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Evaluation and Optimization of Chromium Removal from Synthetic Aqueous Solutions by Powdered Spirogyra

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ABSTRACT

Aims Heavy metals are the main pollutants in nature. Chromium is a heavy metal which is widely used. Hexavalent chromium solubility and mobility in aqueous solutions is so high and it is easily reduced. Biosorption is a process in which heavy metals are uptake through passive binding by nonliving biomass from aqueous solutions. The present study aimed to determine the capability of powdered Spirogyra to remove chromium from synthetic aqueous solutions under the influence of process parameters includes pH, algal dosage, and metal initial concentration.

Materials & Methods This study was empirically carried out in laboratory scale through a batch system in Kashan region, Iran, in September 2014. Hexavalent chromium stock solution (500mg/l) was made by solving 1.417g of dichromate potassium in 1 liter of distilled water. The experiments were conducted with initial concentration of 10, 25, and 40mg/l of hexavalent chromium in pH levels equal to 3, 7 and 11 and algal dosages of 0.2, 0.5 and 1g/l. The repeated-measure test was applied for statistical analysis using SPSS 16 software.

Findings Maximum value of chromium removal was observed at pH=3 (70%). Hexavalent chromium removal value increased with increasing algal dosage from 0.2g/l (45%) to 1g/l (70%) in 100ml samples with 40mg/l concentration of Cr(VI). The amount of Cr(VI) bound by unit weight of biomass were increased from the initial concentration of 10 to 40mg/l about 27mg/g in all levels of pH.

Conclusion Low dosages of powdered Spirogyra can remove hexavalent chromium from wastewater and aqueous solutions.

Keywords Absorption, Physiological; Hexavalent Chromium Ion; Spirogyra; Metals, Heavy

CITATION LINKS

[1] Heavy metal ... [2] Heavy metals in contaminated soils: A review of sources, chemistry, risks and ... [3] Biosorption of Cr(VI) from aqueous solutions by ... [4] Response surface modeling and optimization of chromium (Vi) removal from ... [5] Utilization of waste product (tamarind seeds) for the removal of Cr(VI) from ... [6] Handbook of ... [7] Speciation of dissolved chromium and the mechanisms controlling its concentration in ... [8] Peer Reviewed: In-Situ Treatment of ... [9] Guidelines for ... [10] Organic fouling behavior of superhydrophilic polyvinylidene fluoride (PVDF) ultrafiltration membranes functionalized with ... [11] The role of a combined coagulation and disk filtration process as a pre-treatment to microfiltration and reverse osmosis membranes in ... [12] The past, present, and future trends of ... [13] Investigation of Cr(VI) adsorption onto chemically treated Helianthus annuus: Optimization using response surface ... [14] A review of the biochemistry of heavy metal biosorption ... [15] Biosorption of ... [16] Biosorption: Current perspectives on concept, definition and ... [17] Optimization of Cd(II), Cu(II) and Ni(II) biosorption by chemically modified Moringa oleifera leaves ... [18] Biosorption of cadmium using a novel bacterium isolated from an electronic industry ... [19] Biosorption of copper (II) from aqueous solution by mycelial pellets of ... [20] Bioremediation of industrial effluents containing heavy metals using brewing cells of Saccharomyces cerevisiae as a green ... [21] Sorption and desorption of lead (II) from wastewater by green algae Cladophora ... [22] Determination of the equilibrium, kinetic and ... [23] Zn2+ biosorption by Oscillatoria ... [24] Growth and heavy metals removal efficiency of Nostoc muscorum and Anabaena subcylindrica in ... [25] Standard methods for the examination of water and ... [26] Optimization Of Process Parameters For Biosorption Of ... [27] Removal of chromium and toxic ions present in mine drainage by ... [28] Hexavalent chromium removal from ... [29] Biosorption of metal ions by freshwater algae with ... [30] Removal of chromium(VI) from saline wastewaters by ... [31] Removal of heavy metals by biosorption using ... [32] Biosorption of mercury(II), cadmium(II) and ... [33] Removal of Ni and Cu from single and binary metalsolutions by free and immobilized Chlorella ...

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Introduction

Human industrial affairs lead to production of various environmental pollutants such as toxic organic materials, carcinogenic compounds, and heavy metals. Depending on the type of industrial activity, such pollutants' degree of hazard varies [1]. Heavy metals are the main pollutants in nature and because of their toxicity they are counted as a serious menace for human's and creatures' health in high concentrations. One of the most important hazards of heavy metals is their high tendency to persist in environment and accumulates in food chain [2].

Chromium is a heavy metal which is widely used in plating, textile industries, tannery, wood preservation, and alloy manufacturing and processing [3]. In liquid phase, chromium usually exists in two oxide forms of trivalent (Cr^{+3} or $Cr(OH)^{+2}$) and hexavalent ($Cr_2O_7^{-2}$, CrO_4^{-2} or $HCrO_4^{-}$) generally showed by Cr(VI) [4]. Hexavalent chromium solubility and mobility in aqueous solutions is so high and it is easily reduced [5]. Hexavalent chromium toxicity is more than trivalent chromium, thus Cr(VI) is carcinogenic and mutagenic for human. Chronic exposure to hexavalent chromium leads to cancer in gastrointestinal organs and lungs and severe diarrhea and nausea [3]. Cr(VI) simply enters the cell and produces its toxic effects through oxidation and formation of free radicals. Even in low concentrations, this metal can cause severe allergic reactions like asthma and bronchitis [6, 7]. In vulnerable individuals, long term contact with Cr(VI) might result in anaphylactic shock [8]. Therefore, according to World Health Organization (WHO), Cr(VI) allowed level in potable water is 0.05mg/l [9]. There are several methods to remove chromium ions from water and sewage which includes coagulation, chemical precipitation, reverse osmosis, ion exchange, ultrafiltration and Nano-filtration [10, 11]. As such methods have their drawbacks e.g. incomplete metal removal, high cost and energy, and also generation of toxic compounds and sludge [12, 13], application of new and alternative methods which have a high efficiency and low costs is needed.

In recent years studies have been focused on biosorption of soluble heavy metals by biological mass. Biosorption is a process in which heavy metals are uptake through passive binding by nonliving biomass from aqueous solutions. This implies that removal mechanism in biosorption is not metabolically controlled and metal ions are eventually removed form complexes as a result of being adsorbed on biomasses [14, 15]. In comparison to conventional water treatment methods, biosorption have advantages like reusing biological masses, being applicable *in situ*, not producing chemical sludge and hazardous secondary compounds, being able to integrate with other methods and having low utilization expenses [16, 17].

Various biomasses, e.g. bacteria, fungi, algae, yeasts, molds, and viruses can be used to remove heavy metals from aqueous solutions and industrial wastewater [18-20]. Algae has a high capacity to adsorb metals because of having polysaccharides, proteins, and lipids in its cell wall and by the means of amino-, hydroxyl-, carboxyl-, and sulfate groups [21]. Numerous studies have been done about algae capability for removing heavy metals; Aksu studied biosorption capability of *Chlorella vulgaris* for nickel in reactor with complete combination or a floating bed [22], Davis *et al.* investigated the role of brown algae to remove heavy metals [14], Ahuja *et al.* studied the biosorption of zinc by *Oscillatoria anguistissima* [23], and in a similar work by El Sheekh *et al.*, *Nostoc muscorum* and Anabaena ability for removing heavy metals from industrial wastewater was investigated [24].

Spirogyra is a filamentous algae which commonly lives in dense green masses in surface waters, water pools, and rivers. The present study aimed to determine the capability of powdered Spirogyra to remove chromium from synthetic aqueous solutions under the influence of process parameters includes pH, algal dosage, and metal initial concentration.

Materials & Methods

Preparation of biomass: Spirogyra was collected cross Ghahrood River in Kashan region, Iran in September 2014, being identified by optical microscopy; they were washed with distilled water to remove foreign particles and dirt and then were exposed to open air to dry. They were placed in 60°C oven for 12 hours and finally, were powdered in uniform particle size by a domestic mixer.

Preparation of stock chromium solution and samples containing hexavalent chromium: Hexavalent chromium stock solution (500mg/l chromium) was made through solving 1.417g of 99% dichromate potassium ($K_2Cr_2O_7$) in 1 liter of distilled water. Synthetic aqueous solutions containing various concentrations of hexavalent chromium were prepared made from the stock solution by dilution.

Experimental procedure: The experiments were conducted in 250ml flasks containing 100ml of the synthetic solution with initial concentration of 10, 25, and 40mg/l of hexavalent chromium. The samples were examined by a rotary shaker at 150rpm in pH levels equal to 3, 7 and 11 and algal dosages of 0.2, 0.5 and 1g/l, for 60 minutes in typical laboratory temperature. To adjust the pH value, 0.2M sulfuric acid and 1M sodium hydroxide were used. After mixing time, the adsorbent was separated from the solution through Whatman filter papers (Germany). In order to measure the concentration of hexavalent chromium, the colorimetric method was carried out with 1,5-diphenylcarbazide reagent in acidic solution (i.e. to each amount of 25ml of the filtered sample, 0.5ml of 1,5-diphenylcarbazide was added in an acidic environment and the intensity of the resultant carmine color in each sample determined the residual hexavalent chromium) [25]. In order to read the adsorption level, the visible-spectrophotometer (Model DR/2010, HACH; USA) was used at 540nm. Cr(VI) removal percentage after adsorption was calculated by C_0-C_e/C_0×100 (C_0 is the initial concentration of hexavalent chromium (mg/l) and C_e is the concentration of hexavalent chromium remaining in solution at equilibrium (mg/l).

Statistical Analysis: The repeated-measure test was applied for statistical analysis using SPSS 16 software.

Findings

Effect of pH: The process of removing hexavalent chromium was different at various levels of pH. Maximum value of chromium removal was observed at pH=3 (70%). Increasing the pH up to 7 (43.5%), decreased the removal efficiency and increasing the pH more up to 11 (55.5%) increased the removal efficiency slightly (p=0.004).

Effect of biomass dosage: Hexavalent chromium removal value increased with increasing algal dosage from 0.2g/l (45%) to 1g/l (70%) in 100ml samples with 40mg/l concentration of Cr(VI), pH=3 in 25°C (It was 58% at 0.5g/l; p=0.001).

Effect of initial concentration of metal: The amount of Cr(VI) bound by unit weight of biomass were increased from the initial concentration of 10 to 40mg/l, at pH=3 (4.78 to 27.48mg/g, respectively), pH=7 (2.15 to 20.29mg/g, respectively) and pH=11 (2.73 to 22.23mg/g, respectively). It had about 22% increasing in all levels of pH (p<0.001).

Discussion

In this study, the removal of hexavalent chromium from synthetic aqueous solutions by powdered Spirogyra was investigated in different levels of pH, initial Cr(VI) concentration and biomass dosage in batch experiments.

pH is an influential environmental parameter in liquid phase, with respect to chemical processes such as hydrolysis, complex formation with organic and inorganic compounds, precipitation and reduction. In this study the value of hexavalent chromium removal revealed the best results in acidic pH which is in line with previous studies. In a survey performed on biosorption of chromium by green algae, Valli *et al.* came to this conclusion that maximum removal occurs in pH=2 [26]. The reason probably is that, Cr(VI) ions, which are negatively charge overall surface, are bounded to biomass cell wall, which is positively charge through electrostatic attraction in acidic pH. With increasing pH, overall surface charge of biomass cell wall turns negative and as a result biosorption decreases [27]. As the removal efficiency increased with pH decreasing, the industrial wastewater, which contains a high concentrations of chromium and their pH is between 1 and 3, can be directly treated without adding acid. This can eventually lead to a decrease operating costs of industrial wastewater treatment plants [3, 28].

In biosorption of heavy metals, it was shown in previous studies that the more the initial concentration of metal in solution is, the more the ability of biomass in adsorbing metals would be. Tien concludes by studying the biosorption of heavy metals by fresh water algae that upon increasing metal initial concentration, removal efficiency increases as well [29]. Deng *et al.* have shown that by increasing Pb(II) initial concentration in aqueous solutions, biosorption capability of *Cladophora fascicularis* increases [21]. Based on the resultant outcomes by the current study, increasing Cr^{6+} initial concentration in all levels of pH ($p=0.004$) and the applied algal dosage ($p=0.001$), removal efficiency also increases. It seems that the reason is the high level of Cr(VI) ions availability in solution [30].

Due to the function of various polysaccharides such as cellulose, chitin, glucans and also the presence of sulfate- and carboxyl groups and proteins, algae cell wall has a considerable ability for removing heavy metals. In 2012, Kumar & Oommen examined the *Spirogyra hyalina* ability to remove heavy metals and concluded that this algae have a high efficiency to remove lead and mercury from the aqueous solutions [31]. In 2006, Bayramoglu *et al.* have revealed that *Chlamydomonas reinhardtii* have a truly high capability in uptaking mercury, cadmium, and lead ions from the aqueous solutions and by increasing biomass dosage, removal efficiency increases as well [32]. In 2001, Mehta & Gaur have found that increasing algal dosages in aqueous solutions increases nickel and copper removal by *Chlorella vulgaris* [33]. In the present study also increasing algal dosages caused increased hexavalent chromium removal because of more adsorbent availability in solution. According to the statistical analysis carried out in this study in fixed levels of pH and Cr(VI) initial concentration, an increase in algal dosages lead to increased efficiency of chromium removal ($p=0.001$).

The application of other green algae and biomasses in removing hazardous heavy metals and toxic compounds from aqueous solutions, municipal and industrial wastewaters is recommended for future studies.

Conclusion

Low dosages of powdered Spirogyra can remove hexavalent chromium from wastewater and aqueous solutions.

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