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A REVIEW: REMOVAL OF HEXAVALENT IONS FROM THE INDUSTRIAL WASTEWATER BY ACTIVATED CARBON AND NANO MATERIAL ADSORBENTS.

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ABSTRACT
Industrial wastewater often contains chromium which has raised concerns towards hexavalent chromium as it is carcinogenic to animals as well as it can also cause genetic material alterations, kidney and liver damage, etc. Hence, there are many remedial methods which have been researched for removal of Cr(VI). Out of all the methods, this article talks more about activated carbon and nano material adsorbentsused for the removal of hexavalent chromium. The capacity of various adsorbents areinvestigated for the removal of Cr(VI). The Langmuir and Freundlich adsorption models, which are in common use for describing sorption equilibrium for wastewater-treatment applications, are discussed. Apart from this, the adsorption dosage and capacity of disparate adsorbents are discussed with their kinetic and thermodynamicstudy. This review also includes the equilibrium time at which the maximum adsorption is achieved and optimum pH values for the maximum adsorption.

Keywords: *Hexavalent chromium, wastewater, activated carbon, Nano materialkinetics, thermodynamics, pH.*

INTRODUCTION
Agile industrialization with uncontrolled anthropogenic fluxes related to mining, refining, plating,ammunition, storage cells, metal smelting, and finishing, engine exhausts, industrial emissions andeffluents, heavy metal enrichment of agricultural products, etc. has lead heavy metal break in andpollute the environment [1].A heavy metal is a metallic element which is toxic and has a high density,specific gravity or atomic weight. Heavy metals are largely used by modern industries, including textile, leather, tanning, electroplating and metal finishing [2]. Heavy metals like Cr, Cd, Ni, Pb, Hg,etc...have fatal effects on human physiology and other biological systems [3]. But out of all the heavy metals, Chromium is in limelight because some people are extremely sensitive to Cr (III) orCr (VI). Skin ulcers can happen when skin contact with certain Cr (VI) compounds. Allergenic reactions consisting of severe redness and swelling of the skin have been noted. Several studies have shown that Cr (VI) compounds can increase the risk of lung cancer. The World Health Organization (WHO) has categorized Cr (VI) as a human carcinogen [4].Chromium compounds areextensively used in electroplating, leather industry, anodizing operations, paint and pigments, textile, dyeing, steel fabrication etc.[5]. In aqueous solution, chromium usually exists in trivalent and hexavalent form. But hexavalent Cr is much more like hundred times toxic than trivalent Cr. It is known to be fatal and carcinogenic to living organisms [6]. It is known as strong oxidant. Because of its high toxicity, its discharge levels must be significantly reduced [2]. The maximum permissible limit of hexavalent chromium in drinking water is 0.1mg/l or 100 ppb [7]. The monthlyaverage Cr (VI) maximum value is 0.077 mg/L for industrial wastewater discharges [8].
For the removal of hexavalent Cr from wastewater, various techniques are used such as: chemicalprecipitation, oxidation/reduction, filtration, ion exchangers, membrane separation and adsorption.But among these techniques, ion exchangers and membrane separation are relatively very costly, while chemical precipitation produces great amount of mud. On the other hand, adsorption has advantages such as variety of adsorbent materials and high efficiency at a relatively lower cost. Therefore, adsorption is the most frequently applied

technique[9]. As we have seen that adsorption is better than other techniques for the removal of Cr (VI) from the wastewater, adsorption with activated carbon is widely used amongst other adsorbent as it has benefits such as fast adsorptionrate and effective adsorption of Cr (VI). Beyond this carbon, charcoal, lignin etc. also showed effective adsorption of Cr from wastewater. Comparing to activated carbon high eviction efficiency of nano materials and composites and nano-composites used has higher efficacy as an adsorbents for removal of Cr (VI) [10].

Remediation by using Activated carbon and Nano material for removal of hexavalent Chromium

ACTIVATED CARBON

Several activated carbons, in powder and granular form, prepared from different raw materials andobtained by different activation procedures, were used to remove Cr(VI) from solution[11]. The useof activated carbon for removal of the toxic metal ionic pollutants present in low concentration inaqueous solutions of considerable importance due to their well-developed porous structure comprised of hydrophobic grapheme layers and hydrophilic surface functional groups [12]. KOH- activated carbon showed the maximum adsorption capacity of 315mg/g for Cr (VI) at the optimumpH 3.0 which followed Langmuir isotherm and pseudo second order [13]. Activated carbon prepared from impregnated palm shell with polyethyleneimine showed the adsorption capacity 228.2mg/g at 2-5 pH with adsorbent dosage of 200mg/l [14].A good adsorption capacity 190.3mg/g was exposedby activated carbon prepared from almond shell with sulfuric acid activation [15]. Hazelnut shell activated carbon showed the adsorption capacity of 170mg/g at pH1.0 and followed Langmuir isotherm and pseudo first order with adsorbent dosage of 0.25g/100ml and 72hrs of contact time [16]. Activated carbo-aluminosilicate material from oil shale had the adsorption capacity of 92mg/gat pH 4-8. It followed the Langmuir isotherm and was exothermic in nature[17]. Tytlak in 2014 studied the potential of two biochars produced by the thermal decomposition of wheat straw (BCS)and wicker (BCW) for Cr(VI) ions removing from wastewater was investigated. The Freundlich and Langmuir models were applied for the characterization of adsorption isotherms. The Langmuirmodel has better fitting of adsorption isotherms than the Freundlich model. The sorption process can be described by the pseudo second-order equation. The optimal adsorption capacities were obtained at pH 2 and were 24.6 and 23.6 mg/g for BCS and BCW, respectively [18]. Rubber wood sawdust activated carbon prepared by Karthikeyan showed the adsorption 42.5mg/g at pH 2.0 with200mg/l dosage, ensued Langmuir isotherm and taken 300 min for optimum adsorption [19]. Woodapple shell activated carbon which is an agricultural activated carbon displayed relatively low adsorption capacity of 13.74mg/g at pH 2.0 with 0.5g/l dose, followed Langmuir isotherm and Pseudo second order [20]. Activated alumina and activated charcoal demonstrated less adsorption capacity like 7.44mg/g and 12.87mg/g respectively at pH 4 and 2 respectively with 1gm/100ml adsorbent dose[21]. Coconut shell charcoal (CSC) had its maximum adsorption capacity for Cr (VI) was of 10.88mg/g [22].

NANOMATERIALS

The application of magnetite nanoparticles in the environmental field is mainly due to their much better adsorption and reduction activities than their traditional macro- or micro-counterparts. In addition, magnetite can be easily separated and collected by an external magnetic field. This extraordinary advantage is especially useful for the recovery or reuse of the magnetite nanoparticles. Magnetite nanoparticles have shown favorable activities for the adsorption/reduction of quite a few heavy metal ions like Cr (VI) [23]. Comparative study of Cr (VI)removal using biologically synthesized nano zero valent iron (BS-nZVI) and chemically synthesized nZVI (CS-nZVI), both immobilized in calcium alginate beads was carried.The parameters like initial Cr (VI) concentration, nZVI concentration, and the contact time for Cr (VI) removal were optimized based on Box-Behnken design (BBD) by response surface modeling at aconstant pH 7. Under the optimized conditions (concentration of nZVI = 1000 mg L(-1), contact time = ~ 80 min, and initial concentration of Cr (VI) = 10 mg L(-1)), the Cr (VI) removal by the immobilized BS-nZVI and CS-nZVI alginate beads was 80.04 and 81.08 %, [24]. Wu in 2015 studiedcomposite of nano-zero-valent iron and montmorillonite (NZVI/MMT) was prepared by insertingNZVI into the interlayer of montmorillonite. The unique structure montmorillonite with isolated exchangeable Fe(III) cations residing near the sites of structural negative charges inhibited the agglomeration of ZVI and result in the formation of ZVI particles in the montmorillonite interlayer regions. NZVI/MMT was demonstrated to possess large specific surface area and outstanding reducibility that encourage rapid and stable reaction with Cr (VI). Besides, the intercalation also makes NZVI well dispersed and more stable in the interlayer, thereby improving the reaction capacity by 16 times. The effects of pH value, initial concentration of Cr (VI) and reaction time onCr (VI) removal have also been investigated in detail. According to PXRD and XPS characterization, NZVI/Cr (VI) redox reaction occurred in the interlayer of MMT. The study of NZVI/MMT is instrumental to the development of remediation technologies for persistent environmental contaminants[25]., CS–CA nanoparticle was prepared by Bagheri 2015 for forminga new amide linkage, by grafting the amino groups of CS in the presence of carboxylic groups of CA that acts as cross-linking agent. The as-prepared CS–CA nanoparticle samples were characterized by use of dynamic light scattering (DLS), scanning electron microscopy (SEM), Fourier-transformed infrared spectroscopy (FTIR), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) techniques, which showed that the cross-linking agent preserved during the chemical modifications. The adsorption capacity of the CS–CA nanoparticlesfor the removal of Cr (VI) in aqueous solution was studied. The adsorption equilibrium data takenat the optimized condition, i.e., 25 °C and pH of 3, were analyzed with the Langmuir, Freundlich and Redlich–Peterson isotherm models[26]. Fe/Mn mixed metal oxides were synthesized by Weilongin 2013, facilely by a grinding method and were characterized by TEM, XRD, XPS, and BET. The characterization results revealed that mixed metal oxides were mainly composed of not highly crystallized Fe2O3 and Mn3O4 nanoparticles with a diameter about 3–5 nm. The specific BET surface areas of the composite were affected by the amounts of KCl diluent in the preparation process and about 268 m^2/g of the composite can be achieved. Compared with metal oxide adsorbents existent, the composites showed good adsorption capacity, stability, and regeneration activity for Cr(VI) removal. The enhanced adsorption capacity was speculated to be ascribed to the synergistic effect of the mixed metal oxides. By monitoring the valence change in the adsorption process using XPS characterization, the mechanism for Cr(VI) removal on the composites was found to be a combination of electrostatic attraction and ion exchange. The aboveresults demonstrated that the synthesized metal oxides nanocomposite is of great potential for Cr(VI) removal in the fields of remediation of environmental problems[27]. Chromium (VI) oxyanions were removed selectively from various aqueous systems using magnetic MCM-41 nanosorbents of large surface area (>550 $m^2\ g^{-1}$) and high magnetization (≥8.0 emu g^{-1}) in 2011 by Chen. 10 nm magnetic iron oxide nanoparticles were embedded within 250 ± 50 nm MCM-41to obtain a highly dispersible magnetic material, magMCM-41 that can be easily removed by a magnetic field. A highly selective nanosorbent was obtained by grafting aminopropyls andadsorbing Fe3+ on the pores of the magMCM-41. Chromium oxyanions were selectively removedover the pH range of 2–7 with high adsorption capacity of ca. 1.9 mmol g^{-1} (ca. 100 mg g−1) andKd > 25,000 mL g^{-1} for single and binary component adsorptions from distilled, tap, mountain stream and river waters. The presence of calcium in the tap and natural waters as well as humic compounds in mountain stream and river waters resulted in a slightly lower chromium adsorption, but did not affect its superb selectivity (ca. 97%) [28]. Reductive immobilization of chromium in wastewater by nanoscale zero-valent metal (nZVM) prepared from steel pickling waste liquor wasinvestigated by Fang. A series of characterization techniques were conducted to characterize the properties of the synthesized nanoparticles. Effects of pH, buffer substances, natural organic matter(NOM) and hardness were evaluated to probe the impact of environmental factors. Removal of Cr(VI) benefited from a decrease in pH value and the presences of buffer substances and Ca^{2+}. NOM was found to be suppressive on the activity of ZVM and coupled effect of Ca^{2+} and NOM was additive effect due to their non-interference when operating under acidic condition. The nZVM was proved to be more effective (up to 40.6-fold) than zero-valent iron and nanoscale zero-valentiron for Cr(VI) removal, and its removal capacity in wastewater was 182 ± 2 mg g^{-1}. The removalmechanism included mass transfer on solid–liquid interface, reduction of Cr(VI) and simultaneousco-precipitation as Cr–Fe (oxy)hydroxide on the surface of nanoparticles [29]. Work carried out in 2011 was to create a biocomposite which coupled the reducing capability of iron nanoparticles with the adsorption capacity of cellulose to effectively remove hexavalent chromium fromindustrial wastewater. The iron nanoparticles were synthesized on the orange peel pith using a simple redox precipitation reaction to ensure the biocomposite was inexpensive and easy to produce. The nanoparticles were characterized for size, composition, oxidation state, and distribution before and after the Cr(VI) exposure. The nanoparticles were mostly 20 × 80 nm tubular shapes, but there were also some octahedral crystals around 20–40 nm. The biocompositewith the nanoparticles exhibited twice the Cr(VI) removal of the unmodified orange peel pith andalso possesses over twice the adsorption capacity −5.37 mg/g vs. 1.90 mg/g[30]. Hanif in 2014 conducted a research with an aim to develop such adsorbent system: polymer-coated magnetic nanoparticles which can remove heavy metal and dye from water of different concentration. Synthesis of magnetic iron oxide nanoparticles for contaminated water purification has been one of the outcomes of application of rapidly growing field of Nanotechnology in Environmental Science. In his study, the efficiency of magnetic nanoparticles for removal of Cr(VI) and dye (alizarin) from water solutions of known concentrations were evaluated. The nanoparticles were prepared by co-precipitation method and characterized by X-ray photoelectron spectroscopy, transmission electron microscopy, and Fourier transform infrared spectroscopy. Polymer-coated magnetic iron oxide nanoparticles carrying functional groups on their surface were synthesized by different methods for permanent magnet-assisted removal of heavy metal (chromium) from water.The characterization showed that synthesized nanoparticles were in the size range of 10–50 nm. The adsorption capacities of the Fe3O4 using polyMETAC-coated particles for removal of chromium was found to be 62–91 %. The chromium concentration was determined after magneticseparation using atomic absorption spectrophotometer. Nanoparticles of polymer coated showed the highest removal capacity from water for metal. The developed adsorbents had higher capacityfor removal of heavy metal ions[31].

CONCLUSION

Chromium is absolutely hazardous and has detrimental effect on Environment and human health. Hence, promising technologies are required to remove hexavalent chromium from effluent of leather industry as tanning process contribute a substantial amount of Cr. Higher amount of chromium VI can affect biotic as well as abiotic environment. As a result of which ecosystem willget affected. There are disparate methods which result in 90 percent of chromium removal from the tannery wastewaters. In this review article activated carbon and nano materials were reviewedfor the removal of chromium VI. Abundant low-cost adsorbents are used, but activated carbon is low-cost methods for removal of chromium and its efficacy is very promising. But the only disadvantage is the disposal of activated carbon after use. So, to curb this problem, nano material was used. Compare to activated carbon, nano material showed effective removal rate of Cr(VI). They are expensive but they can be used by industries for removal of hexavalent chromium.

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