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Review of Chromium Residue and Chromium-containing Waste Water Treatment

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Abstract. In August 2011, chrome pollution incident happened in Qujing County, Yunnan, China, which caused the attention of the people all over the world. In this paper, the chrome hazards for the health, the routines of chromium residue and Cr-containing wastewater treatment process and the newest research progress--biological materials adsorption method, biological degradation and urban sludge treatment method were reviewed. Finally, the innovative processing method, "reducing barriers" thoughts were introduced.

Preface

In August, 2011, Qujing County, Yunnan province,China, violated *the chromium residue pollution comprehensive control scheme*, which was issued by China Environmental Protection Administration Bureau in 2005-whose requirement is that by the end of the year2010, all stockpiling chromium residue would realize harmless disposal, thoroughly eliminate chromium residue's threat to the environment. The illegal dumping of chromium residue caused water pollution and a serious threat to the local people's life, health and property safety, which raised people's concern to how Chromium residue exactly produced, its chemical composition, what harm it has to the health of human body and what the usual processing method is. In this paper, the research progress was reviewed.

The Source and Chemical Composition of Chromium Residue

Due to the common metal plating chromium may avoid rusting; especially low price metal plating chromium can produce beautification effect, a lot of chromate enterprise work in the extraction of metallic chromium and chromate chromium compounds. The solid waste of the production is chromium residue. Chromium residue in general, is the loose solid powder, granule or small block. Its overall color is grey or black and yellow or brown inclusion. Long time in the fields, some yellow substance infiltrates from its surface. The main chemical composition is shown in table 1:

TABLE 1 THE MAIN CHEMICAL COMPOSITION OF CHROMIUM RESIDUE

Composition	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	Cr_2O_3	Cr^{6+}
Content (%)	4-11	6-10	23-35	15-33	7-12	2.5-7.5	1-2

The Harm and the Impact to the Human Health of Chromium Residue

After rain, the Cr in the chromium residue in the open air will infiltrate into the soil and groundwater system. Cr as same as most transition metal, has six oxidation states, but the major forms

are Cr (III) and Cr (VI) because of the natural water Eh-Ph range. Within the scope of the low Eh, Cr lies in the forms of Cr^{3+}, $Cr(OH)_2^+$, $Cr(OH)_3^0$ and $Cr(OH)_4^-$,while it exists in the form of $HCrO_4^-$, CrO_4^{2-}, $Cr_2O_7^{2-}$ when oxidation state. Cr enters the human body by air, water, and food. The solubility of Cr (III) hydroxide is lower, so the absorption rate of gastrointestinal tract to Cr^{3+} is lower than hexavalent chromium（Cr^{3+} absorption rate is about 0.5%）. Usually the hexavalent chromium is about 300 times higher toxicity than Cr^{3+}.Cr (VI) to the biology has the harm of cancer, teratogenicity, and also can cause liver damage, pulmonary congestion and skin ulcer. Cr (III) although may cause tumors and skin allergies, it is the important component of animal and plant carbohydrate and fat metabolism [1].

Chromium Residue and Chromium-containing Wastewater Treatment Routine

Chromium Residue Treatment

China's chromium residue treatment process is kept in the three principles: "environmental safety first", " comprehensive utilization and ensure that do not produce secondary pollution" and "ensure the product of the comprehensive utilization be long-term safety".

According to the chromium residue pollution environment protection technology standard (interim) "(HJ/T301-2007), chromium residue treatment points the following several steps to complete: first, in the historical heritage of chromium slag heap, set certain facilities such as the block water weir, block canopy, rain diversion canal to prevent the rain from chromium residue pile; Chromium residue after mining, according to the need, packaging, then the land transport, and to dealing site. Under high temperature, join reductant into chromium residue, and for dry detoxification, that make Cr (VI) into Cr (III); Or wet detoxification, that is, in a certain of the liquid-solid ratio, pH value conditions, join reductant, and make hexavalent chromium reduction. The chromium residue after detoxification can carry on comprehensive utilization, such as used for sub grade materials, concrete aggregate, used in the production of cement, make bricks and blocks, iron, glass coloring and other sintering. Or chromium residue after detoxification, cured, detect the leaching-out toxicity, if each index all less than 7 (HJ/T300), be dumped into the landfill with GB16889 standard; If testing chromium residue after the detoxification and curing ,the chromium leaching-out toxicity less than 8 (HJ/T299), be dumped into the second general industrial solid waste landfill according to standard of GB18599.

Cr-containing Wastewater Treatment

In leather processing, chromium ore acquisition, electroplating, alloy, textile and etc, chromium-contained waste water will produce. The general processing way is that when the pH = 2.0, use reductant to change Cr (VI) into Cr (III), and then add the lime; in alkaline conditions (pH = 9-10), make Cr (III) hydroxyl precipitation. In addition, solidification method, ion exchange, membrane separation technology, adsorption, electrolysis, solvent extraction and etc are used [2].

The New Progress of Chromium-containing Wastewater Treatment Research

Adsorption Method

Adsorption method is applied and researched widely in recent years to remove chrome pollution. At first active carbon was used as adsorbent, however, because of higher expense, its usage was limited. Some wooden cellulose waste, such as sugarcane residue, bark, biomass, chaff, coconut shell, etc is used as adsorbent in the research area in the ascendant.

Among the mechanism of using biological materials adsorption Cr (VI), the more commonly accepted is "adsorption-reductive coupling theory". In the acidic conditions, once adsorption, Cr (VI) begin to direct reduction and indirect reduction process: 1) direct reduction mechanism: Cr (VI) ,at a contact to the biological material around the lower electronic reduction potential donor, can be reduced to Cr (III), which can stay in the water phase, may also form complex with the biological materials Cr linkers; 2) indirect reduction principle, including 3 steps: a. the Cr (VI) with negatively charge is linked with the biological material surface positive-charge groups such as azyl and carboxyl; b. by the adjacent electron donor group, Cr (VI) is reduced to Cr (III); c. Because of the biological

material surface with positive- charge repel phenomenon, the positively charged Cr (III) is repelled into the water, or form complex with adjacent groups [3].

Biological Degradation

Biological degradation is also another highlight in the research of chrome removing. Cervantes [4], Shanker [5], Lasat [6] had reviewed the interaction among chrome and microorganism and plants. Here no longer say. In recent years, researchers not only used some more advanced technology, such as Fourier Infrared Spectrum to study the mechanism, but also to develop in some application area, trying to find some more cheap, effective, easy access biological materials to treat chromium-containing waste water and waste residue.

- The chrome-removing research with the application of bacteria

In some bacteria, strong hexavalent chromium reductive ability was found. Chai [7]separated the Cr (VI) reducing bacteria *Pannonibacter phragmitetus sp* from the chromium residue, found that in 10 days, Cr (VI) removal efficiency was 97.8 %, the bacteria not only can effectively remove water-soluble Cr (VI), but to exchange and carbonate Cr (VI) still have the effect. Zhu [8] researched chromate salt reducing bacteria *Leucobacter sp*. CRB1, separated from the chromium residue, and found its tolerance to hexavalent chromium was 4000 mg/l, and reduction rate was 34.5 %. Cheung [9] found that huge bacillus TKW3 also had hexavalent chromium reduction ability,

The fusiform bacillus [10] and sulfate reducing bacteria [11] researches indicate that the bacteria and chromium ion mechanism is to form extracellular precipitation, that is, to form a lower toxicity of the metal complex.

Because of those researches, the applications of the economy bacteria materials become possible.

- The chrome-removing research with the application of algae

Algae can not only be environment pollution indicator, but also be a kind of effective chromium ion biological adsorbent found by more and more research. Michalak [12] studied *Enteromorpha prolifera* for chrome ion adsorption characteristic, and found that a balance data fit Langmuir, Dubinin-Radushkevich, and Freundlich isothermal adsorption curve. For Cyanobactteria algae [13], Chlorella [14-15], the isothermal adsorption curve for chrome ion also fit the above three, but the optimum curve is different individually. For *Spiridina sp* [16], by the SEM and fluorescence microscope analysis researches, the enormous potential was found to chrome ion adsorption.

- The chrome-removing research with the application of fungi

Ksheminska [17] studied with a different way to screen the chromate salt resistance yeast *Pichia guilliermondii L2*, found in 1.8-2.4 mM chromate salt concentration, the yeast grew well and its extracellular metabolites can effectively reduce chromate salt, and form the Cr (III) biological complex. Kavita [18] researched pretreated *fusarium oxysporum f.* biomass in water solution for Cr (VI) adsorption effect with the batch experimental method. Biomass dose, solution pH and start metal ion concentration, temperature and pretreatment and the way to the influence of adsorption effect. The author found the acid treated biomass for Cr (VI) adsorption is 1.6 times as untreated; At the same time the chrome removal rate increased with the pH decreased, but with Cr (VI) concentration, temperature and biomass dose it was positively correlated. The isothermal adsorption data fit Freundlich adsorption curve. IR showed positively charged amino acids joined into the biological adsorption process. Cr (VI) adsorption curves conformed to level 2 kinetics curve and were spontaneous, endothermic, and highly affinitive to the biomass. Ahluwalia [19] researched 8 living fungal biomass, found that they had different reduction abilities to hexavalent chromium, but for death, dry biomass, it showed a greater reduction activities. *Phanerochaete chrysosporium* could process chrome to the 0.1 mg/l of allowable scope in outflow, and the processing ability could not be influenced by other metal ions (Fe, Zn, Ni). Infrared spectral analysis found that in the cell surface, positively charged amino participated in chromium connection. Experiments prove the by-product of the fermentation industry or the dead yeast biomass from cheap may apply to Cr-containing waste water treatment in a mass.

- The chrome-removing research with the application of plants

Mishra [20] studied the water hyacinth effect on chrome removal, and found in the top 20 mg/l concentrations, Cr removal rate was 84%.Protein content, sugars, biochemical parameters such as chlorophyll declined with Cr accumulation in plant body, but the apparent plant toxic symptoms were not seen. The results showed that the Cr removal of the procedure was safe, which would lead to a large scale, and prosperous application. Agunbiade[21]studied the water hyacinth in polluted coast to remove the heavy metals containing Cr. The research also suggested that water hyacinth not only be used as animal feed, but also as plant extraction and root filter in the phytoremediation technology. Ha [22] studied the large aquatic plant *Eleocharis acicularis* in the abandoned mine tailings and mining waste water, and whose enrichment ability of heavy metals containing the chromium. According to the results, this plant had the huge application prospect. Lai [23] researched 33 kinds of flowers plant for the removal of the heavy metals in the area of central Taiwan, and choose 6 kinds of woody plants and 6 herbs which had the higher removal rate to use as further research.

The Attempt of Sludge in the Treatment of Chromium Wastes

Zhang [24] made a mixture of municipal sludge and chromium residue mixture with some ratio, and found that after the pyrolysis of sludge mixture, the released steam help Cr (VI) reduced, but the reductive ability was related with the heating temperature, particle diameter and the reaction time. In 600 degrees Celsius conditions, it could make the chromium residue with 3384 of mg/Kg Cr (VI) content reduced to the 30 mg/Kg after process. Haroun [25] found that sludge containing high levels Cr in the tannery factory after 50 days compost cycle, tested with different methods of extraction, Cr sequence removal rate significantly increased. Cardoso-Vigueros [26] found that the tannery factory sludge after compost and earthworms composting, chrome content dropped to 562 mg/kg. Zhang [27] studied the Cr detoxification of sewage treatment plant dewatering sludge and concentrate sludge under the microwave radiation condition, found that sludge detoxification effect to chromium residue was related to the quantity of materials containing Cr, detoxification time and etc.

The Prospects and New Ideas in the Treatment of Wastes Containing Chromium

Along with the development of environmental science and raised level of human knowledge, maybe we would make an application of the theory to keep harmonious development among nature, economy and society and to reach the "win-win" or even "multi-win" game idea and the principle of "waste treat waste". Professor Zhang, Huyuan in Lanzhou University found that in the free oxygen supply limited conditions, in the soil and water system, the primary microbial anaerobic breathing could lead to the formation of reductive environment, and the reductive environment could reduce the most heavy metals mobility. Accordingly, he proposed "reduction barriers" original academic ideas, namely an artificial design with a strong anaerobic microbial activity, which comprehensively reduced heavy metal pollutants mobility by the anaerobic reduction environment in this engineering barrier.

Professor Zhang, Huyuan’s research project "the reducing barriers in the waste landfills" (No. 50678075) funded by the national natural science foundation of China (NSFC), was completed in January 2007-December 2009. Prof. Zhang’s existing research results show that compaction sludge with low permeability can intercept metal pollutants transfer by reducing the seepage flow [28]; and that sludge can fix the metal ion without the exogenous nutrients by the microbial anaerobic breath [29,30]; and that sludge is a promising reaction barrier material [31-33]; and that in the aspect of heavy metals environmental risk, sludge barrier is feasible[34]. From those research work, the basic scientific principles of "Reducing barriers" is confirmed.

To our imagination, when the large number of chromium residue in our country a year is taken into the landfills, we can undertake the seal processing. The liner is sludge "reducing barriers". For the historic chromium residues, sludge reduction treatment may be a low expense, a multiple-purpose way. Maybe this is a beautiful new future we can all share.

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