2006, Jianfei *et al.*, 2007). Consequently, modification of the silica gel surface has been performed to obtain solid sorbents with greater selectivity. Silica is most frequently used for producing functionalized materials, because of their high physical strength and chemical inertness (Ponchel *et al.*, 2004).

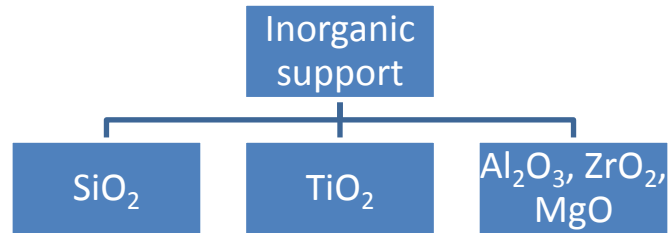


Figure 2.1: Sorbents based on inorganic support

ii) Organic based sorbents

Organic based sorbents may be divided into polymeric and non-polymeric sorbents, as shown in Figure 2.2. In most applications, the sorbents have been synthesized by chemically bonding chelating groups to polymeric cross-linked chains and characterizing their ability to selectively adsorb trace elements.

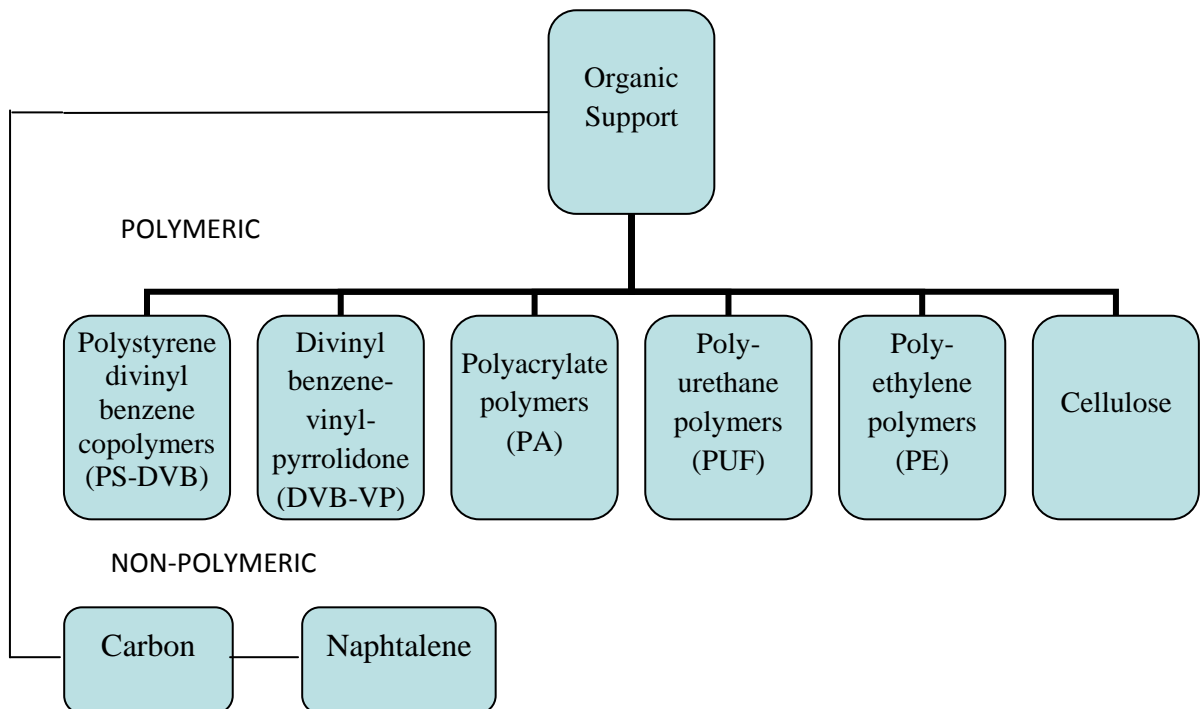


Figure 2.2 : Sorbents based on organic supports

2.4 β -CYCLODEXTRIN

Cyclodextrins are a family of cyclic oligosaccharides composed of α -(1,4) linked glucopyranose subunits (Figure 2.3). There are three main types of cyclodextrin; α -, β -, and γ -cyclodextrin which contain six, seven and eight glucopyranose units (Figure 2.4). The main properties of those cyclodextrins are given in the Table 2.2. They are also known as cycloamylose, cyclomaltooses and Schardinger dextrins. They are produced as a result of intramolecular transglycosylation reaction from degradation of starch by cyclodextrin glucanotransferase (CGTase) enzyme. Cyclodextrins are useful molecular chelating agents. They possess a cage-like supramolecular structure, which is the same as the structure formed from cryptands, calixarenes, cyclophanes, spherands and crown ethers (Martin, 2004). The C-2-OH group of one glucopyranose unit can form a hydrogen bond with the C-3-OH of the adjacent glucopyranose unit (Astray *et al.*, 2009). In the cyclodextrin molecules, a complete secondary belt is formed by these H-bonds; therefore the β -CD rather rigid structure. This intramolecular hydrogen bond formation is probably the explanation for the observation that β -CD has the lowest water solubility of all CDs.

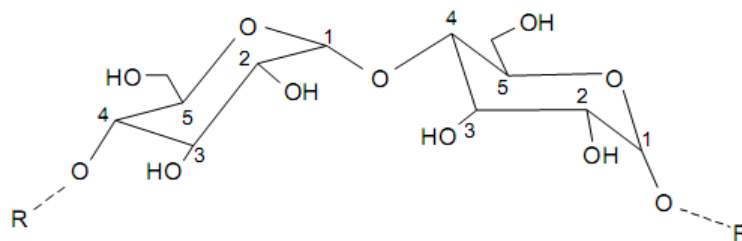


Figure 2.3: Glycosidic oxygen bridge alpha (1,4) between two molecules of glucopyranose.

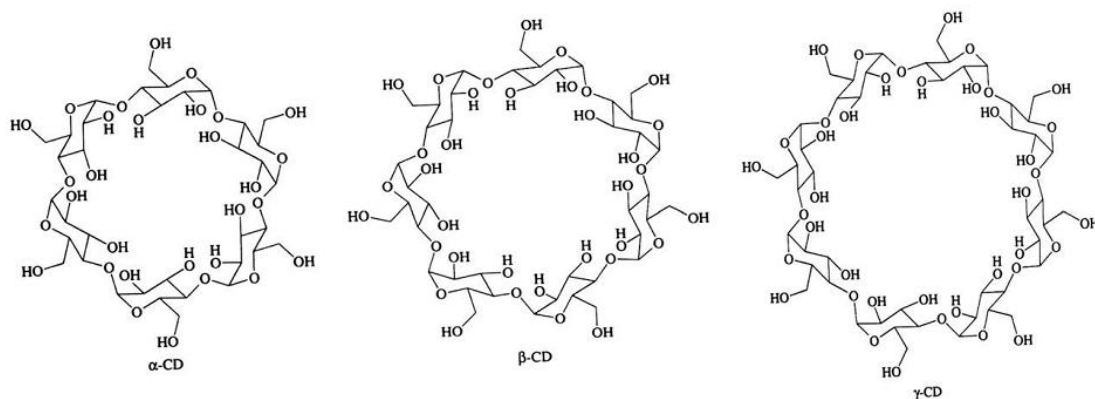


Figure 2.4: Chemical structure of α -cyclodextrin, β -cyclodextrin, γ -cyclodextrin

Table 2.2 : Properties of cyclodextrin

Property	α -cyclodextrin	β -cyclodextrin	γ -cyclodextrin
Number of glucopyranose units	6	7	8
Molecular weight (g/mol)	972	1135	1297
Solubility in water at 25°C (% w/v)	14.5	1.85	23.2
Outer diameter (Å)	14.6	15.4	17.5
Cavity diameter(Å)	4.7-5.3	6.0-6.5	7.5-8.3
Height of torus (Å)	7.9	7.9	7.9
Cavity volume(Å ³)	174	262	427

2.4.1 Inclusion complex formation

The most notable feature of cyclodextrins is their ability to form solid inclusion complexes (host-guest complexes) with a very wide range of solid, liquid and gaseous compounds by a molecular complexation. In this complexation, a guest molecule is held within the cavity of the cyclodextrin host molecule. Complex formation is a dimensional fit between host cavity and guest molecule (Munoz-Botella *et al.*, 1995). No covalent bonds are broken or formed during formation of the inclusion complex (Schneiderman and Stalcup, 2000). The main driving force of complex formation is the release of enthalpy-rich water molecules from the cavity. Water molecules are displaced by more hydrophobic

guests molecules present in the solution to attain apolar-apolar association and decrease of cyclodextrin ring strain resulting in a stable lower energy state (Szejtli, 1998; Schneiderman and Stalcup, 2000). The binding of guest molecules within the host cyclodextrin is not fixed or permanent but rather is a dynamic equilibrium. Binding strength depend on how well the 'host-guest' complex fits together and on specific local interactions between surface atoms. Complexes can be formed either in solution or in the crystalline state and water is typically the solvent of choice. Inclusion complexation can be accomplished in a co-solvent system and in the presence of any non-aqueous solvents.

The potential guest list for the molecular encapsulation in cyclodextrins is quite varied and includes such compounds as straight or branched chain aliphatics, aldehydes, ketones, alcohols, organic acids, fatty acids, aromatics, gases and polar compounds such as halogens, oxyacids, and amines. Due to the availability of multiple reactive hydroxyl groups, the functionality of cyclodextrins is greatly increased by chemical modification.

The ability of a cyclodextrin to form an inclusion complex with guest molecules is a function of two key factors. The first is steric and depends on the relative size of the cyclodextrin to the size of the guest molecules or certain key functional groups within the guest. If the guest is of the wrong size, it will not fit properly into the cyclodextrin cavity. The second critical factor is the thermodynamic interaction between the different components of the system which as between cyclodextrin, guest and solvent. For a complex to form there must be a favorable net energetic driving force that pulls the guest into the cyclodextrin. In this process, entropy and enthalpy changes have an important role.

2.4.2 Synthesis of β -cyclodextrin-based as an adsorbent

β -cyclodextrin is a polysaccharide which is a stereoregular polymers of monosaccharides (sugars), are unique raw materials in that they very abundant natural polymers, renewable resources, stable and hydrophilic biopolymers, and modifiable. They also have biological and chemical properties such as non-toxicity, biocompatibility, biodegradability, chirality, chelation and adsorption capacities. The excellent adsorption behavior of polysaccharides is mainly attributed to:

- i) high hydrophilicity of the polymer due to the hydroxyl groups of glucose units;
- ii) presence of a large number of functional groups (hydroxyl groups);
- iii) high chemical reactivity of these groups; and
- iv) flexible structure of the polymer chain.

β -cyclodextrin can be synthesized using two main ways, which can be classified as :

- i) Crosslinking reactions.

β -cyclodextrin can be crosslinked by a reaction between the hydroxyl groups of the chains with a coupling agent to form water-insoluble crosslinked network (Yilmaz *et al.*, 2007; Chin *et al.*, 2010). Crosslinking occurs when a reagent introduces intermolecular bridges and/or crosslinks between β -cyclodextrin macromolecule. The crosslinking agent can react with macromolecules linear chains (crosslinking step) and/or itself (polymerization step) in an alkaline medium. The crosslinked polymers are obtained in homogeneous or heterogeneous conditions by using reticulation with bi- or polyfunctional crosslinking agents. Kawaguchi *et al.*, (1982) investigated the behavior of

aromatic compounds in water on β -cyclodextrin polyurethane resins which polymer containing cyclodextrin units as specific sorption sites prepared by crosslinking β -cyclodextrin with isocyanates. Besides, Zha *et al.*, (2008) was investigated to adsorb hydroquinone by prepared glutaraldehyde activated chitosan beads bearing β -cyclodextrin cross-linked 1,6-hexamethylene diisocyanate. Water insoluble β -cyclodextrin polymer crosslinked by citric acid was prepared and investigated by Zhao *et al.*, (2009) as adsorbent for the removal of organic pollutants and heavy metals in water.

ii) Immobilization of β -cyclodextrin

Immobilization of β -cyclodextrin on insoluble supports by coupling or grafting reactions in order to give hybrid or composite materials. According to the literature, the cyclodextrin can be immobilized with silica using four principal approaches: (i) the impregnation of the oligosaccharides on the support, (ii) the polymerization, (iii) the sol-gel process and (iv) the chemical grafting without or with a spacer arm. This last approach has been widely studied and consists of covalent bonding native or chemically modified cyclodextrins onto the support to prevent the leaching of cyclodextrins. Composite materials combine the physical and chemical properties of both inorganic and organic materials. Porous silica is one of the ideal rigid supports, which can be made with large and narrow pore size distribution. Native cyclodextrins have been directly bonded to silica gel by the reaction of cyclodextrin with chlorinated silica gel (Shiraishi *et al.*, 1986) or through a spacer arm by the reaction of cyclodextrins on a silica previously modified by an organosilane agent terminated by an epoxy function (Armstrong, 1985). This last procedure led to the immobilization of cyclodextrin via the primary (Armstrong, 1985) or secondary hydroxyl position (Monacu *et al.*, 2001).

2.4.3 Application of β -cyclodextrin-based as an adsorbent

Water pollution due to the toxic metals and organic compounds remains a serious environmental and public problem. Water pollution also has become a major source of concern and a priority for most industrial sectors. Heavy metal ions, aromatic compounds (including phenolic derivatives, and polycyclic aromatic compounds) and dyes are often found in the environments as a result of their wide industrial uses. They are common contaminants in wastewater and many of them are toxic and carcinogenic. Table 2.3 shows the applications of different types of derivatives of β -cyclodextrin which were used as adsorbents to adsorb pollutants.

Table 2.3: Application of β -cyclodextrin and its derivatives as an adsorbent.

No	Adsorbent	Adsorbate	Reference
		DYE	
1.	3-Glycidyloxypropyl silica bonded with cyclodextrin (Si-GLY- β CD)	Methyl orange	Poncle <i>et al.</i> , 2004.
2.	β -cyclodextrin crosslinked epichlorohydrin (EPI) in presence of carboxymethylcellulose (CMC), (CD/CMC)	C.I. Basic Blue 9	Crini and Peindy, 2006.
3.	β -cyclodextrin based polymers using 4,4'-methylene-bis-phenyldiisocyanate (MDI) and hexamethylene diisocyanate (HMDI)	Congo Red	Ozmen, and Yilmiz, 2007.
4.	β -cyclodextrin crosslinked epichlorohydrin (EPI) in presence carboxymethylcellulose (CMC)	C.I. Basic Green 4 (Malachite Green)	Crini <i>et al.</i> , 2007.
5.	β -cyclodextrin crosslinked using hexamethylene diisocyanate(HMDI)	Azo dyes	Yilmaz <i>et al.</i> , 2007.

Table 2.3 : Application of β -cyclodextrin and its derivatives as an adsorbent (continued)

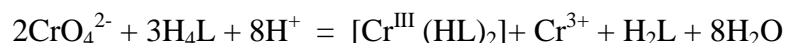
6.	β -cyclodextrin polymer crosslinked by citric acid	Methylene blue	Zhao <i>et al.</i> , 2009.
7.	β -cyclodextrin crosslinked with 4,4'-methylene-bis-phenyldiisocyanate (MDI) and hexamethylene diisocyanate (HMDI)	Azo dyes (Evans Blue and Chicago Sky Blue)	Yilmaz and Memon, 2010.
		AROMATIC COMPOUND	
8.	β -cyclodextrin using epichlorohydrin (EPI) as crosslinked agent	4-cresol (isomeric phenol)	Li <i>et al.</i> , 2009
9.	β -cyclodextrin bonded with silica gel	phenol	Shiraishi <i>et al.</i> , 1986.
10.	β -cyclodextrin bonded with silica (CDS)	phenol, 3-nitrophenol, 4-nitrophenol, 2-nitrophenol, 2,4-dimethylphenol, 4-chloro-3-methylphenol, 2,4-dichlorophenol	Fan <i>et al.</i> , 2003.
11.	β -cyclodextrin bonded with silica (CD-HMS), nanoporous framework	<i>p</i> -nitrophenol, <i>p</i> -nitroaniline, <i>m</i> -nitrophenol, <i>p</i> -chlorophenol, phenol	Bibby and Mercier, 2003.
12.	β -cyclodextrin crosslinked with 4,4'-methylene-bis-phenyldiisocyanate (MDI) and hexamethylene diisocyanate (HMDI)	benzidine, <i>p</i> -nitroaniline, α -naphthalamine	Yilmaz and Memon, 2010.
13.	β -cyclodextrin-2-hydroxyethyl methacrylate (β -CD-HEMA)	4-tert-butyl benzoic acid (TBBA)	Janus <i>et al.</i> , 1999.

Table 2.3 : Application of β -cyclodextrin and its derivatives as an adsorbent (continued)

14.	methacryloyl- β -cyclodextrin derivatives grafted/coated onto silica	<i>p</i> -nitrophenol, pentachlorophenol, (2,4-dichlorophenoxy)acetic acid	Phan <i>et al.</i> , 2002.
15.	cyclodextrin grafted chitosan	<i>p</i> -nonylphenol, bisphenol A.	Aoki <i>et al.</i> , 2003.
16.	Glutaraldehyde activated chitosan beads bearing β -cyclodextrin cross-linked by HMDI (β CD-HMDI-Chi)	hydroquinone	Zha <i>et al.</i> , 2008.
17.	β -cyclodextrin polymer crosslinked epichlorohydrin (EPI)	dibenzofuran, 2-hydroxy-dibenzofuran, 2-methoxy-dibenzofuran, 3-amino-2-methoxy-dibenzofuran	Romo, and Penas, 2004.
18.	β -cyclodextrin polymer crosslinked by citric acid	phenol	Zhao <i>et al.</i> , 2009.
19.	Cyclodextrin polymer crosslinked using epichlorohydrin(EPI), succinyl chloride, hexamethylene diisocyanate (HMDI), toluene-2,4-diisocyanate (TDI).	phenol, <i>o</i> -cresol, <i>m</i> -cresol, <i>p</i> -cresol	Romo <i>et al.</i> , 2008.
20.	β -cyclodextrin crosslinked polymer using toluene-2,4-diisocyanate (TDI) and hexamethylene diisocyanate (HMDI)	methyl-, ethyl-, propyl-, benzylparaben	Chin <i>et al.</i> , 2010.

2.5 1,5-DIPHENYLCARBAZIDE AS A CHELATING AGENT

1,5-diphenylcarbazide (DPC) is a chelating agent, which can form a complex with chromium(VI) in acidic medium. Cr-complex with DPC is very sensitive and inexpensive procedure and also permits the speciation of chromium. Cr-complex with DPC will form red-violet coloured chromophore and it is a chelate of Cr(III) and diphenylcarbazone. The latter is produced and simultaneously combines with chromium when diphenylcarbazide is oxidized by Cr(VI). The reaction can be summarized as follow:



where ; H_4L is diphenylcarbazide $(\text{C}_6\text{H}_5)-(\text{NH})_2-\text{C}=\text{O}-(\text{NH})_2-(\text{C}_6\text{H}_5)$

H_2L is diphenylcarbazone $(\text{C}_6\text{H}_5)-\text{N}=\text{N}-\text{C}=\text{O}-(\text{NH})_2-(\text{C}_6\text{H}_5)$

Direct reaction of Cr(III) with diphenylcarbazone does not occur to any appreciable extent on account of the well known inertness of the Cr(III) aquo-complex (Gardner and Comber, 2001).

In recent years, many works have been reported for the determination of chromium species using Cr-complex with DPC. Padaruskas *et al.*, (1998) have developed a simple HPLC technique for the on-line preconcentration and determination of Cr(VI) traces in natural waters using selective pre-column complexation with 1,5-diphenylcarbazide. This on-line preconcentration technique was applied successfully to the determination of Cr(VI) in water samples and the recoveries of added chromium were in the range 94-104%. Tunceli and Turker (2002) have developed a procedure with the column preconcentration of Cr(VI), which Cr(VI) has been preconcentrated as its diphenylcarbazone complex onto a column containing Amberlite XAD-16. In this work, the developed method has been

successfully applied to the separation, preconcentration and speciation of chromium in tap water. Besides, Pehlivan and Cetin, (2009) have analyzed Cr(VI) and was carried out colorimetrically with 1,5-diphenylcarbazide method by using UV-Visible spectrometer. This work was used macroporous resin which contain quarternary amine groups (Lewatit MP64 and Lewatit MP 500). These anion exchangers are thus attractive sorbents for the treatment of wastewater containing Cr(VI) ion at trace levels.