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Research article

# Immobilization in cement mortar of chromium removed from water using titania nanoparticles

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A B S T R A C T

Because of the high toxicity of chromium, particularly as Cr (VI), it is removed from industrial effluents before their discharge into water bodies by a variety of techniques, including adsorption. Ultimate disposal of the sludge or the adsorbate, however, is a serious problem. While titania, in nanoparticle form, serves as a very good adsorbent for chromium, as an additive, it also helps to increase the compressive strength of mortar and concrete. Combining these two properties of the material, titania nanoparticles were used to adsorb chromium and then added to mortar up to a concentration of 20% by weight. The compressive strength of the resulting mortar specimens that replaced 15% of cement with chromium laden titania showed an improved strength than that without titania, thus confirming that this material had positive effect on the mortar strength. Leachate tests using the Toxicity Characteristics Leaching Procedure (TCLP) confirmed that the mortar sample chromium leachate was well within the permissible limits. The proposed technique thus offers a safe and viable method for the ultimate disposal of toxic metal wastes, in general, and those laden waste chromium, in particular.



## 1. Introduction

Chromium a naturally occurring element found in rocks, soil, animals, plants and volcanic dust and gases, is one of the most abundant element in the Earth's crust. It exists in oxidation states ranging from −IV to +VI inclusively, with the most stable forms being trivalent (III) chromium and hexavalent (VI) chromium (Becquer et al., 2003). In nature Cr is chiefly found in the trivalent form (Kotaś and Stasicka, 2000) while Cr (VI) in the environment is almost totally derived from human activities (Schneider et al., 2012). Whereas, the metallurgical, chemical, and refractory industries are the fundamental users of chromium (Dayan and Paine, 2001), leather tanning and chrome plating processes are the major sources of chromium pollution (Sharma et al., 2012).

Chromium in the hexavalent oxidation state, Cr (VI) is of grave concern because of its toxicity, high solubility, and mobility in water (Rashid et al., 2011) makes it 500 times more toxic than the Cr (III) and it has been recognized as a pulmonary carcinogenic along with causing other health effects such as respiratory, skin, carcinogenic, renal, hepatic, haematological problems while being genotoxic and mutagenic (Saha et al., 2011). Cr (VI) is carcinogenic to rats and mice after chronic oral exposure (Stout et al., 2009). Penetration of Cr (VI) in skin will cause painless erosive ulceration "chrome holes" with delayed healing and increased stomach and lung cancer risks in humans due to Cr (VI) exposure has also been reported (Beaumont et al., 2008). Toxic effects of accumulated Cr on plant growth and development include alteration in the germination process and effect on the growth of roots, stems and leaves has also been observed (Shanker et al., 2005).

Methodologies have been developed in removing chromium from industrial wastewater by chemical precipitation, ion exchange, electrochemical treatment, membrane filtration, flotation, coagulation flocculation and adsorption (Barakat, 2011). Although, precipitation method is used for its simplicity process and is inexpensive but, it is ineffective when metal ion concentration is low and can produce large amount of sludge which needs to be treated with great difficulties (Fu and Wang, 2011). Thus, adsorption is considered as one of the most suitable chromium removal methods due to its cost effectiveness, higher efficiency, and ease of operation (Djellabi and Ghorab, 2015) and the availability of a wide range of adsorbents like silica composites (Kumar et al., 2007), activated carbon (Sekhar et al., 2012), fly ash (Veni and Ravindhranath, 2012) and microbes (Liu et al., 2013). Further, various low cost adsorbents (Bailey et al., 1999) and microbial

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biomass (Ahluwalia, 2014) have also been observed previously for heavy metal chromium removal. Titania nanoparticles have also proven themselves to be excellent adsorbents for chromium removal due to their unique features like physical and chemical stability, low cost, non-toxicity and the resistance to corrosion (Hung et al., 2007). In one study titania showed highest capacity for Cr (VI) removal out of other photo-catalysts including zinc oxide and cadmium sulfide (Joshi and Shrivastava, 2011). Titania also helps in the photo-catalytic reduction of Cr (VI) to Cr (III) (Malaviya and Singh, 2011).

No matter how chromium is removed from an effluent, the ultimate disposal of the concentrate or sludge with concentrated chromium still remains a major problem. In what follows, we propose a viable solution for safe and permanent disposal of such concentrated wastes by incorporating it in cement mortar.

While, the major applications of titania based photo-catalytic building materials include environmental pollution remediation, self-cleaning and self-disinfection (Chen and Poon, 2009), there is potential for using chromium-tanned leather residue in civil engineering to obtain technical, economic and environmental benefits (de Oliveira Andrade and Mattje, 2012). The application of titania for decreasing oxides of nitrogen and volatile organic compounds has gained a greater attention of the civil engineering community because of potential benefits with decreasing pollution (Cárdenas et al., 2012). White cement containing titania possessing photo-catalytic properties allows maintaining the aesthetic characteristics of concrete over time, while eliminating dangerous pollutants from the urban environment. White cement also increases the mechanical strength of concrete (Cassar et al., 2003). Similarly, partial replacement of cement with nanophase titania particles improves the compressive strength of mortar and concrete (Nazari et al., 2010).

On the other hand, several nanomaterials including titania can be used in cementitious matrices to improve their physicochemical behavior in cement, mortar and concrete (Chen et al., 2012). The addition of nano-titania powders in cement mortar significantly decreased the porosity and accelerated the hydration rate of the cementitious materials at early ages. Thus, compressive strength of the mortar was enhanced, practically at the early stage (Meng et al., 2012).

Removal and ultimate disposal of the heavy metals, from industrial waste water, in general, and chromium, in particular, is of critical importance. Safe disposal of the chromium wastes generated from steel and other alloys production, chrome plating, pigments and leather tanning industries to protect human health and environment is an issue of grave concern (Wang and Vipulanandan, 2000).

Since there have been reports in the literature where the chromium metal has been immobilized within solid matrices including geo-polymers and concrete for final disposal (Giergiczny and Król, 2008), this opens up the possibility of immobilizing chromium, in mortar and concrete, in such a manner that the probability of leaching is considerably reduced, leading to a safe and permanent solution for the disposal of hazardous waste containing chromium. A technique is introduced whereby Cr (VI), from aqueous solution is photo-catalytically reduced to Cr (III) and adsorbed on titania nanoparticles the latter being incorporated into mortar blocks with improved mechanical properties and showing little leaching of the toxic metal.

## 2. Materials and methods

### 2.1. Test materials

All the chemicals used in this research were of analytical grade. Accurately weighted $TiO_2$ (GPR, BDH chemicals Ltd. Poole England), potassium dichromate, diphenylcarbazide (DPC), acetone, sulphuric acid, glacial acetic acid, sodium hydroxide, and nitric acid (analytical grade) were used in this study. Cement and sand were obtained from local sources whereas distilled water was used throughout the experiments.

#### 2.1.1. Mortar test specimens

For the mortar specimen used in this research, a water to cement ratio of 0.5 was used. Ordinary Portland cement was used with sand to cement ratio of 1. The volume of mortar specimen used was 125 $cm^3$ and cement mortar density of 2162 $kg/m^3$ was selected in this research work. Dry mass of mortar specimen calculated was 270.25 g containing 135.12 g of cement and same amount of sand. Total number of mortar specimens cast were 15 with 3 samples each for 0%, 5%, 10%, 15% and 20% cement replacement with chromium laden titania as shown in Table 1.

#### 2.1.2. Preparation of chromium stock and standard solution

The concentration of chromium in aqueous solutions was determined using the Diphenylcarbazide (DPC) standard method (APHA 3500-CR). Potassium dichromate stock solution of 500 ppm was prepared by dissolving 141.4 mg of dried potassium dichromate in 100 ml distilled water in a volumetric flask. DPC solution was prepared by dissolving 250 mg of 1,5 diphenylcarbazide powder in 50 mL acetone. To adjust the pH of the solution to pH 2, 0.2 N sulphuric acid was used. Then standards ranging from 0 mg $L^{-1}$ to 1 mg $L^{-1}$ were prepared from the chromium stock and DPC solutions.

### 2.2. Test equipment

The morphology of titania nanoparticles was determined by scanning electron microscope (JEOL JSM-6460). Energy-dispersive spectroscopy (EDS, JEOL JSM-6460) was used to identify the elements present in the nanoparticles. Crystalline phase and size of nanoparticles was analyzed by X-ray diffraction (XRD, JEOL JDX-II). The photo-catalyst (Titania) was separated from solution by Centrifugation using centrifuge instrument (D3752O Sigma). The quantitative determination of chromium was done by UV/Vis spectrophotometer (HACH DR 2400). A pH meter (CyberScan 500 Eutech) was used to adjust the pH of the chromium stock solution, with 0.2 N sulphuric acid. Strength test machine manufactured by 'CONTROLS' was used to determine the compressive strength of mortar specimen.

### 2.3. Test procedures

#### 2.3.1. Synthesis of titania nanoparticles

Titania nanoparticles were synthesized using liquid impregnation (LI) method. For this purpose, 50 g of titania powder was added in 300 ml distilled water and allowed to stir for 24 h. The solution was then allowed to settle for another 24 h. Then slurry type mixture was placed in oven for 12 h at 105 °C for drying. Dried slurry was crushed and placed in muffle furnace (NEY-525 SRIES II) for 6 h at 550 °C for calcination. The resultant powder was allowed to cool down at room temperature giving clear crystalline form of titania nanoparticles (Fan et al., 2011).

#### 2.3.2. Characterization of nanoparticles

*2.3.2.1. Scanning electron microscopy (SEM).* The topography and morphology of the titania, was carried out using scanning electron microscope (JEOL JSM-6460) at 10,000x magnifications. Scanning Electron Microscopy was used for the direct observation of particle size and morphology of sample powders.