

Removal of Chromium in quest for clean and sustainable environment: A Review

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Abstract

Millennium development goal in its list of targets have improved health and environment sustainability among other things. Environmental protection guarantees environmental sustainability and directly as well indirectly improves societal health. In the quest to protect the environment, removal of heavy metals which are either carcinogenic or mutagenic has taken the lead. Chromium exist in two oxidation states in the environment (Cr^{3+} and Cr^{6+}) with the later being more toxic. The use of different adsorbents in the removal of chromium from the environment has been reviewed in this article and areas that need further attention that will improve and enhance its removal were reported. It is hoped that the concerns reported this article will be useful in solving environmental problems caused as a result of chromium contamination.

Keywords: Environmental sustainability, Carcinogenic, Chromium, Adsorbents

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Introduction

Water is one of the basic needs of human being and also essential for various industrial activities [1]. Water pollution has become a serious concern to the world at large and the continuous deterioration of our water body is no doubt a concern to the environmentalists. Various discharges from industrial activities have been directly or indirectly the major source of pollutants in water bodies. Pollutants released from industrial activities range from organics through various anionic pollutants and to inorganic pollutants. Heavy metals are one of the major pollutants released into the water body as they are widely used in various industrial activities, as they have found great applications in electroplating processes, plastic and fertilizer manufacturing, mining and metallurgical activities among others [2]. Heavy metal are found to persist in the environment as they are non biodegradable and hence causing serious health problems, for instance heavy metal in drinking water can lead to serious health problems such as cancer [3]. Various heavy metals such as cadmium (Cd), Chromium (Cr) and Nickel (Ni) due to their toxicity have been classified by International Agency for Research on Cancer (IARC) as group- 1 carcinogen [4]. Although chromium is an essential metal required by human in trace amounts, its mechanisms of action in the body and the amounts needed for optimal health are not well defined. The health hazards associated with exposure to

chromium are dependent on its oxidation state, the trivalent chromium (Cr^{3+}) which is chemically basic and the most stable form of the element because of its strong tendency to form kinetically inert hexacoordinate complexes with water, ammonia, organic acids, sulfate, halides, and urea. This characteristic has great relevance to the behavior of trivalent chromium in biological systems. The hexavalent chromium (Cr^{6+}) is acidic and is the most commercially, biologically, and environmentally important state of chromium. Hexavalent forms of chromium are almost always linked to oxygen and are, therefore, strong oxidizing agents. Characteristically, acidic hexavalent chromium forms chromate (CrO_4)²⁻ and dichromate (Cr_2O_7)²⁻ ions [5]. Hexavalent chromium is the toxic form that results from industrial pollution and its toxicity is about 500 times more than the trivalent one [6,7]. Chromium has found great use in various industrial processes including chromium compound manufacturing, electroplating, leather tanning, welding chrome paint, dyeing, hardened steel, fungicides and corrosion resistance, ceramic and glass industry, in photography, chrome alloy and chromium metal production. Hence the effluents generated by these industries are highly loaded by this pollutant [8].

Various conventional methods exists for the removal of heavy metals in waste water but they are both economically unfriendly and with various limitations and therefore the

need for economically friendly and effective way of dealing with these pollutants. Biological materials (biomass) have been found to satisfy this quest as they can be used to remove at a very low cost even small amount of toxic heavy metals from industrial effluents and the process that utilizes biological material for the uptake of heavy metals from aqueous solutions has been referred to as biosorption. Biosorbents usually contain variety of functional sites and metal sequestering by different parts of the cell can occur via various processes: precipitation, complexation, chelation, coordination, ion-exchange, reduction [9,10]. Various sorbents ranging from natural materials such as clay and minerals, synthetic materials and to low cost adsorbents such as bacteria, fungi and algae, industrial wastes, agricultural wastes and other polysaccharide materials have found great use in the removal of metals and dyes from effluents [11]. The toxicity of Cr^{6+} has called for a special attention and its removal using various sorbents has been investigated over the years by various researchers. This literature review paper highlight and provides an overview of researchers' efforts in the recent years on the removal of this problematic toxicant (Cr^{6+}) in the quest for a cleaner environment.

Clay materials and minerals

Clay materials have certain properties that make them an excellent adsorbent for the removal of both organic and inorganic pollutants. They have high specific surface area, chemical and

mechanical stabilities, and a number of surface and structural properties. The adsorption capacity of clay has been traced to its high surface area and the net negative charge on the silicate minerals which in adsorption process is neutralized by the positively charged cations such as cationic dyes or heavy metals [12-13]. Clay materials includes bentonite which is composed mainly of montmorillonite, a clay mineral of the smectite and Kaolin (China clay) which mainly contain kaolinite with others components such as quartz, mica, feldspar, illite, and montmorillonite. Common clay and shale basically contains illite and chlorite [12].

Bhattacharyya and Gupta [14] compared the efficiency of kaolinite and its various modified forms for the removal of Cr (VI), the sorbent were reported to be fully characterized and studies such as effect Cr (VI) concentration, amount of adsorbent, pH of the solution, sorbate-sorbent interaction time and temperatures were reported. The adsorption parameter was analyzed with both Langmuir and Freundlich adsorption isotherm. XRD analysis as reported showed expansion of basal base for acid-activated kaolinite which was accompanied decrease in intensity from 23.14 to 21.32% while the relative intensity of a low angle was reported to increase also. The specific surface area for kaolinite, acid-activated kaolinite, poly(oxozirconium) kaolinite (ZrO-kaolinite) and tetrabutylammonium kaolinite (TBA) was reported to vary from 3.8m²/g to 15.6 m²/g to 13.4 m²/g and to

14.0 m²/g respectively. Maximum adsorption was reported to occur at pH of 7, adsorption reached near equilibrium at about 240 minutes and percentage was reported to increase for all the sorbent as the sorbent dose increased. The adsorption data fitted well into both Langmuir and Freundlich adsorption isotherms. Fonseca et al [15] investigated and reported the use of natural Vermiculite for the uptake of Cr³⁺ and three other metal ion in aqueous solutions. The sorbent was characterized, various parameters investigated for the adsorption process and the adsorption data analyzed using Langmuir isotherm. The FTIR analysis was reported to reveal that functional groups present in the clay are responsible for sorption and the X-ray pattern was reported to reveal high purity and crystallinity. The principal mechanism for the metal uptake was reported to be majorly ion exchange and the quantity of exchange for Cr³⁺ was reported to be 0.48 mmol g⁻¹.

Ghorbel-Abid et al [16] investigated the efficiency of natural bentonitic clay in the uptake of Cr (III). Batch adsorption of Cr (III) was carried out at room temperature, pH range of 3 to 5, initial metal ion concentration used in the tests range between 10 and 300 mg/l, constant agitation speed of 130 rpm and the experiments were reported terminated at contact time of 16hrs. It was reported that natural clay adsorption capacity increased when the initial pH of the solution increased from 3 to 5 and also increase in initial metal ion

concentration also increases chromium uptake. The use of natural clay for the uptake of Cr⁶⁺ has also been reported by another researcher, the utilized clay was reported to have high purity. Batch adsorption studies were carried out at neutral pH, varying temperature and initial concentration of adsorbate. The mechanism of adsorption and potential rate controlling step were studied using pseudo-first order equation, pseudo-second order equation, Elovich equation and intraparticle diffusion equations. With increase in initial concentration of chromium (VI) from 20 to 100mg/L, adsorption capacity of chromium (VI) was reported to increase from 45.5 to 141.51mg/kg, with an increase of temperature from 303 to 333K, the adsorption capacity at equilibrium of chromium (VI) onto the natural clay was reported to increase from 141.51 to 361 mg/kg while contact time was reported to have no effect on adsorption capacity at high temperature [17]. Akar et al [18] reported the efficiency of natural clay, heat and acid activated clay and hexadecyltrimethylammonium bromide montmorillonite clay in the uptake of Cr (VI). Batch adsorption studies were carried out and the effects of pH, contact time, and initial metal ion concentration were reported. Adsorption data was analyzed using Langmuir, Freundlich and Dubinin-Radushkevich isotherm models. Adsorption was reported to be pH dependent and maximum adsorption was reported to occur at pH of 1.0. Adsorption equilibrium was reported established in 7 hours.

Increases in the initial metal ion concentration and contact time were also reported to increase the removal of Cr (VI) ions. Adsorption capacity of modified clay with hexadecyltrimethylammonium bromide was reported to be higher than that of acid and heat treated ones. The experimental data was reported to fit well with Langmuir and D-R isotherm models. The effect of ionic strength on the adsorption of copper and chromium using Vermiculite pure clay mineral has been reported, KCl, NaCl and NH_4Cl were the electrolyte used. Batch adsorption was carried out at room temperature, optimum adsorbent dosage (1.25 g/L), different initial concentration of Cr (III) and Cu (II) and shaking time of 24 hours. Low sorption was reported for metal ion solution with high ionic strength, since heavy metal sorption onto clay minerals in low ionic strength solution takes place onto both planar and edge sites while an increase in ionic strength brings about competition between the positive ions and the heavy metal ions. The maximum sorption capacities were reported as 46.948 mg/g and 43.668 mg/g for Cr (III) and Cu (II) respectively. Competitive adsorption studies was also carried out and it was reported that in Cu(II)-Cr(III) binary mixture the amount of Cr (III) adsorbed by vermiculite pure clay mineral increased while while Cu(II) showed a corresponding displacement from the clay surface into the surrounding solution [19].

The use of illiitic clay for the uptake of Chromium and cadmium has also been reported; the natural clay was

characterized and as well purified before use. The batch adsorption studies was carried out at room temperature, varying pH and varying agitation time and the adsorption data was reported analyzed using Langmuir and Freundlich isotherms. The purified clay was reported to have increase in adsorption of metal ions with increase in pH of the solution and equilibrium was attained at 8 hours and 20 hours respectively for cadmium and chromium ions. The adsorption capacities for the Cr (III) and Cd (II) by purified clay were reported to be 35.70 mg/g and 52.5 mg/g in the single-element systems. Significant increase was reported in the chromium uptake in the metal binary solution (94 mg/g) while for cadmium there was decrease in its uptake (23mg/g) [20]. Raw and modified montmorillonite have been characterized and the efficiency of modified montmorillonite in the uptake of Cr (VI) investigated and reported. Batch adsorption experiment was conducted at agitation speed of 150rpm, kinetic studies was also reported to have been carried out for a predetermined time (1, 2, 3, 4, 5, 10, 20, 40, 60, 90 and 120 min). The effect of temperature, initial adsorbate concentration and pH were also studied and reported. The pH of the solution and environmental temperature was reported to have significant influences on the adsorption of Cr^{6+} . The optimal pH and suitable temperature for the removal of Cr^{6+} was reported to be about 4, and 298K respectively. All adsorption processes was reported to be rapid during the first 5 min

and reached equilibrium in 20 min [21]. Brick clay fired at varying temperature (200, 400 and 600°C) have been investigated for its Chromium removal efficiency, Cr(VI) solutions of initial concentrations varying from 5ppm to 40 ppm and agitation time varying from 1 to 20 minutes were used for this investigation. Brick clay fired at 200°C was reported to show the highest removal at all stirring time periods attempted as compared to that fired at 400°C and 600°C [22]. Identification, characterization and Cr (VI) adsorption potential of two natural clays has also been reported. The clay materials were also subjected to thermal analysis by raising the temperature from room temperature to 900°C, adsorption studies was carried out by varying contact time, temperature and initial adsorbate concentration. The adsorption data were analyzed using Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherms. One of the two clay samples was identified to contain majorly smectite (Montmorillonite) while the major constituent of the other was reported to be kaolinite and illite. The FTIR analysis was reported to reveal among other groups –OH and Si–O, montmorillonite clay was reported to have a higher specific surface area, total pore volume, internal porosity, pore size and has higher purity when compared with the kaolinite. 60 minutes was established as the equilibrium time for both clay samples, Cr⁶⁺ ions removal was reported to be favoured at a slightly acid solution for both clays and the Cr(VI) ions

capacities was reported to decrease as temperature increases while the metal retention reaches its maximum at 20°C for both clay samples. The adsorption data fitted well into Langmuir model [23]. Natural and acid-activated sepiolite samples functionalized with (3-Mercaptopropyl) trimethoxysilane have been characterized and investigated for chromium adsorption efficiency. The Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherms were used to describe the sorption of Cr (VI) species from solution onto the surface of the functionalized sepiolites. It was reported that XRD analysis show no distinct difference between the raw and the modified sepiolite whereas FTIR result shows that the organic matter in the sepiolite decreased after the acidic treatment. At varying pH of the solution, it was reported that the adsorption of Cr (VI) was very negligible, the adsorption of Cr (VI) by modified natural and acid activated sepiolites were reported to increase with increasing pH of the solution. Higher adsorption capacity (8.03mg/g) was reported for modified acid activated sepiolite at pH 3 compared with the other pH range used for its adsorption. The modified acid activated sepiolite was reported to adsorb higher than the modified raw sepiolite. The adsorption data was reported to be well explained using the Dubinin–Radushkevich model [24]. Raw clays subjected to purification have also been investigated for the removal of Chromium (III) ion and two other metal ions. The two raw clays have been earlier characterized

and reported to have the following major composition kaolinite, illitic, orthose and quartz, feeble quantities of albite and montmorillonite. The removal of Cr (III) by sorption to clay surfaces at pH-7 was reported to be more effective than the other two metal ions and adsorption rate was reported to increase with increase in pH [25]. Natural red clay modified with hexadecyltrimethylammonium bromide (HDTMA) has been investigated for its potential in the uptake of Cr (VI) and phenol. The raw and modified clay samples were reported fully characterized. The following conditions was reported for adsorption studies; initial concentration of phenol and Cr (VI) $c_{in} = 0.0005 \text{ mol/dm}^3$, volume of the aqueous phase = 100 ml and mass of the solid phase = 0.4 g. Six hours was selected as agitation time. The FTIR analysis of the modified clay revealed the bending vibration of water and the presence of -OH functional group, The optimal pH range for maximum Cr (VI) adsorption was reported to be between 4–6.5 and increase in pH resulted into decrease in Cr(VI) adsorption. Percentage adsorption of Cr (VI) was reported to decrease with increasing concentration of chromium in the initial solution and slight decrease in adsorption of the studied pollutants was observed at increased temperature [26]. Rashmi et al [27] reported the comparison of the adsorption capacities of intercalated clay compounds of montmorillonite (ZrO-B) and bentonite (ZrO-M), the prepared sorbents were fully characterized using the scanning electron

microscope (SEM) and fourier transform infra red (FTIR). It was reported that adsorption was carried out at room temperature but the effect of pH, adsorbent dose and adsorbate concentrations were studied. FTIR reveals the presence of O-H functional group and SEM shows that modified clays are microporous. The optimum pH was reported to be pH 6 and this pH, chromium adsorption was reported to be 83.7% and 87.1% for ZrO-B and ZrO-M respectively. At optimum pH (pH 6), 0.4g/l adsorbent dose recorded the maximum adsorption which was reported to be 99.8 % for ZrO-M and 99.9 % for ZrO-B. Percentage Chromium uptake for both sorbent over the concentration range considered was reported to be between 70-99 %. Dodecylamine modified sodium montmorillonite has been prepared and investigated for its effectiveness in the removal of Cr^{6+} . The prepared material was characterized using FTIR, SEM and XRD and nitrogen adsorption. The prepared material was applied to both synthetic and real effluents; batch and column experiment studies were carried out. It was reported that the FTIR revealed the peak corresponding to the O-H group among others, the surface area of the prepared material was reported to be $23.18 \text{ m}^2/\text{g}$ for a pore of radius 9.0nm. For batch adsorption studies, the highest percentage adsorption which was reported to be greater than 98% was obtained at 0.5g adsorbent dose, pH point of zero charge was reported to be 3.62 and hence adsorption of Cr (VI) was best at low pH. For column experiment, adsorption of

Chromium was reported to be up to about 99% for sample volume up to 300ml, above the said sample volume, adsorption of chromium was reported to reduce. Adsorbent regeneration was done using 1.0 mol L⁻¹ NaOH as the eluent and the performance of the adsorbent was reported to be very good with elution efficiency of greater than 90% for 4 adsorption-desorption cycles and beyond four cycles, the removal efficiency was reported to decrease gradually by about 10%. The Langmuir adsorption capacity was reported to be 23.69 mg/g [28].

Some adsorbents in the silica family have also been investigated for their efficiency in the removal of this problematic toxicant chromium. Diatomite modified by microemulsion (DMM) and manganese oxide (MnO) has been investigated and reported to have chromium ion (III) adsorption capacity from aqueous solution. The prepared materials were characterized, adsorption studies were carried out at varied concentration and pH and the adsorption data was analyzed using the Langmuir adsorption isotherm. The FTIR analysis of the raw and the modified diatomite was reported to show variation as some bands disappeared after modification. Bands revealed after modification was reported to reveal groups like O-H and Mn-O among others. The adsorption of chromium ion was reported to increase over the pH range used for the experiment (pH = 2.2-6.3), the chromium ion (III) removal of DMM varies from 35% to 70% and that of MnD varies from 33% to 59% with maximum

adsorption recorded at pH 4. Chromium ion removal was reported to increase with increase in initial metal ion concentration and solution volume. As solution volume increases from 0 to 2500 mL, both their removals was reported to improve from lower than 10% to higher than 90%. Optimal equilibrium time for maximum removal was established to be 36 h for MnD and 24 h for DMM (Li et al, 2009). Khamis et al [29] reported the use of various types of sand (White, yellow and red sands from the United Arab Emirates) for the uptake of Cr (III) and Cr (VI). It was reported that the soil samples was distributed into different particle sizes, treated with dilute nitric acid for the removal of carbonate and the metal ion content of the sand investigated. Adsorption study was carried on using varying pH and adsorbent dose and the adsorption data was analyzed using the Langmuir and Freundlich adsorption isotherms. The red sand was reported to compose majorly of particles size $\geq 300\mu\text{m}$, yellow sand particles are predominantly in the range 150–300 μm while white sand was reported to have a significant proportion of large, medium and small size fractions. Red and yellow sand was reported to be richer in Al, Fe, K, Mg and Ni while white contain more Ca and Na. It was reported that the minimum sand dosage required for complete removal of Cr (III) is 20, 40 and 100 g/l for white, yellow and red sand, respectively. The adsorbents were established to be unsuitable for the removal of Cr (VI). The rate of Cr (III) removal was reported to increase with increase in

pH while pH less than 6.0 was prescribed. The equilibrium adsorption data was reported to fit well into the Langmuir isotherm.

Yadav et al [30] investigated and reported the use of modified sand for the removal of Cr (VI) ion from aqueous solution. The modified sand was characterized using SEM, FTIR and EDX. Adsorption studies were carried with varying temperature, pH, adsorbent dose, contact time and initial concentration. It was reported that the EDX analysis revealed that the major constituent of the adsorbent is silica (as Silicon Oxide, SiO_2), SEM revealed increase in surface area while the FTIR analysis further confirms the presence of SiO_2 in the adsorbent peaks corresponding to Si-O bond was detected. It was reported that Cr removal decreased from 80.40% to 62.42% with the increase in temperature from 25 to 35 °C for the initial concentration of 5 mg L⁻¹, increasing the initial concentration resulted decrease in Cr (VI) percentage adsorption from 80.40 to 67.24%, Cr(VI) removal was reported to increase proportionally with the amount of the modified sand dose until a constant was reached and as the pH of the solution increases the percentage adsorption decreases.

Synthetic materials

In the quest for highly efficient adsorbent, various materials have been synthesized and others coated with synthetic materials for their investigation in the removal of problematic toxicants from waste waters.

Guo et al [31] reported the use of zerovalent zinc assisted with silica gel for total removal of Cr (VI). The specific surface area of Zn and silica gel was determined using BET and adsorption studies was reported with respect to varying pH and adsorbent dose at room temperature. It was reported that, with silica gel (pH = 6), less than 5% removal of Cr (VI) ion was obtained while percentage removal rose to 64% with zerovalent Zn. When zerovalent Zn was used along with silica gel, both the rate of adsorption and the percentage adsorption increased. It was reported that the percentage adsorption depends on the particle size of silica gel. It was also reported that the reduction of Cr (VI) with zerovalent Zn alone decreased with increasing pH while in presence of silica gel the reduction of Cr (VI) was improved even in alkaline condition. Great acceleration of Cr (VI) reduction was reported for various increases in the silica gel and zerovalent Zn.

Ballav et al (2012) prepared, characterized and studied the sorption efficiency of Glycine doped polypyrrole-glycol(PPy-gly) adsorbent, the adsorbent was prepared via insitu polymerization. It was reported that FTIR revealed bending vibration of C=O and the stretching and asymmetric stretching of NH_3 group among others, Field emission scanning microscopic (FE-SEM) and the SEM images revealed agglomerated spherical particles with sizes in the range between 153-538 nm and between 150–250 nm respectively. Cr (VI) ion removal efficiency by PPy-gly was reported to decrease with

increase in solution pH from 99.87% at pH 2 to 16% at pH 11.0, in the case of adsorbent dose, removal efficiency was reported to change from 50% at a dose of 0.025 g to 99.87% at a dose of 0.100 g and remains unchanged after dose 0.100 g. Adsorption isotherm data was reported to fit better into Langmuir isotherm than the Freundlich isotherm. Adsorption-desorption experiment was carried out for five consecutive cycles and it was reported that the removal efficiencies remain unchanged for the first three cycle (above 99%) and subsequently dropped to 85% and 58% respectively.

Polypyrrole-polyaniline (PPy-PANI) nanofibers as adsorbent of Cr (VI) has also been prepared and characterized. The various bands as shown by the ATR-FTIR spectrum confirm the presence of both PPy and PANI polymeric moieties in the synthesized nanofibers. It was reported that the FE-SEM analysis revealed the presence of nearly spherical particles of PPy homopolymer with tendency to form randomly distributed aggregates. For the adsorption studies, the removal efficiency of the prepared sorbent was reported to decrease with increasing pH of the solution with 99.83% removal observed at pH 2.0, percentage adsorption efficiency was reported to increase from 57.3% to 99.8% with an increase in adsorbent dose from 10 mg to 50 mg. The equilibrium data was reported to fit well into Langmuir and Freundlich isotherm models. It was reported that co-existing cation had no effect on the removal of Cr (VI) and hence the prepared

adsorbent is selective in nature. It was reported that the regeneration of the adsorbent and the desorption of Cr (III) was carried out using NaOH and HCl respectively. In four adsorption-desorption cycle the adsorption capacity of regenerated sorbent of the first two cycle remain almost unchanged and in the subsequent third (93.43 mg/g) while for the fourth cycle great decrease was reported (25.37 mg/g) [32].

The preparation, characterization and Chromium ion uptake of Thiocarbamoyl chitosan (TC-Chitosan) has been investigated and reported. Characterization of the prepared materials was done using SEM, EDAX, BET and FTIR, Cr (VI) adsorption studies in real and synthetic effluents were reported using varying pH. FTIR analyses was reported to reveal bands corresponding to amine, hydroxyl and amide among others, as pH of the solution increases 1 to 2, the amount adsorbed also increases from 72.5% to 89.2% and further increase in pH was reported to result in decreased adsorption. It was reported that the isotherm analysis of adsorption data fitted well into the Langmuir isotherm with adsorption capacity for Cr (VI) been $(434.8 \pm 2.6 \text{ mg/g})$ [33].

The removal of Chromium ion using epoxy functionalized poly (ether-sulfone) (PES) has also been reported. The prepared membranes were characterized by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), pure water flux, water content, porosity and

contact angle technique. Proton Nuclear magnetic resonance ($^1\text{H NMR}$) analysis revealed electrophilic substitution on the end phenyl group while FTIR revealed $-\text{OH}$ and $\text{C}=\text{O}$ groups among others. It was also reported that the SEM analyses of both cellulose acetate (CA) and the functionalized acetate (EPES) revealed more open pores for the functionalized acetate. As reported, AFM revealed large 'nodules' for pure CA and as the concentration of EPES increased the "nodules" decreased to significant extent at 80/20 blend composition. It was also reported that increase in the concentration of EPES in the blend system resulted in enhanced chromium ion rejection [34].

Kumar et al [35] investigated and reported the efficiency of tetraoctylammonium bromide impregnated with chitosan in the adsorption for chromium (VI). Column experiment was reported, the adsorption data was analyzed using Langmuir, Freundlich, Redlich–Peterson (R–P), Dubinin–Radushkevich, Elovich isotherm, Temkin isotherm. It was reported that FT-IR spectral analysis showed distinct characteristic bands corresponding to O–H and N–H stretching vibrations at 3450 cm^{-1} and 3358 cm^{-1} respectively while SEM analyses revealed that the adsorbent material is porous with a dense and homogenous surface. The optimum pH for the quantitative adsorption of chromium was reported to be between 3–4 and adsorbent dose between 0.2–0.3 g in 25 mL sample volume gave percentage adsorption of $99.0\pm$

0.35%. The column experiment was reported to be very efficient with removal upto $98.7\pm 0.2\%$ till a sample volume of 700 mL.

Biomaterials

Biosorption involves the use of biomaterials in the selective sequestering of metal soluble species. Metal sequestering by different parts of the cell can occur via various processes such as complexation, precipitation, coordination, chelation, ion exchange or reduction. Sometimes sorption of metal may be the result of more than one mechanism, for example, metal complexation may be followed by metal reduction or metal precipitation. The removal of toxic hexavalent chromium from aqueous solution by biosorption has been reported and it is often associated with the simultaneous reduction of Cr(VI) to Cr(III) [5,7,36].

Activated Carbon prepared from biomaterials

Activated carbon is known to have high porosity as well as high surface area hence very effective in the removal of a wide range of pollutants including heavy metals. The commercial activated carbon because of their precursor (coal or petroleum pitch) are not economically friendly as well as non renewable and therefore alternative sources such as wood, coconut shells and various other lignocellulosic materials are been utilized by researchers. Activated carbons can be prepared either by physical or chemical methods. The physical method of production follows the order, production of

charcoals by pyrolysis followed by activation by gasification using carbondioxide, water vapour or air or a combination of any of the above. Chemical activation employs dehydrating agents such as strong acid which acts as activating agent, other methods employ pyrolysis followed by chemical activation. Activation usually creates more pore size in the carbonaceous materials to increase its absorptivity [37-39]. Activated carbons prepared from low cost adsorbent have also been composite with species (iron oxide, aluminium oxide e.t.c) that can increase their sorption efficiency [40].

Industrial wastes

Various industrial wastes and by products of industrial processes have also found use in the removal of this problematic toxicant. The various industrial waste have been found to contain functional groups suitable for complexing metal ions and others modified to introduce site suitable for uptake of metal ions.

Inoue et al [41] reported the use of persimmon waste in the uptake of Cr (VI) among other metal ions. Persimmon waste contains polyphenol and polysaccharide hydroxyl groups which was crosslinked using concentrated sulphuric acid. Batch adsorption studies were reported as a function of pH, contact time and adsorbent dose. High adsorption was reported for Cr (VI) at pH less than 3 and beyond this pH, adsorption of Cr (VI) decreased. The adsorption capacity was reported to be 7.18 mol/Kg. Column studies were reported for

the separation of Cr (VI) from Zn (II) and mutual separation between the two ions was reported. The uptake of chromium (VI) ion using carbonaceous product obtained from fertilizer waste (carbon slurry) has also been reported. Column adsorption studies and regeneration of spent carbonaceous material were also reported. It was reported that carbon slurry was organic in nature, Cr (VI) removal was favoured in the acidic media with maximum adsorption (15.24mg/g) occurring at pH 2. Adsorption was also reported to increase with decrease in particle size and desorption studies was investigated using deionized water, ammonium hydroxide, sodium chloride, hydrochloric acid, and nitric acid, and it was reported that the desorption of the metal ion occurred by 1% HNO₃ [42]. Anandkumar and Mandal [43] reported the use of cashew husk based tannery residual biomass in the uptake of Cr (VI). The waste was pyrolysed and chemically activated with HCl using different ratio of adsorbent to HCl. Batch adsorption studies were reported varying pH, temperature and adsorbate concentration. Sorption capacity was reported to increase with increased ratio of acid, maximum uptake of Chromium ion was reported to occur at pH 2. The effect of other cations reportedly reduced the percentage removal of Cr (VI) ion. Maximum adsorption capacity of this activated industrial waste was reported to be 217.39mg/g. By product of bear modified with acid has also been investigated for the uptake of Cr (VI) ion and the surface of the sorbent were characterized.

Batch adsorption studies were carried out as a function of pH and initial concentration. Regeneration studies were also carried out. FTIR analysis revealed hydroxyl and carbonyl group among others and uptake of Cr (VI) decreases with increasing pH. 2mol L⁻¹ HCl was used as regenerating agent. Panda et al [44] reported the use of dolochar waste from iron sponge industry for the uptake of Cd (II) and Cr (VI). Proximate, ultimate and chemical composition of the sorbent was reported, batch adsorption studies was also reported as a function variables agitation time, metal ion concentration, pH, adsorbent dosages, temperature and the desorption studies also reported. Chemical composition of dolochar ash as reported revealed that SiO₂ is its major constituent. It was reported that adsorption decreased as particle size increases, percentage removal of Cr (VI) increased with increased adsorbent dose and the optimum pH for the uptake of Cr (VI) was reported to be 6.6. Adsorption was reported to increase with increased temperature and the maximum adsorption capacity for Cr (VI) was reported to be 2.1mg/g. Desorbing agents used are water, 0.1 and 0.2 M NaOH and water was reported to achieve very insignificant desorption.

Nanomaterials

The properties of materials can be greatly enhanced by reducing their size hence the property of nanomaterials is greatly dependent on its size. Materials in the nano scale (1–100 nm range) often exhibit high adsorption characteristics due

to larger surface area. Nanomaterials vary from zero-dimensional nanocrystals to one-dimensional nanowires, nanotubes to two-dimensional, nanofilms and nanowalls [45,46]. A composite of magnetic nanoparticles with others such as agricultural waste, clays, etc which serves as base materials have also found great use in environmental remediation. Magnetic nanoparticles combine its large surface area with its magnetic characteristics in the uptake of metals [47-49]. The adsorption capacity of various nanomaterials/nanocomposites varies basically based on their efficiency coupled with variable conditions used by different researchers. Figure-1 depicts the maximum adsorption capacity as reported by different researchers.

Concern for further research

Recovery of pollutants from the regenerant solution calls for concern as this will still be released into the environment. Batch experiment has been well reported, only few reported column experiment. Column experiment finds more applications industrially. The waste water that is released by these industries comes with a host of other pollutants including salts, dyes and other metals. Therefore for effective industrial applications of sorbent, sorption of a particular pollutant should be carried out in the presence of other species. Studies utilizing binary or ternary solution, investigations on the effect of ionic strength, metal sorption in the presence of organic compound such as dye should be more

reported. Many researcher utilized synthetic effluent hence the use of real industrial effluent will expose the efficiency of sorbents.

Conclusion

Chromium exists in two oxidation states in the environment i.e Cr³⁺ and Cr⁶⁺ with the later being highly soluble in water and more toxic and hence the focus of researchers is on the removal of Cr⁶⁺ [50]. Cr⁶⁺ may exist in solution as HCrO₄⁻, H₂CrO₄, Cr₂O₇²⁻ or CrO₄²⁻ with the stability of each being majorly pH dependent. Although the uptake of metal ion from solution depends on the surface area of the sorbent but more importantly is the pH of the aqueous solution, net surface charge of the sorbent and other factors. The surface of the sorbent can bare a

net negative, positive or no charge. The pH at which the net total charge is zero is called the pH point of zero charge (PZC). The surface of the sorbent usually has a net negative charge at pH above the PZC and a net positive charge at pH below the PZC. Although the aspect of the PZC was not reported by many of the researchers reviewed, but many reported maximum Cr VI removal in the strongly acidic (≤ 3). In low pH solution, the surface of the sorbent is highly protonated and hence high binding of anionic chromium to the sorbent occurs [50]. One widely used method for the removal of Cr (VI) is chemical reduction of Cr (VI) to Cr (III) followed by precipitation [31]. The reduction of chromium (VI) using biomaterial can said to proceed as follows;



Sorbents such as zerovalent metals proceeds as follows;



Functional group(s) introduced unto the surface of a particular sorbent can also be responsible for the Cr (VI) reduction.



The binding of anionic chromium and the reduction of Cr (VI) to Cr (III) is highly favoured at low pH [53] and hence most researchers have reported optimum adsorption capacity at low pH. Although sorption provides simplicity and economic advantages, the success of sorption is in the ability to regenerate the sorbent.

Regeneration of the sorbent used should be considered an important aspect of sorption studies as it usually determines the reusability of a particular biomass and aids environmental protection [54-56]. Pollutants are either loosely physically bonded to the face of the sorbent or chemically bonded or combination of both and hence the

mechanism of pollutant uptake by biomass determines the desorbing agent. Loosely bonded ion can be easily recovered using distilled water while chemically bonded ions or ions sorbed via ion exchange will require a stronger desorbing agent such as acid or alkali. Desorption in an acidic media can be described by an ion exchange mechanism as heavy metals are known to be soluble at low pH [56], since the medium is highly protonated, H^+ replaces the chromium ion on the surface of the sorbent. The desorption of Cr^{6+} have greatly been reported in basic media (high pH), as a result of strong electrostatic repulsion between the negatively charged surface and the negatively charged chromium ions. Hydroxyl

ion has also been reported to release chromium ions by ion exchange mechanism at high pH and hence the suitability of NaOH and other alkali for Cr^{6+} desorption [57, 58]. Complexing agent such as EDTA can also be used for desorption, it selectively remove the metal ions from the surface of the sorbent by forming a complex with the metal.

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Table 1: Modified and unmodified biomaterials used in the uptake of Chromium ion: pH, regeneration studies and other parameters.

Biomaterials	Chemical treatment/Modification	Type of study	Optimum pH	Maximum uptake / percentage removal	Regeneration studies	References
Pine needle	Nil	Batch adsorption studies using synthetic effluent	2.0	371.1mg/g	Nil	Park <i>et al</i> , 2008
Sun flower	Boiling and Formaldehyde	Batch adsorption using synthetic effluent	2.0	4.9 mg/g for boiled and 3.6 mg/g for formaldehyde activated	Nil	Jain <i>et al</i> , 2009
Ocimum americanum L. seed pods	Nil	Batch adsorption studies using synthetic effluent	1.0- 1.5	83.33 mg/g	Nil	Levankumar <i>et al</i> , 2009
Boiled mucilaginous seeds of <i>Ocimum americanum</i>	Nil	Batch and column studies using synthetic effluents	1.5	32mg/g	Nil	Lakshmanraj <i>et al</i> , 2009
Bael fruit shell	H ₃ PO ₄	Batch adsorption studies using synthetic effluent	2.0	17.27 mg/g	Nil	Anandkumar and Mandal, 2009
Aligator weed	Nil	Batch	1.0	123.45mg/g	0.2 mol/L	Wang <i>et al</i> , 2009

		adsorption using synthetic effluent			NaOH used as desorbing agent	
Saw dust	Nil	Batch adsorption using synthetic effluent	1.0	45.5 mg/g	1 N NaOH and 1 N HCl used as desorbing agents	Gupta and Babu, 2009
Wall nut hulls	Nil	Batch adsorption using synthetic effluent	1.0	97.3%	Nil	Wang <i>et al</i> , 2009
Saw dust	Nil	Continuous fixed bed column experiment using synthetic effluents	1.0	74.5%	Nil	Gupta and Babu, 2009
Rubber wood saw dust	Nil	Batch adsorption using synthetic effluent	< 2.0	100%	1 M HCl used as desorbing agent	Zakari <i>et al</i> , 2009
<i>Posidonia oceanica</i> fibres	Nil	Batch adsorption using synthetic effluent	2.0	1.64 mg/g	Nil	Ncibi <i>et al</i> , 2009
<i>Coriolus versicolor</i>	Thermal inactivation	Batch adsorption using synthetic effluent	2.0	62.89mg/g	Nil	Sanghia <i>et al</i> , 2009

<i>Oedogonium hatei</i>	Raw and acid treated	Batch adsorption using synthetic effluent	2.0	31mg/g for raw and 35.2mg/g acid treated	0.1M NaOH used as desorbing agent	Gupta and Rastogi, 2009
Lechuguilla plants	Nil	Column adsorption using synthetic effluent	4.0	95mg /g	Nil	Romero-González, 2009
Boiled sunflower head waste	Nil	Batch adsorption using synthetic effluent	2.0	7.9 mg/g	Nil	Jain <i>et al</i> , 2009
seaweed, <i>Hydrilla verticillata</i>	Nil		1.8	247 mg/g	Nil	Baral <i>et al</i> , 2009
Wheat residue	Diethylenetriamine	Batch adsorption using synthetic effluent	1.6	322.58 mg/g	Nil	Chen <i>et al</i> , 2010
Bracken fern	Nil	Batch and column adsorption studies using synthetic effluent	4.0	1.60mmol/g	Nil	Lopez-Garcia <i>et al</i> , 2010
Dried leaves of <i>Pinus densiflora</i>	Nil	Batch adsorption using synthetic effluent	4.0	> 95%	Nil	Park <i>et al</i> , 2011
Egg shell membrane	Layered double hydroxides and composite with	Batch adsorption studies using	> 3.0	27.9 mg/g > 90%	Nil	Guo <i>et al</i> , 2011

	MgAl-CO ₃ ²⁻	synthetic effluent				
Wheat straw	Cross linking of amine group	Batch and column adsorption using synthetic effluent	< 6.0	5.68 mmol/g	Distilled water and HCl used as desorbing agents	Xu <i>et al</i> , 2011
Spent mushroom (Tricholoma lobayense)	Dodecyl dimethyl benzyl ammonium bromide	Batch adsorption using synthetic effluent	3.39	43.86 mg/g	NaNO ₃ used as desorbing agent	Jing <i>et al</i> , 2011
Gracilaria verrucosa	Acids, alkalis and organics	Batch adsorption using synthetic effluent	-	113 mg/g	0.1 M HCl, HNO ₃ and NaOH, 0.2 M CaCl ₂ , 0.01 and 0.1 N EDTA used as desorbing agents	Ata <i>et al</i> , 2012
Wall nut shell	Citric acid	Batch adsorption studies using synthetic effluent	2.0	0.596 mmol/g	0.5M HCl used as desorbing agent	Altun and Pehlivan, 2012
Osage orange peel and pulp	Nil	Batch adsorption using synthetic effluent	2.0	78% for peel and 88% for pulp	Nil	Pehlivan <i>et al</i> , 2012
Corn stalk	Modified with organic	Column experiment	-	93.41 mg/g	Nil	Chen <i>et al</i> , 2012

	compounds	using synthetic effluent				
Palm shell powder	Treated with acid and steam and modified with formaldehyde	Batch and column experiment using synthetic effluent	~1.0	313 mg/g	0.1 M EDTA, 0.1 M NH ₃ and 0.1 M HCl used as desorbing agents	Kushwaha <i>et al</i> , 2012
Tea waste	Cellulose treated	Batch adsorption using synthetic effluent	1.5	47,67 mg/g	Nil	Ng <i>et al</i> , 2013

Figure-1: Comparing the maximum adsorption capacities of different nanomaterials and nanocomposite.

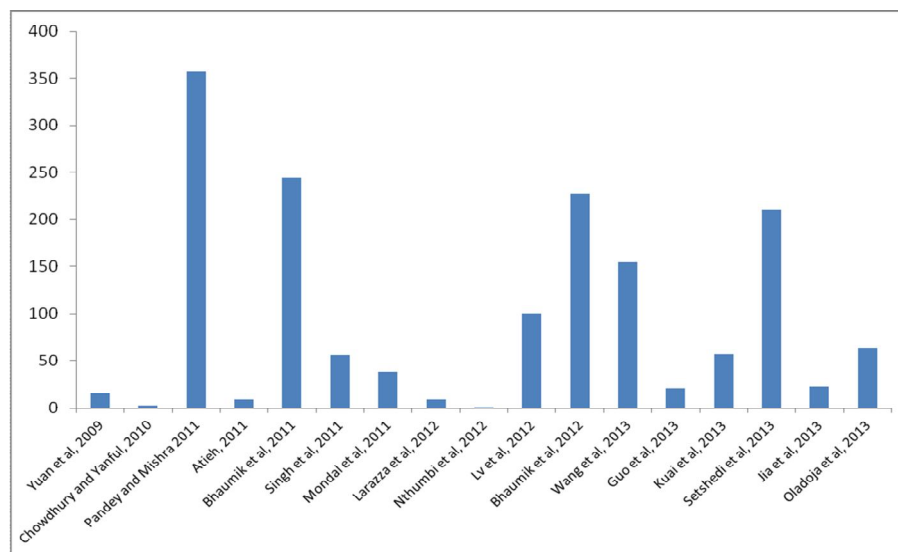


Table 2: Activated carbon prepared from various biomaterials used in the uptake of Chromium ion: pH, regeneration studies and other parameters

Base material	Method of activated carbon production	Type of study	Optimum pH	Maximum uptake / percentage removal	Regeneration studies	Reference
Rice husk	H ₂ SO ₄ at 150°C	Batch adsorption using synthetic effluent	2.0	48.31mg/g	Various concentration (ranging from 0.0125 to 0.150M) of KI and HCl	Bansal <i>et al</i> , 2009
Tamarind wood	ZnCl ₂	Batch adsorption using synthetic effluent	1.0	28.019 mg/g	Nil	Acharya <i>et al</i> , 2009
Tamarind seed	H ₂ SO ₄	Batch adsorption using synthetic effluent	1.0	29.7mg/g	Desorption studies carried out by increasing the solution pH	Gupta and Babu 2009
<i>Chrysophyllum albidum</i> (Sapotaceae) seed shells	Pyrolysis followed by H ₂ SO ₄ activation and Chitosan modification	Batch adsorption using synthetic effluent	4.5-5.0	59.63mg/g for acid activated and 76.23mg/g for chitosan modified carbon	Nil	Amuda <i>et al</i> , 2009
Pomegranate husk	H ₂ SO ₄	Batch adsorption	1.0	35.21mg/g	0.1N NaOH used as	Nemr, 2009

		using synthetic effluent			desorbing agent	
Leather shaving Wastes	Pyrolysis followed CO ₂ activation and impregnation with H ₃ PO ₄ and ZnCl ₂ followed by heat treatment	Batch adsorption using synthetic effluent	2.0	126.6, 138.9 and 133.3 for physically activated carbon , ZnCl ₂ and H ₃ PO ₄ activated respectively	Nil	Kantarli and Yanik, 2010
Peach stone	Pyrolysis followed by N ₂ /steam activation	Batch adsorption using synthetic effluent	2.0	143mg/g	Nil	Duranoğlu <i>et al</i> , 2010
Trapa natans husk	Impregnated with H ₃ PO ₄ followed by pyrolysis and further modified with Fe	Batch adsorption using synthetic effluent	2.0-3.0	11.83 mg/g	Distilled water and 0.1–2.0 mol/L NaOH used as desorbing agent	Liu <i>et al</i> , 2010
Algae bloom residue	H ₃ PO ₄	Batch adsorption using synthetic effluent	1.0	155.52mg/g	Nil	Zhang <i>et al</i> , 2010

Bamboo	$\text{Fe}_2(\text{SO}_4)_3$ and H_2SO_4 impregnation followed by microwave heating	Batch and column studies using synthetic effluent	2.0	91%	Nil	Wang <i>et al</i> , 2011
oak wood and oak bark	Pyrolysis	Batch adsorption using synthetic effluent and contaminated surface and ground water	2.0	4.93 mg/g and 7.51 mg/g for oak wood and oak bark respectively	Nil	Mohan <i>et al</i> , 2011
Sugar cane bagasse	ZnCl_2	Batch adsorption studies using synthetic effluent	8.58	87%	Nil	Cronje <i>et al</i> , 2011
Apricot stone	Impregnated with H_3PO_4 followed by pyrolysis	Batch adsorption using synthetic effluent	2.0	262mg/g	Nil	Özdemir <i>et al</i> , 2011
Pterocladia capillacea	H_2SO_4	Batch adsorption using synthetic effluent and simulated sea water	1.0	66.67mg/g	Nil	Nemr <i>et al</i> , 2011

<i>Syzygium jambolanu</i> m nut	Impregnated with H ₂ SO ₄ followed by thermal activation in CO ₂	Batch adsorption studies using synthetic effluent	2.0	100mg/g	10 % H ₂ O ₂ with 1 M NaOH was used as desorbing agent	Muthukumara n and Beulah, 2011
Peanut shell	Impregnated with KOH and followed by carbonization	Batch adsorption studies using synthetic effluent	2.0	8.31mg/g	Nil	Al-Othman <i>et al</i> , 2012
Prawn shell	Impregnation with H ₂ SO ₄ followed by thermal treatment	Batch adsorption using synthetic effluent	-	99%	1% HCl, H ₂ SO ₄ and NaOH used as desorbing agent as HCl/H ₂ SO ₄ /NaOH	Arulkumar <i>et al</i> , 2012
Corn cob	Pyrolysis followed by CO ₂ activation	Batch adsorption using synthetic effluent	5.0	84.64 mg/g	Nil	Fonsecca <i>et al</i> , 2013
peanut shell, lapsi seeds and energy grass	H ₂ SO ₄ /HNO ₃	Batch adsorption using synthetic effluent	1.0	226.4, 204.8 and 230.5 mg/g for peanut , lapsi seed and energy grass charcoal respectively	Distilled water at pH 1.1	Varga <i>et al</i> , 2013

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