Chapter 1: Introduction

Chromium (Cr) is a frequently occurring contaminant in surface water and groundwater from effluents of several industries such as tannery, electroplating, mining, metallurgy, steel manufacturing, textile, etc (Bayazit & Kerkez, 2014). Chromium mainly exists in trivalent and hexavalent states. Trivalent Cr^{3+} is an essential nutrient for glucose, lipid and protein metabolism in mammals (Mertz, 1976). Its deficiency may cause cardiac problems, disruptions in metabolic processes and diabetes. However, high levels of Cr^{3+} can bind to DNA, having a detrimental effect on cellular structures and its components (Anderson, 1998; Glinsmann & Mertz, 1966) resulting in several health problems. Exposure to Cr^{6+} may lead to skin irritation, kidney, liver and gastric damage as it can very easily diffuse into cell membranes (Katz & Salem, 1993). It may also cause lung cancer and is a potential carcinogen. Hexavalent chromium is also toxic to plants and causes yellowing of leaves of wheat and paddy.

Trivalent chromium may exist as Cr^{3+}, $Cr(OH)_2^{+}$ or $Cr(OH)_2^{+}$ species in aqueous solutions depending on the solution pH values (Ponder, Darab, & Mallouk, 2000) while Cr^{6+} primarily exists in the form of highly water soluble chromate (CrO_4^{2-} and $HCrO_4^{-}$) and dichromate ($Cr_2O_7^{2-}$), which are highly toxic (Zelmanov & Semiat, 2011). The permissible limit of Cr^{6+} in drinking water according to WHO guidelines is 0.05mg/L (WHO, 1996). BIS (Bureau of Indian Standard-10500-2012) also have recommended an acceptable limit of 50µg/L of chromium in drinking water. Indian rivers were reported to have chromium concentration exceeding the tolerance limit of 50µg/L. (River Data Directorate Planning & Development Organisation, 2014).

It is thus important to develop cost-effective and reliable techniques to remove chromium from industrial effluents before being discharged into aquatic systems. Conventional methods for the removal of chromium include Chemical precipitation (Golbaz, Jafari, Rafiee, & Kalantary, 2014; Rajput, Pittman, & Mohan, 2016; D. Wang et al., 2016), Electrolytic recovery (Sirajuddin et al., 2007), Ion exchange (Fan, Wang, & Wang, 2013; Pakzadeh & Batista, 2011), Electrodialysis (ED) (Nataraj, Hosamani, & Aminabhavi, 2007), Membrane separation (Kozlowski & Walkowiak, 2002; Sudha et al., 2014) and Liquid liquid extraction (Mahmoud, Obada, & Kassem, 2013; K. P. Yu et al., 2016).

The techniques mentioned above though are of high efficiency and utility also have some disadvantages that limit their applications, such as toxic waste production, high cost and huge energy consumption. Chemical methods require large amounts of chemicals and generate toxic sludge that needs further treatment. Adsorption is a preferred technique as it is economically most favorable. However, the selection of environmental friendly and cost effective adsorbents is a matter of great significance (Albadarin et al., 2012).

The adsorbents widely used for removal of chromium can be classified as:

- ***Agricultural waste and by products***

These are abundant in nature widely derived from agricultural processing and have been considered to have enormous commercial potential and application feasibility (Bohumil Volesky, 2007) like eucalyptus bark (Sarin & Pant, 2006), cereal by products (Arris, Bencheikh Lehocine, & Meniai, 2016), Brown seaweed S. Siliquosum (Cabatingan, Agapay, Rakels, Ottens, & van der Wielen, 2001), Chemically treated Helianthus annuus (Jain, Garg, & Kadirvelu, 2011), Activated Neem Leaves (Babu & Gupta, 2008a), Sphagnum moss peat (D. C. Sharma & Forster, 1994b), Activated Tamarind seeds (Babu & Gupta, 2008b), Coconut husk fiber (W. T. Tan, Ooi, & Lee, 1993), Pine needles (Dakiky, Khamis, Manassra, & Mer'eb, 2002), Sugar beet pulp (D. C. Sharma & Forster, 1994a), Palm pressed fibers (W. T. Tan et al., 1993), Maize cob(D. C. Sharma & Forster, 1994a), Sugar cane bagasse. (D. C. Sharma & Forster, 1994a), Almond (Dakiky et al., 2002), Cactus(Dakiky et al., 2002), Biomass residual slurry (Namasivayam & Ranganathan, 1993), Waste tea (Orhan & Buyukgungur, 1993), Walnut shell (Orhan & Buyukgungur, 1993) Agricultural waste biomass (Garg, Kaur, Garg, & Sud, 2007) Rice husks (Sumathi, Mahimairaja, & Naidu, 2005), Soya Cake (Daneshvar, Salari, and Aber 2002), Teff straw (Wassie & Srivastava, 2016), Chemically modified banana peels (Ali & Saeed, 2016), Melaleuca diosmifolia (Kuppusamy et al., 2016),Powdered and granular Peganum Harmala seeds (syrian rue) (Khosravi, Fazlzadehdavil, Barikbin, & Taghizadeh, 2014), Bone Char (Hyder, Begum, & Egiebor, 2015), Grapefruit peelings (Rosales, Meijide, Tavares, Pazos, & Sanromán, 2016), cereal by-products (Arris et al., 2016), Raw and acid treated Oedogonium hatei (V K Gupta & Rastogi, 2009), Lignin (Lalvani, Hubner, & Wiltowski, 2000), Hazelnut Shell (Cimino, Passerini, & Toscano, 2000), Mangrove leaves (Elangovan, Philip, & Chandraraj, 2008), Water Lily (Elangovan et al., 2008), Red rose waste (Shafqat, Bhatt, Hanif, & Zubair, 2008), Lignocellulosic Substrate Extracted from Wheat Bran (Dupont & Guillon, 2003) and Rice straw (Gao et al., 2008) to name a few. At lower pH the surface of biosorbent becomes protonated due to H^+ ions. Strong electrostatic attraction between the positively charged surface and $Cr_2O_7^{2-}$ and $HCrO_4^-$ anions, chemical bonding between Cr^{6+}/Cr^{3+} and functional groups attached to the surface of waste biomass as well as van-der Waals forces are reported to be responsible for removal of chromium using agricultural biomass (Z Aksu & Akpinar, 2000; Zümriye Aksu & Akpinar, 2001; Bansal, Singh, & Garg, 2009; Vinod K. Gupta & Saleh, 2013).

- ***Industrial wastes***

Sawdust (S. Gupta & Babu, 2009), By product of Lentius edodes (G. Q. Chen et al., 2006), Tea Factory waste (Malkoc & Nuhoglu, 2007), Polymer grafted sawdust (Raji & Anirudhan, 1998), Maple sawdust (L. J. Yu, Shukla, Dorris, Shukla, & Margrave, 2003), Distillery sludge (Selvaraj, Manonmani, & Pattabhi, 2003), Calcined bauxite (Baral, Das, Rath, & Chaudhury, 2007), Fly ash impregnated with aluminum (Banerjee, Joshi, and Jayaram 2005), Coir pith (Suksabye, Nakajima, Thiravetyan, Baba, & Nakbanpote, 2009), Treated waste newspaper (Dehghani, Sanaei, Ali, & Bhatnagar, 2016), Iron Complexed Protein Waste (Fathima, Aravindhan, Rao, & Nair, 2005), Dolochar (Panda, Das, Rao, & Mishra, 2011) and Fertilizer industry waste material (Vinod K. Gupta, Rastogi, & Nayak, 2010) are some examples of industrial waste or by products used as adsorbents. The mechanism of removal depends on the composition of industrial waste and can range from weak van-der waal forces to electrostatic attraction and chemisorption.

- ***Biosorbents***

Biosorbents which involve the use of microbes, biopolymers as well as agricultural wastes are more environmentally benign in nature and hence are considered as greener adsorbents.

Microbes-The functional groups inherently available on the surface of bacteria, fungi or algae help in metal complexation and ion exchange during heavy metal remediation (Xie et al., 2016). Compared to live microbial cells which require continuous nutrient supply, dead microbes have the advantages of easy storage and handling and have higher surface area. Detoxification of metals by non-living biomass is by passive biosorption and is metabolism independent process in comparison to living biomass (B Volesky, 2001). It has been reported by Park et al. (Park, Yun, Jo, & Park, 2005) that with biomass involving chromium adsorption, there is a probability of adsorption coupled reduction mechanism through the adsorption of anionic Cr^{6+} on the biosorbent surface followed by its reduction to Cr^{3+}. Some of the biosorbents used for chromium reduction and removal include Trichoderma fungal species (Vankar & Bajpai, 2008), Mucor hiemalis (Tewari, Vasudevan, & Guha, 2005), *C. vulgaris* (Cetinkaya Donmez, Aksu, Ozturk, & Kutsal, 1999), *Rhizopus nigrificans* (Bai & Abraham, 2002), Pleurotus ostreatus (Javaid, Bajwa, Shafique, & Anwar, 2011), *S. obliquus* (Cetinkaya Donmez et al., 1999), *Aeromonas caviae* (Loukidou, Zouboulis, Karapantsios, & Matis, 2004), Alligator weed (X. S. Wang, Tang, & Tao, 2009), Zooglera ramigera (Veglio' & Beolchini, 1997), *Chlorella vulgaris* (Veglio' & Beolchini, 1997), *Rhizopus arrhizus* (Prakasham, Merrie, Sheela, Saswathi, & Ramakrishna, 1999), Spirogyra (Kratochvil & Volesky, 1998), Leaf mould (D. C. Sharma & Forster, 1996), Aspergillus versicolor (Das, Mukherjee, & Guha, 2008), Aspergillus niger (Mungasavalli, Viraraghavan, & Jin, 2007) and *Spirulina* sp. (Rezaei, 2013). However direct applications of biomass for large scale treatment has some drawbacks in terms of leaching of microbes, low regeneration capacity and loss of biomass. Hence immobilisation of microbes on various supporting matrices to attain good mechanical strength and porosity and modification of microbes was performed by several researchers (Dodson et al., 2015; Jiang, Xu, Li, Lv, & Wang, 2013) thereby increasing adsorption efficiency. A modified fungal biomass of Penicillium chrysogenum by grafting polyethylenimine on its surface (Deng & Ting, 2005) showed good efficacy towards adsorption of Cr^{6+}. Aspergillus sp immobilized on sodium montmorillonite is reported to have good potential for Cr^{6+} removal with an adsorption capacity of 45.67mg/g (Sathvika, Manasi, Rajesh, & Rajesh, 2015b). The same group also reported the application of yeast immobilized on cellulose for efficient removal of Cr^{6+} with an adsorption capacity of 23.61mg/g (Sathvika, Manasi, Rajesh, & Rajesh, 2015a).

Biopolymers- Use of biopolymers including cellulose and chitosan are a common practice for chromium detoxification. Chitosan has gained pronounced attention as biosorbent due to its physicochemical properties like chemical stability, high reactivity, excellent chelation behaviour and high selectivity towards pollutants (Elwakeel, 2010a, 2010b; Owlad, Aroua, Daud, & Baroutian, 2009). Further, properties like biocompatibility and biodegradability has resulted in increased usage of chitosan in waste water treatment as well as flocculation (Alves & Mano, 2008; Dabrowski, 2001; Muzzarelli, 1973; Rinaudo & Ã, 2006). Recently alginate biopolymer obtained from brown algae (Bertagnolli, da Silva, & Guibal, 2014; Gopalakannan & Viswanathan, 2015; Lagoa & Rodrigues, 2009; Lazaridis & Charalambous, 2005; Šillerová, Komárek, Liu, Poch, & Villaescusa, 2015; Tirgar, Golbabaei, Hamedi, & Nourijelyani, 2011) and its biocomposite with starch (Gopalakannan & Viswanathan, 2016) have been employed for the removal of hexavalent chromium. Presence of electron donor atoms like nitrogen and oxygen in the biopolymer may induce reduction of Cr^{6+} into less toxic Cr^{3+} (Gopalakannan & Viswanathan, 2016).

Gums- In addition to biopolymers, Gums such as Cassia marginata Seed Gum (Singh, Sharma, Kumari, & Tiwari, 2008), Poly(methylactrylate) functionalized guar gum (Singh, Kumari, Pandey, & Narayan, 2009) , Copolymers of N-Vinyl-2-Pyrrolidone grafted onto guar gum (R. K. Sharma & Lalita, 2011), Poly(methylacrylate) grafted on Guar gum (Singh et al., 2009) have also been investigated as adsorbents for chromium.

- ***Polymers***

Polymeric adsorbents are superior to other adsorbents due to their large surface area, tunable surface chemistry and feasible regeneration under mild conditions. Polymers with specific functionalities can be obtained, by either synthesizing new monomers bearing the functional groups capable of interacting with the target metal ions, followed by polymerization, or by converting the groups on the existing polymers or co-polymers with suitable chemical reactions into the desired functional groups. Polyacrylamide (Önnby, Pakade, Mattiasson, & Kirsebom, 2012) and Polyethylene imine (P. A. Kumar & Chakraborty, 2009) have been used for adsorption of chromium (Bhaumik, Maity, Srinivasu, & Onyango, 2012). Vetriselvi et al. used a redox polymer, Polyacrylic acid integrated with Catechol-hydroquinone for the adsorption of Cr^{6+} and Pb^{2+} from tannery effluents (Vetriselvi & Jaya Santhi, 2015).

Conducting Polymers- In recent studies polypyrrole and polyaniline have been reported as excellent adsorbents for the removal of Cr^{6+}. An intrinsically conducting polymer, polyaniline (PANI) is one of the most extensively investigated conducting polymers because of its good stability, low cost and being environment friendly (Bhadra, Khastgir, Singha, & Lee, 2009). PANI has shown very high removal capacity for hexavalent chromium due to reductive adsorption of hexavalent chromium (Chiou & Epstein, 2005; Xiao Guo, Fei, Su, & Zhang, 2011; J. Huang & Kaner, 2006).

❖ ***Ion Exchangers***

Ion exchangers, due to their high Cr^{6+} removal capacity (higher than 150 mg/g), good adsorption kinetics and regeneration properties (Edebali & Pehlivan, 2010; Mihciokur & Peker, 2013; Pehlivan & Cetin, 2009; W. Q. Wang, Li, & Zeng, 2012a) are extensively being used for removal of chromium. Strong Alkaline Anion Exchange Fiber (SAAEF) a unique kind of fabric absorption and separation material was used for removal of Cr^{6+}. The process was observed to be spontaneous, entropy driven and endothermic (Wenqing Wang, Li, & Zeng, 2012, 2015; W. Q. Wang, Li, & Zeng, 2012b). Imidazole-modified silica (Z. Wang, Ye, Wang, & Li, 2013), Mesoporous silica such as NH_2-MCM-41 (Bao et al., 2015; Cao, Wu, Jin, Yilihan, & Huang, 2014) have been used for the removal of Cr^{6+} from aqueous solutions while MCM-41 and MCM-48 were investigated for the adsorption of arsenate and chromate (Benhamou, Basly, Baudu, Derriche, & Hamacha, 2013).

Natural zeolites have been used as cationic exchange materials for the remediation of heavy metals and other contaminants due to their excellent properties as adsorbents. Surfactant modification of zeolitic materials changes their surface characteristics from hydrophilic to hydrophobic, which makes them amenable for use in adsorption processes to remove anionic contaminants (Serrano-Gómez, López-González, Olguín, & Bulbulian, 2010). Zeolite-rich tuff from the state of Chihuahua, preconditioned with sodium chloride and subsequently modified with hexadecyltrimethylammonium bromide was used for the removal of Cr^{6+} from aqueous systems (Salgado-Gómez, Macedo-Miranda, & Olguín, 2014).

Clay minerals, due to their large surface area and high cation exchange capacity have been studied for potential applications as environmental remediation agents and in removal of heavy metals and organic contaminants from water, particularly after modification with organic compounds. Silica based adsorbent (Qiua et al., 2009), Bentonite Clay (Tahir & Naseem, 2007), Jordanian pottery materials (Al-Sou'od, 2012), Natural and modified Brazilian smectite (Guerra, Oliveira, da Costa, Viana, & Airoldi, 2010), River bed sand (Y. C. Sharma & Weng, 2007), Red mud

Erdem (Erdem, Altundogan, & Tumen, 2004), Turkish montmorillonite clay and HDTMA modified Turkish montmorillonite clay (Akar, Yetimoglu, & Gedikbey, 2009), Moroccan stevensite (A. Benhammou, Yaacoubi, Nibou, & Tanouti, 2005), Hydroxyaluminum modified montmorillonite clay (B. Hu & Luo, 2010) and Acid activated kaolinite (Bhattacharyya & Gupta, 2006) were reported as adsorbents for removal of chromium.

There are many other researchers who have used natural and modified clay minerals for Cr^{6+} reduction (Brigatti et al., 2000; Eloussaief, Kallel, Yaacoubi, & Benzina, 2011; Parthasarathy, Choudary, Sreedhar, Kunwar, & Srinivasan, 2003; Shi, Zhang, & Chen, 2011; Stucki, 2006; Y. Wu, Zhang, Tong, & Xu, 2009) Clays modified by cationic surfactants and used in chromate removal from water, include Bentonite (smectite) (S. A. Khan, Riaz-ur-Rehman, & Khan, 1995; Krishna, Murty, & Jai Prakash, 2001; Z. Li & Bowman, 1998; Majdan, Maryuk, Gładysz-Płaska, Pikus, & Kwiatkowski, 2008), Stevensite (A. Benhammou et al., 2005; Abdelaziz Benhammou, Yaacoubi, Nibou, & Tanouti, 2007), Kaolinite (Z. Li & Bowman, 2001; Z. Li & Gallus, 2007), Illite (Z. Li, Alessi, Zhang, & Bowman, 2002), Palygorskite and Sepiolite (Z. Li, Willms, & Kniola, 2003). Vinuth et al. explored the use of Fe^{2+}-montmorillonite, for the reduction of Cr^{6+} in aqueous solution (Vinuth, Bhojya Naik, & Manjanna, 2015). Simultaneous adsorption of Cr^{6+} and phenol on a modified natural red clay was investigated by Gladysz-Plaska et al.(Gładysz-Płaska, Majdan, Pikus, & Sternik, 2012). HCl activated Akadama clay was used by Zhao et al. for removal of Cr^{6+} (Y. Zhao, Qi, Chen, Ji, & Zhang, 2015a). Lightweight Expanded Clay Aggregate (LECA) modified with an aqueous solution of magnesium chloride $MgCl_2$ and hydrogen peroxide H_2O_2 was used to remove Cr^{6+} from aqueous solutions (Kalhori, Yetilmezsoy, Uygur, Zarrabi, & Shmeis, 2013).

- **Layered Materials**

Layered double hydroxides (LDHs) or hydrotalcite-like compounds are a large family of two-dimensional (2D) anionic clay materials represented by the general formula of $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}$ $[A^{n-}_{x/n}]mH_2O$, where M^{2+} and M^{3+} are di- and trivalent metal cations and A^{n-} is a counter anion, x=0.17-0.33 and is the $M^{3+}/(M^{2+}+M^{3+})$ ratio (Cavani, Trifiro, & Vaccari, 1991). The interlayer anions are linked within the positively charged host layer by means of electrostatic as well as hydrogen bonding interactions through the interlayer water molecules or hydroxyl groups. LDHs can provide a flexible confined space that can be adjusted by changing the size and the structure of the interlayer molecules. Layered double hydroxides (LDHs) have been demonstrated to be effective adsorbents for the removal of hexavalent chromium (Crepaldi, Pavan, & Valim, 2000; Q. Wang et al., 2013; M. X. Zhu, Li, Xie, & Xin, 2005). Lu et al. have used Ni-Fe-LDH for methyl orange and Cr^{6+} adsorption (Lu et al., 2016).

Recently, many studies have been done on the effect of LDH structure for Cr^{6+} removal. Carriazo et al. compared the chromate uptake capacity of MgAl-Cl LDH with its carbonate counterpart. The results showed that MgAl-Cl samples were better adsorbents than calcined MgAl-CO_3 samples with 17mg/g Cr^{6+} removal (Carriazo, del Arco, Martín, & Rives, 2007). Wang et al. (Wenwen Wang, Zhou, Achari, Yu, & Cai, 2014) studied the Cr^{6+} uptake using MgAl, NiAl and ZnAl LDHs with molar ratio (M^{2+}/M^{3+} = 3). The authors found that ZnAl-LDH exhibits excellent sorption capacity (68.07mg/g) and good regeneration performance. Zhang et al. (F. Zhang, Du, Li, Liu, & Hou, 2014) reported the removal of Cr^{6+} onto MgAlFe–NO_3 LDHs synthesized by a mechano hydrothermal method with varying Mg^{2+}/Al^{3+} molar ratio. The resulting LDHs had higher removal efficiency for Cr^{6+} compared to that prepared by conventional mechanochemical method. The influence of interlayer anions such as NO_3^-, SO_4^{2-} and Cl^- on Mg-Al hydrotalcites for Cr^{6+} removal from aqueous solution was studied by Khitous et al. (Khitous, Salem, & Halliche, 2015). The removal behaviors of Cr^{6+} and Se^{6+} on $Mg_{3x}Ca_xFe$-LDHs (x = 0-1.5) was studied by Zhou et al. (Jizhi Zhou et al., 2015). Jaiswal et al. synthesized layered double hydroxides (LDHs) with Co/Bi=3 via urea hydrolysis method and applied it for removal of Cr^{6+} (Jaiswal, Mani, Banerjee, Gautam, & Chattopadhyaya, 2015). LDHs remove Cr^{6+} from solution by both surface sorption and anion-exchange (Lazaridis, Pandi, & Matis, 2004). Recently, amine groups functionalized graphene sheets were synthesized and used for hexavalent chromium removal (A. S. K. Kumar, Kakan, & Rajesh, 2013; L Zhang et al., 2015).

- ***Carbons***

Activated carbons due to their wide availability with amenable physical and chemical properties (Di Natale, Erto, Lancia, & Musmarra, 2015; Mohan, Singh, & Singh, 2005) have been widely used for the adsorption of Cr. The adsorption in activated carbons is usually physical adsorption through van-der waals forces (Jianguo

Zhou et al., 2016). However, the small pore size and low pore volume within the activated carbons led to a quite slow mass transport rate. Mesoporous carbons are promising alternatives with fast adsorption rate owing to their high specific surface area, well developed mesoporous channels and large pore volumes (Hartmann, Vinu, & Chandrasekar, 2005). Mesoporous carbons have been used for removal of Cr^{6+} (H. Chen, Yan, & Jiang, 2014; J. Zhu et al., 2014) and are reported to display high adsorption capacities. Activated carbon derived from acrylonitrile-divinylbenzene copolymer (Duranoglu, Trochimczuk, & Beker, 2012), Coconut Shell based Activated Carbon (Alaerts, Jitjaturunt, & Kelderman, 1989), Activated Charcoal (Mor, Ravindra, & Bishnoi, 2007), Coal (Dakiky et al., 2002), ACASC (acid-treated Chrysophyllum albidum seed shells carbon) (Amuda, Adelowo, & Ologunde, 2009), Chemically Activated High Temperature Syzygium jambolanum nut Carbon (Muthukumaran & Beulah, 2011), Algal bloom residue derived activated carbon (H. Zhang et al., 2010), mesoporous carbon microspheres are some of the carbons that have been used for chromium removal (Jianguo Zhou et al., 2016). However, activated carbon is difficult to regenerate and the processing cost is higher, thus restricting their extensive application (Yang, Yu, & Chen, 2015).

This has resulted in increased research focus for the production of alternative low-cost and highly efficient activated carbons using relatively cheap raw materials with a high carbon content such as agricultural residues, biomass and various solid substances. Some of the raw materials that have been used for preparation of activated carbon and applied for removal of chromium include Rice husk and straw (Bishnoi, Bajaj, Sharma, & Gupta, 2004; Gao et al., 2008; Hsu et al., 2009), Hazelnut shell (Kobya, 2004), Coconut shell (Babel & Kurniawan, 2004), Cornelian cherry, Apricot stone, Almond shells (Demirbas, Kobya, Senturk, & Ozkan, 2004), Casurina Equisetifolia Leaves (Ranganathan, 2000), Tamarind wood (Acharya, Sahu, Sahoo, Mohanty, & Meikap, 2009), Hevea Brasilinesis sawdust (Karthikeyan, Rajgopal, & Miranda, 2005), Date palm seed (El Nemr, Khaled, Abdelwahab, & El-Sikaily, 2008), Olive Bagasse (Demiral, Demiral, Tümsek, & Karabacakoğlu, 2008), Peach Stone (Duranoglu, Trochimczuk, & Beker, 2010), Bael fruit shell (Gottipati & Mishra, 2010), Sugarcane Bagasse (Cronje, Chetty, Carsky, Sahu, & Meikap, 2011), Eichhornia crassipes root (Giri, Patel, & Mandal, 2012), Trapa natans husk (W. Liu, Zhang, Zhang, Wang, & Li, 2010), Terminalia arjuna nuts (Mohanty, Jha, Meikap, & Biswas, 2005) and Longan seed (Yang et al., 2015).

Biochar a carbon-rich product similar to activated carbon with its abundant functional groups and lower cost is considered as the best alternative for commercial activated carbon (T. Chen, Zhou, Xu, Wang, & Lu, 2015; Tytłak, Oleszczuk, & Dobrowolski, 2015). Biochar is obtained by pyrolysis of waste biomass such as sugar beet tailing (Dong, Ma, & Li, 2011) and Wheat (X. S. Wang et al., 2010) under relatively low temperature (<700°C) and oxygen deficient conditions (Tytłak et al., 2015). Though the specific surface area and micropore volume of biochars are much lesser (T. Chen et al., 2014) in comparison to activated carbons their adsorption capacity is comparable. Biochar has gained considerable interest due to its potential in soil amendment, crop fertilization, carbon sequestration and environmental remediation of heavy metals and organic pollutants as well (T. Chen et al., 2014; X. Tan et al., 2016). Generally, there are different kinds of mechanisms for Cr^{6+} removal by biochars and activated carbons: (i) electrostatic interaction of negatively charged Cr^{6+} species on the positively charged surface of sorbent; (ii) adsorption of Cr^{6+} species followed by reduction (iii) reduction of Cr^{6+} species to Cr^{3+} form followed by adsorption or chelation (iv) adsorption coupled with reduction, where Cr^{6+} ions are partially adsorbed onto the sorbent and partially are reduced to Cr^{3+} (Tytłak et al., 2015; L. Zhou et al., 2016).

❖ ***Nanomaterials***

Nano sized materials are now a day’s widely used in wastewater due to their high surface area and adsorption capacity (Nowack & Bucheli, 2007; Savage & Diallo, 2005). When nanomaterials are used as adsorbents mass transport resistance is greatly reduced due to size of adsorbents (S. S. Kumar, Venkateswarlu, Rao, & Rao, 2013). Magnetite nanoparticles have been used for the removal of chromium from waste water (Padmavathy, Madhu, & Haseena, 2016) . $CoFe_2O_4$ nanoparticles have been used by Srivastava et al. for the adsorption of Cr^{6+} ions from synthetic wastewater as well as printing press wastewater (Srivastava, Kohout, & Sillanpää, 2016). Akagancite Nanocrystals (Lazaridis, Bakoyannakis, & Deliyanni, 2005), Modified Jacobsite $MnFe_2O_4$ nanoparticles (J. Hu, Lo, & Chen, 2005) are also used as adsorbents for chromium removal.

❖ ***Metal Oxides***

In comparison with activated carbons, metal oxides are more promising adsorbents due to the following advantages: (i) They are commonly occurring and have good selectivity to heavy metal ions; (ii) ease of preparation into suitable adsorbent form such as granules (K. Wu et al., 2011). For instance, iron oxide is a low cost, eco-friendly and widely investigated adsorbent for anionic pollutants removal (Zeng, Li, & Liu, 2004). Iron hydroxides are reported to effectively adsorb and immobilize Cr^{6+} (K. Xu, Li, Liu, & Peng, 2011). Zirconium oxide has strong affinity to Cr^{6+} and high resistance to attacks from acids, alkalis, oxidants, and reductants (Rodrigues, Maschio, da Silva, & da Silva, 2010). Iron-zirconium bimetal oxide originating from the combination of iron oxide and zirconium oxide showed a great potential for Cr^{6+} removal than their simple individual metal oxides (Y. Wang, Liu, Lu, & Huang, 2015). Hydrous zirconium oxide has been used for removal of Cr^{6+} (Rodrigues et al., 2010). Activated Alumina (Mor et al., 2007), HCl-activated Akadama clay (Y. Zhao, Qi, Chen, Ji, & Zhang, 2015b), Fe^{3+}/Cr^{3+} hydroxide (Namasivayam & Ranganathan, 1993)etc. are other metal oxides that have been recently investigated.

❖ ***Metal Organic Frameworks***

Metal-organic frameworks (MOFs), known as metal organic coordination polymers, commonly recognized as soft analogues of zeolites, are a new class of porous structures composed of different transition metal ions (or clusters) and rigid-rod-like organic linkers (N. A. Khan, Hasan, & Jhung, 2013). Such a composition not only provides MOFs with tunable options, organic functionality, high thermal and mechanical stability, open metal chelating sites in the skeleton, large pore sizes, and high surface areas, but can also be easily prepared in one pot (T. Liu et al., 2014). A MOF based on copper-benzene tricarboxylates was applied to the adsorption of hexavalent chromium from aqueous solution by Maleki et al. (Maleki, Hayati, Naghizadeh, & Joo, 2015).

❖ ***Composites***

During the use of conventional adsorbents, practical problems such as adsorbent agglomeration and adsorbent loss during the separation process are often encountered. Further bulk adsorbents have inherent limitations of mass transfer resistance due to large surface areas and large diffusion lengths. To overcome these limiting factors, adsorbents with some nano features are incorporated so that chromium species has rapid access to high surface area thereby enhancing internal mass transport kinetics (Hristovski, Baumgardner, & Westerhoff, 2007). Nanocomposites can be developed by embedding the nanoparticles in bulk materials. The LDH/PAN nanocomposite film was used as an effective adsorbent for Cr^{6+} removal (Gore, Omwoma, Chen, & Song, 2016). Magnetic natural zeolite-polypyrrole composite has been used as an effective adsorbent for Cr^{6+} removal from water (Mthombeni, Onyango, & Aoyi, 2015). Titanium dioxide (TiO_2) loaded on carbon microspheres (Qian, Hu, Liu, Zhou, & Guo, 2012) and Hydrogen peroxide treated carbon black/TiO_2 (Li Zhang & Zhang, 2014) were also used for Cr^{6+} removal. Calcined graphene/MgAlLDH was found to remove Cr^{6+} with capacity of 172.55mg/g (X. Yuan et al., 2013). Cellulose-NaMMT (Sodium montmorillonite) composite (A. S. K. Kumar, Kalidhasan, Rajesh, & Rajesh, 2012), LDH (layered double hydroxide)/ESM (Eggshell membrane) composite (Xiaoxiao Guo et al., 2011), Bacterial cellulose-magnetite composites (Stoica-Guzun et al., 2016) and Titanium Oxide-Ag composite (S. S. Liu et al., 2011) are few other nanocomposites recently reported for removal of Cr^{6+}.

Magnetic nanocomposites - Magnetic nanoparticles have been used as components with other adsorbents to assist in separation of adsorbents as well as to enhance removal of Cr^{6+} (Pang et al., 2011). For instance, it is difficult to separate Graphene oxide (GO) from aqueous solution using conventional centrifugation and filtration techniques after the adsorption process due to its small particle size. Therefore, magnetic graphene-based adsorbents with large specific surface areas and magnetic separation have begun to be used in the field of environmental remediation. Liu and Zhu et al. synthesized magnetic graphene composites for Cr^{6+} removal (M. Liu et al., 2013; J. Zhu et al., 2012). A ternary magnetic composite consisting of graphene oxide (GO), diethylenetriamine and Fe_3O_4 nanoparticles was synthesized and applied as a magnetic adsorbent for the Cr^{6+} removal from aqueous solutions with easy magnetic separation (D. Zhao et al., 2016). Other magnetic composites used for chromium removal include polypyrrole/Fe_3O_4 magnetic nanocomposite (Bhaumik, Maity, Srinivasu, & Onyango, 2011), Bacterial Cellulose-Fe_3O_4 composite A (Stoica-Guzun et al., 2016), Polypyrrole coated fly ash - iron composite (Q. Zhou, Yan, & Luo, 2016), Magnetic polypyrrole nanocomposite hydrogel (Ahmad et al., 2016), Polypyrrole coated fly ash-iron composites (Q. Zhou et al., 2016), Polypyrrole nanocomposite hydrogel particles (Ahmad et al., 2016), Polypyrrole/Fe_3O_4 (Bhaumik, Setshedi, Maity, & Onyango, 2013), Iron oxide modified polyglycidyl methacrylate graft copolymer (PGMA) hybrid adsorbent (PGMAFe) (Duranoglu, Buyruklardan Kaya, Beker, & Senkal, 2012) and Polypyrrole-titanium (IV) phosphate (Baig, Rao, Khan, Sanagi, & Gondal, 2015).

Techniques for monitoring and detection of Chromium

It is vitally important to develop methods for the fast, facile, sensitive and selective detection of Cr^{6+} from the viewpoint of environmental monitoring and protection. Up to now, many methods and materials have been used to detect Cr^{6+}, including UV-Vis spectrophotometry (Balasubramanian & Pugalenthi, 1999; Ravindran et al., 2012; L. Zhao, Jin, Yan, Liu, & Zhu, 2012), Surface plasmon field enhanced resonance light scattering method (Han, Qi, Shen, Liu, & Chen, 2007), Electrochemical techniques (Jin, Wu, & Chen, 2014; Y. Li & Lin, 2006), Fluorescence sensors (Hosseini et al., 2012; Sun, Zhang, & Jin, 2013; Zheng et al., 2013), Inductively coupled plasma-mass spectrometry (H. J. Wang et al., 2010), Chromatography (Arancibia, Valderrama, Silva, & Tapia, 2003), Inductively couple atomic emission spectrometry (Balasubramanian & Pugalenthi, 1999), Atomic absorption spectroscopy (Chwastowska, Skwara, Sterlińska, & Pszonicki, 2005), Photoelectrochemical methods, Surface enhanced Raman scattering (SERS), and electro deposition (An, Park, Kwon, Bae, & Jang, 2013; Q. Wei et al., 2014; Ling Zhang et al., 2013). Although these methods are highly sensitive, most of them suffer disadvantages such as high cost, time-consuming, a complicated pretreatment process and the operation of sophisticated instruments, which limit their wide applications.

- ***Colorimetry***

The diphenylcarbazide technique is the most widely used technique for the determination of Cr^{6+} (Clesceri, Greenberg, & Eaton, 1998). In an acid medium, 1,5-diphenylcarbazide (DPC) reacts with Cr^{6+} and a red-violet colored complex is produced. The molar absorption spectra based on Cr^{6+} at the wavelength of 540 nm are recorded. However, the DPC is insoluble in water and the solution prepared with acetone is stable just for one week. Furthermore, the color reaction between DPC and Cr^{6+} needs the participation of sulfuric acid and phosphoric acid to avoid interference, which makes the process complicated and inconvenient. Therefore, developing a new, simple, selective and rapid colorimetric assay for the determination of trace Cr^{6+} in aqueous solution is important to monitor the environment.

There are many colorimetric methods for Cr^{6+} determination that have been recently investigated by researchers (Bardiya, Hwang, & Bae, 2004; Clesceri et al., 1998; Long, Miró, & Hansen, 2005; Rajesh, Agarwal, & Aarthy, 2008; Singer Pressman & Aldstadt Iii, 2005). An extractive spectrophotometric method for the chemical speciation of Cr^{3+} and Cr^{6+} species in aqueous media has been developed by Shahawi et al. The method is based upon the extraction of the complex ion-associate formed between the chloro chromate (CrO_3Cl^-) anion and the ion-pair reagent tetraphenylarsonium chloride ($TPAs^+Cl^-$) or tetraphenylphosphonium bromide (TPP^+Br^-) at acidic pH in chloroform followed by direct spectrophotometric measurement at 355 nm (El-Shahawi, Hassan, Othman, Zyada, & El-Sonbati, 2005). A colorimetric method for determination of Cr^{6+} was developed by Li et al. based on the peroxidase substrate-2,2-azino-bis(3-ethylbenzo-thiazoline-6-sulfonic acid) diammonium salt (ABTS) as the color developing agent (J. Li, Wei, Guo, & Wang, 2008).

Of late, fiber optic-linear array detection spectrometers (FOLADS) based on CCD-detector have been used in spectroscopy. Simultaneous determination of analytes using multi wavelength data acquisition is possible with CCD linear array spectrophotometry. Further, optical fibers have high light focalization that makes them suitable for pre-concentration applications in which micro liter volume of extraction solvent is used (Gangopadhyay, 2004; Johansson, Cauchi, & Sundgren, 2002; Lee, 2003). Chromium speciation analysis was performed by Yousefi et al. using sodium dodecyl sulfate (SDS) as both ion-pairing and disperser agent. Cr^{6+} ions were converted into their cationic complex with 1,5-diphenylcarbazide (DPC) and then extracted into 1-octanol dispersed in aqueous solution. Cr^{3+} ion also can be determined by this procedure after oxidation to Cr^{6+}. After extraction and phase separation, upper organic phase was transferred to a micro cell of a fiber optic-linear array detection spectrophotometry (FO-LADS) for determination (Yousefi & Shemirani, 2013).

- ***Fluorescence***

Fluorescence sensors have also been designed for Cr^{6+} detection, such as organic fluorophores (Z. Yuan, Cai, Du, He, & Yeung, 2014), Quantum dots (Lan et al., 2014) and Metal nanoparticles (Dang, Li, Wang, Li, & Wu, 2009). The photophysical properties of rhodamine (Mao, He, & Liu, 2010) and naphthalimide modified rhodamine isomers have been reported to be used in Cr^{3+} sensing by fluorimetry (Z. Zhou et al., 2008). Conjugated polymers such as photoluminescent o-phenylenediamine–m-phenylenediamine copolymer nanospheres (Song, Sun, Yang, Zhao, & Liao, 2016) have been used for selective and sensitive detection of chromium ion. Using graphitic carbon nitride (g-C_3N_4) nanosheets, an effective and facile fluorescence sensing approach for the label-free and selective determination of Cr^{6+} was developed by Rong et al (Rong et al., 2015). Lei et al. fabricated two sensors for Cr^{3+} ion based on poly(amidoamine) dendrimers with 1-phenyl-3-methyl-5-pyrazolone fluorescent unit based on the mechanism of of ring-opening and photo induced electron transfer (PET) (Lei, Su, & Huo, 2011). Another PET based sensor was reported by M.Sarkar et al (Sarkar, Banthia, & Samanta, 2006). Forster resonance energy transfer (FRET) based sensors (K. Huang et al., 2008; Z. Zhou et al., 2008) were used for monitoring chromium.

❖ ***Nanoparticles as Sensors***

Nanoparticle based sensors using gold, silver, copolymer spheres, carbon materials have been developed taking advantage of their fluorescence and surface plasmon resonance (Ravindran et al., 2012; Sun et al., 2013; Zheng et al., 2013). Bifunctionalization of silver nanoparticles with 6-mercaptonicotinic acid and melamine was performed by Modi et al. for simultaneous colorimetric sensing of Cr^{3+} and Ba^{2+} ions (Modi, Mehta, & Kailasa, 2014). Polyethyleneimine protected silver nanoclusters were used for sensing of Cr^{6+} by Xu et al. (N. Xu, Zhu, Kong, & Meng, 2016). This NPs-based sensor was reported to have several advantages, including (i) simple and low-cost preparation; (ii) high selectivity and sensitivity to Cr^{3+} and Cr^{6+}; (iii) a marked red/blue shift in the UV-Vis extinction spectra and a visible color change. Akash et al. used single-walled carbon nanotubes (SWCNTs) functionalized with a phosphinic acid derivative‘bis(2,4,4-trimethylpentyl) phosphinic acid’ as sensors for Cr^{6+} (Deep, Sharma, Tuteja, & Paul, 2014). Ghosh et al. used highly luminescent Gd_2O_3:Eu^{3+} nanoparticles for detection of Cr^{3+}(Ghosh & Luwang, 2016). Kaur et al. showed binding affinity of Cr^{3+} with fluorescent glutathione-based tripeptide and imine linked organic nanoparticles (FONs) (Kaur et al., 2015). Kollbek et al. used TiO_2 NPs for detection of Chromium ion (Kollbek et al., 2015). Mondal et al. developed a novel organic-inorganic hybrid, Polypyrrole nano particles grafted with functionalized silica gel for selective binding of Cr^{6+} (Mondal, Roy, Bayen, & Chowdhury, 2011). Rong et al. used graphitic carbon nitride (g-C3N4) nano sheets (Rong et al., 2015) for sensing Cr^{6+}. Song et al. used o-phenylenediamine-m-phenylenediamine Copolymer Nanospheres for detection of Cr^{6+}(Song et al., 2016).

- ***Luminescence***

Highly luminescent crystalline polyimide (PI) nanosheets were used by Xiao et al. for selective sensing of chromium ions in aqueous solution, without the interference of other metal ions, such as potassium, calcium, cadmium, plumbum, manganese, mercury, magnesium, cobalt, copper, and zinc (Xiao et al., 2013).

- ***Electrochemical sensors***

Electrochemical techniques have emerged as interesting alternatives as they offer rapid detection of the analyte in different matrices because they do not require prior separation and can be used in the presence of turbidity.

Potentiometry- The use of ion selective electrodes led to lower detection limits as compared to techniques like colorimetry and AAS. A Cr^{3+} specific potentiometric sensor using aurin tricarboxylic acid modified silica has been developed. Tri-*O*-thymotide (I) and 5-amino-1-phenyl-1H-pyrazole-4-carboxamide have been used to prepare matrices for Cr^{3+} sensing by potentiometry (V. K. Gupta, Jain, Kumar, Agarwal, & Maheshwari, 2006; Zamani et al., 2009). Other ISEs include 4-amino-3-hydrazino-6-methyl-1, 2, 4-triazin-5-one as a neutral ionophore (Zamani, Rajabzadeh, & Ganjali, 2006) and membranes with N,N,N,N-tetrakis(3-aminopropyl)-1,4-butanediamine ionophore (Choi, Minoura, & Moon, 2005) for selective determination of chromium.

Voltammetry - Adsorptive stripping voltammetric methods have been reported by several researchers (Brett, Filipe, & Susanna Neves, 2003). Jorge et al. (Jorge, Rocha, Fonseca, & Neto, 2010) presented an adsorptive stripping voltammetric protocol coupled with a rotating disc bismuth film electrode obtaining very low limit of quantification (LOQ), in the range on nM, at pH 4.6 using acetate buffer. Lin et al. (Lin, Lawrence, Thongngamdee, Wang, & Lin, 2005) described an adsorptive stripping voltammetric protocol at a bismuth-coated glassy-carbon electrode for trace measurements of Cr^{6+} for pH between 4.5 and 7.5. Grabarczyk (Grabarczyk, 2008) developed a quantitative method to extract total Cr^{6+} (soluble and insoluble forms) from a solid sample, detecting Cr^{6+} in the extract by catalytic adsorptive stripping voltammetric technique at pH between 5 and 6. On the other hand, Bergamini et al. (Bergamini, dos Santos, & Zanoni, 2007) and Sanchez-Moreno et al. (Sanchez-Moreno, Gismera, Sevilla, & Procopio, 2010) reported detection of Cr^{6+} at pH 2 and 3 using solid-state sensors coupled to amperometric or voltammetric detectors. Fiol et al. (Fiol, de la Torre, Demeyere, Florido, & Villaescusa, 2007) prepared vegetable waste-based sensors with selectivity for Cr^{6+} and Hg^{2+} at pH 2-3 with LOD of about 2 mM and sensitivity of -61mV. Relatively more sophisticated modified electrodes have also been used for sensing chromium. For instance, Svancara et al. (Svancara, Vytras, & Foret, 2004) reported Cr^{6+} sensor based on pre-concentration of the chromate anion at a carbon paste electrode modified in situ with quarternary ammonium salts working at pH 1 to 3. Hallam et al. (Hallam, Kampouris, Kadara, & Banks, 2010) described screen printed electrodes (SPE) with platforms based on graphite for Cr^{6+} sensors, working at pH 1 obtaining a limit of detection (LOD) of about 0.4 M, a limit of quantification (LOQ) of 2 M. Graphite and gold screen printed electrodes for monitoring chromium have been reported (Hallam et al., 2010; Metters, Kadara, & Banks, 2012). Welch et al.(Welch, Nekrassova, & Compton, 2005) found that Cr^{6+} in pH 1 solutions can undergo chemically irreversible reduction on the surface of diamond electrodes, doped with gold, glassy carbon and boron with an LOD of 4 M. Application of screen printed working electrodes for Cr^{6+}, detection and quantification has been reported by few researchers at higher pH values (Bergamini et al., 2007; Dominguez-Renedo, Ruiz-Espelt, Garcia-Astorgano, & Arcos-Martinez, 2008; Grabarczyk, 2008; Sánchez-Moreno, Gismera, Sevilla, & Procopio, 2010). Simple, low-cost and acid-resistant carbon-based screen-printed electrodes (SPEs) for detection of Cr^{6+} species, in sulfuric acid at pH about 1, were prepared by Miscoria et al. (Miscoria, Jacq, Maeder, & Martín Negri, 2014).

Other electrochemical techniques that have been used include impedimetry and electrocatalytic detection. Wei et al. reported Ultrasensitive and ultra selective impedimetric detection of Cr^{6+} using crown ethers as high-affinity targeting receptors (J. Wei et al., 2015). Korshoj et al. reported Methylene blue-mediated electrocatalytic detection of Cr^{6+} (Korshoj, Zaitouna, & Lai, 2015).

Photoelectrochemical Sensors- It is a kind of sensing technique based on photoinduced electron transfer processes at electrode/interfaces. They have remarkable sensitivity, portability, and easy integration. Few studies have focused on this technique for sensing chromium. Li et al reported PEC sensing of Cr^{6+} based on its selective inhibition of quercetin oxidation on a TiO_2 photoanode (H. Li et al., 2013). Ultrasensitive photoelectrochemical determination of Cr^{6+} in water samples by ion-imprinted/formate anion-incorporated graphitic carbon nitride nanostructured hybrid has been reported by Fang et al. (Fang, Yang, Zhang, & Gong, 2016).

While electro chemical techniques are simple, inexpensive and portable, they are subjected to interferences resulting from the sample matrices or analyte reaction product and it is necessary to clean up the electrode surface prior to the next cycle detection, which is time-consuming. Alternative techniques include

- ***Biosensors***

lt is known that heavy metal ions inhibit the activity of enzymes. Enzyme inhibition-based biosensors appear to be very efficient for determining ions of these hazardous toxic elements, with high sensitivity and specificity. The most used enzymes are urease, tyrosinase, acetylcholine esterase (AChE) and horseradish peroxidase. Renedo et al. used tyrosinase to develop an amperometric sensor for detection of Cr^{3+} (Dominguez Renedo, Alonso Lomillo, & Arcos Martinez, 2004). Attara et al. fabricated a amperometric horse radish peroxidase based sensor for determination of chromium (Attar, Emilia Ghica, Amine, & Brett, 2014).

- ***Lab on chip sensors***

In recent years, lab-on-chip (or microfluidic), Lab on paper and Lab on cloth devices for sensing chromium have been developed. A lab-on-a-chip or paper is a miniaturized device that integrates onto a single chip one or several analyses which are usually done in a laboratory. Such devices have the potential ability to reduce reaction solution consumption and assay time, and to realize highly-integrated, automated and compact flow assay system. a simple rapid and portable lab on chip microchip sensor for Cr^{6+} has been established with Au-Ag-Pt three-electrode system by Li et al. (D. Li et al., 2013).

Single-walled carbon nanotubes (SWCNTs) have been functionalized with a phosphinic acid derivative 'bis(2,4,4-trimethylpentyl) phosphinic acid' (PA/d) for sensitive and selective electrochemical sensing of Cr^{6+} ions (Deep et al., 2014).

Although the above mentioned detection techniques possess attractive analytical "figures of merit", each of them has one or several undesirable limitations. For example, ICP-MS, as the most sensitive and multielement detection technique (Y. Zhang, Xu, Wang, Toledo, & Zhou, 2007), is a rather bulky (i.e. unsuitable for the in situ field monitoring) (Taylor, 2001), expensive and not selective to the different charge states and chemical forms of an element. While electrochemical techniques are simple, inexpensive and portable, they are subjected to the interference resulting from the sample matrixes or analyte reaction product and it is necessary to clean up the electrode surface prior to the next cycle detection, which is time consuming.

In order to achieve higher selectivity and sensitivity, these analysis techniques were coupled with extraction and pre-concentration techniques such as liquid-liquid extraction (LLE), solid phase extraction (SPE) and co-precipitation, solid phase micro extraction (SPME), liquid phase micro extraction (LPME) and dispersive liquid-liquid microextraction (DLLME) (Yousefi & Shemirani, 2013).

Thus, the development of new, practical and rapid assays for the determination of Cr^{6+} still remains a challenge. Facile colorimetric assays with more attractive detection limits using nanoparticles could potentially eliminate the use of analytical instruments and are paid more and more attention.

Due to major shortcomings of conventional treatment methods mentioned above including the high cost of safely disposing the sludge, expensive chemicals necessary for Cr^{6+} reduction and incomplete reduction of Cr^{6+}, adsorption processes are considered to be the appropriate method. Adsorption, an effective and versatile method when combined with suitable desorption steps solves the problem of sludge disposal. We have seen that a number of low cost adsorbents have been used for the removal of chromium from waste waters However, many of these adsorbents have low chromium adsorption capacity or slow process kinetics or difficulty in separation. Thus, there is a need to develop innovative low cost adsorbents useful both for industry and for the environment such as biopolymers and nanocomposites.

The objective of our present work is thus :

(1) Use of adsorbents based on biopolymers such as Chitosan derivatives and composites for removal of Chromium

(2) Use of Polymers with redox behavior like Polyaniline for removal of Chromium

(3) Use of capped silver and gold nanoparticles for detection of Chromium

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