Microparticles Immobilized *Tamarindus Indica* Extract Bioremediates Toxic Chromium in Tannery Effluent and Contaminated Soil

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Research Article

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Abstract

Bioreduction of certain environmental toxic metals using plant-derived antioxidants has been proven effective and promising bioremediation approach. The Redox state of specific metals, in particular chromium, determines its environmental solubility and toxicity. Antioxidant-rich extract of tamarind leaves was extracted and its Cr(VI) reduction potentials in tannery effluent and Cr(VI) contaminated soil determined under acidic and neutral pHs. Microparticles immobilized tamarind extract were produced and similarly tested for Cr(VI) reduction capacity in tannery effluent and contaminated soil. The particles were initially characterized to evaluate their physicochemical properties, encapsulation efficiency as well as release kinetics. The particles produced were irregular in shape with a very high extract adsorption efficiency (87.06%). The particles shows high release kinetic constant and a lower half-life. About, 50 and 60% Cr(VI) reduction was achieved by tamarind extract immobilized microparticles in tannery effluent and 60 and 80% in Cr(VI) contaminated soil after 4hrs at pH 6.7 and 2.0, respectively. Cr(VI) in tannery effluent and contaminated soils was efficiently reduced and immobilization enhanced and preserved the extract effectiveness for a longer period of time. Therefore, immobilization of antioxidant-rich extract into microparticles was found to be essential in attaining maximum Cr(VI) reduction. Therefore, findings from this work could be very helpful in industrial waste treatment and environmental cleanliness.

Introduction

Environmental pollution due to growing industrial activities is undeniably one of the most indispensable problems of this century[1]. Effluent from leather tanning industries has been described to contain a considerable amount of substances which are released into the environment[2]. This action in particular, results in serious environmental contamination to water bodies and soil[3]. These toxic materials not only cause human health hazards but also affect other life forms[4]. Tannery effluent contains large amounts of lime sludge, sulfides, acids, toxic metals salts, in particular chromium salts, which are toxic, non-biodegradable and hardly disposable[5]. Tanneries are one of the major sources of chromium pollution ranging from 40–25,000 mg/L of wastewater[6,7]. Other sources of chromium in the environment includes the activities of numerous industries including welding, electroplating, painting, pigments production and chemicals industries[8]. In the environment, chromium exists commonly in trivalent (Cr(III)) and hexavalent (Cr(VI)) form[9]. Meanwhile, Cr(VI) is highly toxic, soluble, mobile and carcinogenic to humans and animals[10], Cr(III) is considered an essential component of human and animal nutrition in trace amounts[11]. Due to Cr(VI) carcinogenicity and mutagenicity, the Environment Protection Agency (EPA) has designated chromium as a class A or priority pollutant[12]. The maximum tolerance of total chromium and Cr(VI) in public drinking water is 2 mg/L and 0.05 mg/L, respectively[7]. Structural similarity of chromate (CrO_4^{2-}) to sulfate (SO_4^{2-}), enables it cross cell membranes via the sulfate transport system[13]. Exposure to Cr(VI) has been linked to various types of cancer, epigastric pain, nausea, vomiting, severe diarrhea and hemorrhage at concentration less than 0.10 mg/g of body mass[14]. Therefore, owing to this characteristic toxicity and solubility, Cr(VI) reduction to Cr(III) has been useful as a remediation technology for Cr(VI)-

contaminated environment[10,15]. Chemical reduction significantly reduce Cr (VI) to Cr (III)[16], but requires high reagents concentration and introduced secondary contamination[17]. Several works emphasize on the use of reductant of biological origin as an alternative chemical remediation approach[17,18]. Biological reductant are cost-effective because of their low energy requirement, low toxicity, availability and augmented removal efficiency[19]. Herein, we determined Cr(VI) removal capacity of microparticles immobilized Tamarindus indica methanolic leaves extract in tannery effluent and Cr(VI) contaminated soil. We earlier reported on tamarind extract to contain a vast number of antioxidant phytochemicals some of which were reported with excellency in converting Cr(VI) to less toxic and immobile form[20]. Tamarind plant is one of the most commonly abundant and under-utilized plant native of tropical Africa[21].

Methods

Reagents

Potassium dichromate (Fisher Scientific; Pittsburgh, PA, USA) was used as a source of hexavalent chromium, diphenylcarbazide (Merck Germany), sulfuric acid (98%), hydrochloric acid (85%) and sodium hydroxide were all of analytical reagent grade and obtained from Sigma (St. Louis, MO, USA). Deionized water was used for all solutions and dilutions.

Extraction of Tamarind Leaves

Tamarind leaves were collected by a research assistant from Pharmacognosy Research Laboratory, Ahmadu Bello University Zaria. The leaves were washed with clean water and dry before ground into fine powder. Extraction was carried out by maceration through soaking 500g leaves powder in 70% methanol for two days. The solution was decanted and filtered through Whatman No.4 filter paper. The mixture was concentrated to a thick consistency and the resulting extract kept in a desiccator for further use.

Preparation of Reagents

The extract solution was prepared by dissolving 0.1g in deionized water and subsequently diluted to 100mL to obtain a 1mg/ml extract solution. Stock Cr (VI) solution (50 mg L − 1) was prepared by dissolving 0.05 g $K_2Cr_2O_7$ (294.18 g mol − 1) in1 L of deionized water. The pH of Cr(VI) solution was adjusted to 7.0 using 0.1 M NaOH or 0.1 M HCl before filtered using a 0.45-µmWhatman filter paper and sterilized. The working solution was prepared by diluting the stock solution with deionize water to give the appropriate concentration (10 mg L−1) of the solution and 0.20 g of 1,5 Diphenylcarbazide was added in 100ml of 95% acidified ethanol and store in sterilized and dried brown colored bottle.

Collection of Sample

Contaminated soil and tannery effluent were collected from Nigerian Institute of Leather Science and Technology (NILEST). While, uncontaminated soil sample was collected from a random location and

thereafter identified as sandy soil with the following characteristics of < 18% clay and > 68% sand, weak structure, 33–47% porosity, 25% field capacity, pH of 6.7, 95% hydraulic conductivity, 45% infiltration rate and bulk density of 1.6g/cc are commonly recorded[22]. Loose particles and plant debris were removed manually, the sample were ground into fine powder and passed through 0.149mm sieve [23]. Normal tap was used to prepare a 5mg/L Cr(VI) solution for simulation of contaminated water.

Determination of Cr(VI) Concentration

The experiment for the reduction of Cr (VI) was conducted as described by Chen et al.[16] with some modifications. The reaction mixtures were obtained by adding a source of Cr(VI) into a 250mL Erlenmeyer flask, and Tamarindus indica methanolic leaves extract or equivalent amount of particles. The initial pH of the solution was adjusted with sulfuric acid solution (0.5M) and/or sodium hydroxide solution (1.0M). All experiments were conducted at room temperature (25oC) unless otherwise specified. Hexavalent chromium was measured spectrophotometrically at 540nm using 1, 5 - diphenylcarbazide.

Preparation of Extract-immobilized Microparticles

Guinea corn (Sorghum bicolor) stalk was obtained from a farm, dried and grounded into powder. The microparticles were prepared by simple adsorption through mixing the extract solution with lignocellulosic powder as described by Sharma et al.[24] with little modifications. About 1g of lignocellulose powder was dissolved in 100ml of 1mg/ml extract and the solvent allowed to evaporate at 40^{o}C, while the extract absorbed into the powder. The samples were kept in an airtight container at 4^{o}C until needed.

Characterization of Microparticles

The size and morphology of the microparticles produced were determined according to the method described by Harris et al.[25], with the aid of Scanning Electron Microscopy (SEM) Analysis. The particles were mounted on metal stubs with double-side adhesive, and coated with gold in vacuum. The morphology was viewed on the screen and then captured at different magnifications.

Microparticles Adsorption Efficiency

Tamarind leaves extract adsorption efficiency was carried out according to Harris et al.[25]. Extract adsorbed in microparticles was quantified by Folin–Ciocalteu method with respect to total phenolic content by dissolving 30 mg of the particles in 20 mL of deionized water. The experiments were carried out in triplicate to minimize error.

Kinetic Release Studies on Microparticles

Tamarindus indica methanolic leaves extract release kinetics was determined according to Harris et al.[25]. Microparticles (150 mg) were suspended in deionized water at 37 ◦C and shake at 100 rpm (Rotabit horizontal shaker, Selecta, Barcelona, Spain). The suspension was aliquoted in 1 mL tubes after different

time intervals, centrifuged at 15,000 rpm for 30 min. One milliliter of deionized water was added into the suspension to replace the amount taken in each step. The release of the extract was quantified using Folin–Ciocalteu method and the experiments were carried out in triplicate.

Determination of Cr(VI) Reduction by Microparticles in Contaminated Water Model

Cr(VI) reduction capacity of microparticles in contaminated water was determined based on the method reported by Kassama and Misri,[26]. Accurately weighed extract loaded microparticles equivalent to ~ 1mg and 0.5mg of free extract and empty particles as control were placed in a predetermined 20ml of Cr(VI) solution (5mg/L). The system was maintained at a predetermined condition of room temperature, acidic and neutral pH, and time. The aliquots of 1.5ml were collected after shaking the dissolution flask at regular time intervals (1-4hours) and residual Cr(VI) quantified using 1, 5- diphenylcarbazide method. The absorbance was measured at 540nm by using a UV spectrophotometer.

Determination of Cr(VI) Reduction by Microparticles in Contaminated Soil Model

The method described by Okello et al.[27] was used to determine the reduction of Cr(VI) in contaminated soil model. Accurately, 3 g of finely ground soil was mixed with 6 ml of Cr(VI) solution (5 mg/L) in an Erlenmeyer flask and kept for 2 hours prior to the reduction studies. Appropriate weight of the microparticles corresponding to 1mg and 0.5 tamarind extract were added to the mixture and shake. At different time intervals an aliquot of 1mL was withdrawn and added 9 mL of deionized water and centrifuged at 3500xg for 10 minute, 1mL supernatant was assayed for residual Cr (VI) concentration. This same procedure was also used on empty microparticles as a control.

Determination of Cr(VI) Reduction in Tannery Effluent

Chromium (VI) reduction capacity of microparticles in tannery effluent was determined based on the method reported by Kassama and Misri,[26]. Accurately weighed extract loaded microparticles equivalent to ~ 1mg and 0.5mg of extract and empty particles as control were placed in 20ml tannery effluent in a separate Erlenmeyer flask. The system was maintained at a predetermined condition of room temperature, acidic and neutral pH and time. The aliquots of 1.5ml were collected after shaking the dissolution flask at regular time intervals (1-4hours) and quantified for residual Cr(VI) concentration. This same procedure was repeated using empty microparticles as a control.

Determination of Cr(VI) Reduction in Contaminated Soil

The method described by Okello et al.[27] was used to determine the reduction of Cr(VI) in contaminated soil. Accurately, 3 g of finely ground contaminated soil was placed in an Erlenmeyer flask and kept for two days prior to the reduction studies. Appropriate weight of the microparticles corresponding to 1mg and 0.5 tamarind extract were added to the mixture and shake. At different time intervals an aliquot of 1mL was withdrawn and added 9 mL of deionized water and centrifuged at 3500xg for 10 minute, 1mL

supernatant was assayed for residual Cr (VI) concentration. This same procedure was repeated using empty microparticles as a control.

Statistical Analysis

All the experiments were carried out in triplicate and the results presented as mean ± SD.

Results

Characterization of Microparticles

Free and extract immobilized lignocellulosic microparticles were produced through a simple adsorption method and the particles depicted [Plate 1]. The microparticles are irregular in shape and morphology with a defined particle size range. The microparticles produced show a very efficient adsorption capacity and the particles shows high release kinetic constant and a lower half-life [Table 1].

Table 1
Physicochemical Characteristics of *Tamarindus indica* Methanolic Leaves Extract Loaded Microparticles.

CHARACTERISTICS	
Appearance/Morphology	Irregular
Average Diameter (µm)	100 - 43
Half life ($t_{1/2}$ (min^{-1}))	29.25
Adsorption Efficiency (%)	87.06 ± 0.26
Controlled Release Rate Constant (min^{-1})	2.4×10^{-2}
Correlation Coefficient (r^2)	0.740

Cr (VI) reduction by Immobilized Extract in Contaminated Water Model

Chromium (VI) reduction was carried-out with tamarindus indica methanolic leaves extract immobilized microparticles system on a simulated Cr(VI) contaminated water at pH 2 and 7 [Figures 1 and 2]. About 61.2 and 38.9% Cr(VI) reduction was achieved after 4hrs with 1mg and 0.5mg concentration of extract immobilized microparticles at pH 7. Whereas, the reduction reached 100% at pH 2 after 1hr for the two concentrations. In addition, insignificant reduction of Cr(VI) was also observed with empty microparticles at both neutral and acidic pHs examined.

Cr (VI) reduction by Immobilized Extract in Contaminated Soil Model

Chromium (VI) reduction was carried-out in a contaminated soil model with a known concentration of Cr (VI) at neutral and acidic pHs [Figures 3 and 4]. Cr(VI) reduction using the immobilized system is only slightly higher in lower pHs. About, 38.3% and 11.5% reduction was achieved using tamarind extract

immobilized microparticles after 4hrs at neutral pH. However, Cr(VI) reached 51.7 and 20.3% for 1mg and 0.5mg extract immobilized microparticles at acidic pH after 4hrs. Nearly, 10.5% reduction was achieved by the empty microparticles at acidic pH, while no reduction observed at neutral pH.

Cr (VI) reduction by Immobilized Extract in Tannery Effluent

Cr(VI) reduction using extract immobilized microparticles in tannery effluent was determined [Figures 7 and 8]. Cr(VI) reduction was about 50 and 60% at pH (6.7 and 2.0), 1mg/ml after 8hrs, and the same pattern was observed at lower concentration. The Cr(VI) reduction was continuously increasing until it became steady after 8hrs at both the concentrations.

Cr (VI) reduction by Immobilized Extract in Contaminated Soil

Chromium(VI) reduction was carried-out with tamarindus indica methanolic leaves extract microparticles immobilized system at pH 2 and 6.7 [Figures 5 and 6]. About 60 and 80% Cr(VI) reduction was achieved after after 8hrs and 6hrs using at pH 6.7 and 2.0 and optimized condition of 45 oC and pH (2.0), respectively. The reduction pattern was concentration-dependent with control having little or negligible reduction.

Discussion

The mechanisms of redox interactions between Cr(VI) and antioxidants have been characterized and it involved a rapid pre-oxidative equilibrium forming chromate ester intermediates[9,28]. The chromate ester decomposes with a concomitant transfer of three electrons to the Cr(VI) center [29], although, literature has established the general mechanism of anti-oxidation by phenolics through single electron transfer reaction[30]. In this work, immobilization of extract was carried-out in order to preserve the stability of bioactive compounds, prevent undesirable interactions due to environmental factors and also promote a controlled release of the encapsulated compounds [31]. Cr(VI) reduction by free extract was sharp at first 2hrs and attained steady state after 8hrs at both pHs. This pattern was similar to the findings of Dubey et al.[32] and Okello et al.[27], they reported Cr(VI) reduction using Sorbaria sorbifolia aqueous leaf extract and quercetin derivatives, respectively. The decline in Cr(VI) reduction observed after 8hrs at pH 2.0 could be due to complete exhaustions of the available reducing groups presence in tamarind extract. Equally, tamarind extract efficiency could be affected due to interactions with other components of the reaction medium or processing conditions. Comparable patterns of Cr(VI) reduction achieved using immobilized microparticles could be attributed to the controlled release and stability of the extract provided by immobilization technique. This is in agreement with the suggestion of Qi et al.[33], they reported similar findings using microcapsules loaded with rutin-Cr(III) complex for the treatment of Cr(VI) contaminated wastewater. Less pronounced reduction noticed with free extract in contaminated soil at pH of 6.7 could be due to the effects of many other soil component. This coincide with a study by Brose and James,[34] and Okello et al. [27], they reported Cr(VI) reduction using a mixed tartaric acid, isopropyl alcohol and Mn(II), and quercetin derivatives with palladium nanoparticles as a catalyst, respectively. In another work,

Thierno et al.[35], indicated on the influence of soil organic matter on Cr(VI) reduction using iron nanoparticles. While, the excellent reduction observed by microparticles under both pHs indicated sustained extract release and stability of the active compounds present in tamarind extract. Other soil components may also play significant role in potentiating the reduction reaction. This agrees with the outcomes of a work carried out by Christiana et al.[36], they use nano irons synthesized from five plant extract and juice. Christiana suggested that the higher Cr(VI) reduction than anticipated observed in their work could be due to the contribution of other coexisting substances in the suspension. Banks et al.[37], suggested that conversion of Cr(VI) to Cr(III) can be potentiated by inorganic, organic, or biological agents present in soil. The increase in Cr(VI) reduction from 4hrs to 8hrs is a useful indication that the rate of extract release is gradual and the activity retain for longer period. It further confirmed the stability of immobilized extract and the excellent role of immobilization techniques in Cr(VI) remediation from contaminated soil and tannery effluent. Insignificant Cr(VI) reduction observed from the empty particles may resulted from the functional group attached to the cellulose polymer or diminutive adsorption mechanism. This is because the particles were also reported as good biosorbent in heavy metals adsorption studies[38–40]. Christiana et al.[36] affirmed this claim in their work using nanoirons synthesized from five plant extract and juice, that higher Cr(VI) reduction than anticipated could be due to the contribution of other co-existing substance in the suspension. Comparatively, a steady increase in Cr(VI) reduction by microparticles at the beginning of the reaction could be due its high extract release rate. This outcome is consistent with the observation of Mystrioti and Xenidis,[36], they explain this gradual decline in the performance of green tea synthesized nZVI (Zinc nanoparticle) as a kinetic limitation.

Conclusion

Microparticles immobilized extract were synthesized and examined to be irregular in shape. Cr(VI) reduction by immobilized tamarindus indica methanolic leaves extract in tannery effluent and contaminated soil was carried out. This research has demonstrated that Cr(VI) reduction was highest in contaminated soil indicated by a higher efficacy. Therefore, tamarind extract immobilization proved efficient in sustaining Cr(VI) reduction and further facilitating the reduction mechanism. Findings from this studies could be of utmost importance in industrial waste water treatment and environmental land cleanliness.

Declarations

Ethics approval and consent to participate

Not applicable

Consent for publication

Not applicable

Availability of data and materials

All data generated during this study are included in this published article

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Authors' contributions

B S; Laboratory, Data Collection and Analysis, Manuscript preparation and Corrections

A M; Design, manuscript corrections and supervision

A A; Laboratory, Data analysis, and manuscript preparation

A B S; Concept and design of the work and supervision

All authors read and approved the final manuscript.

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Figures

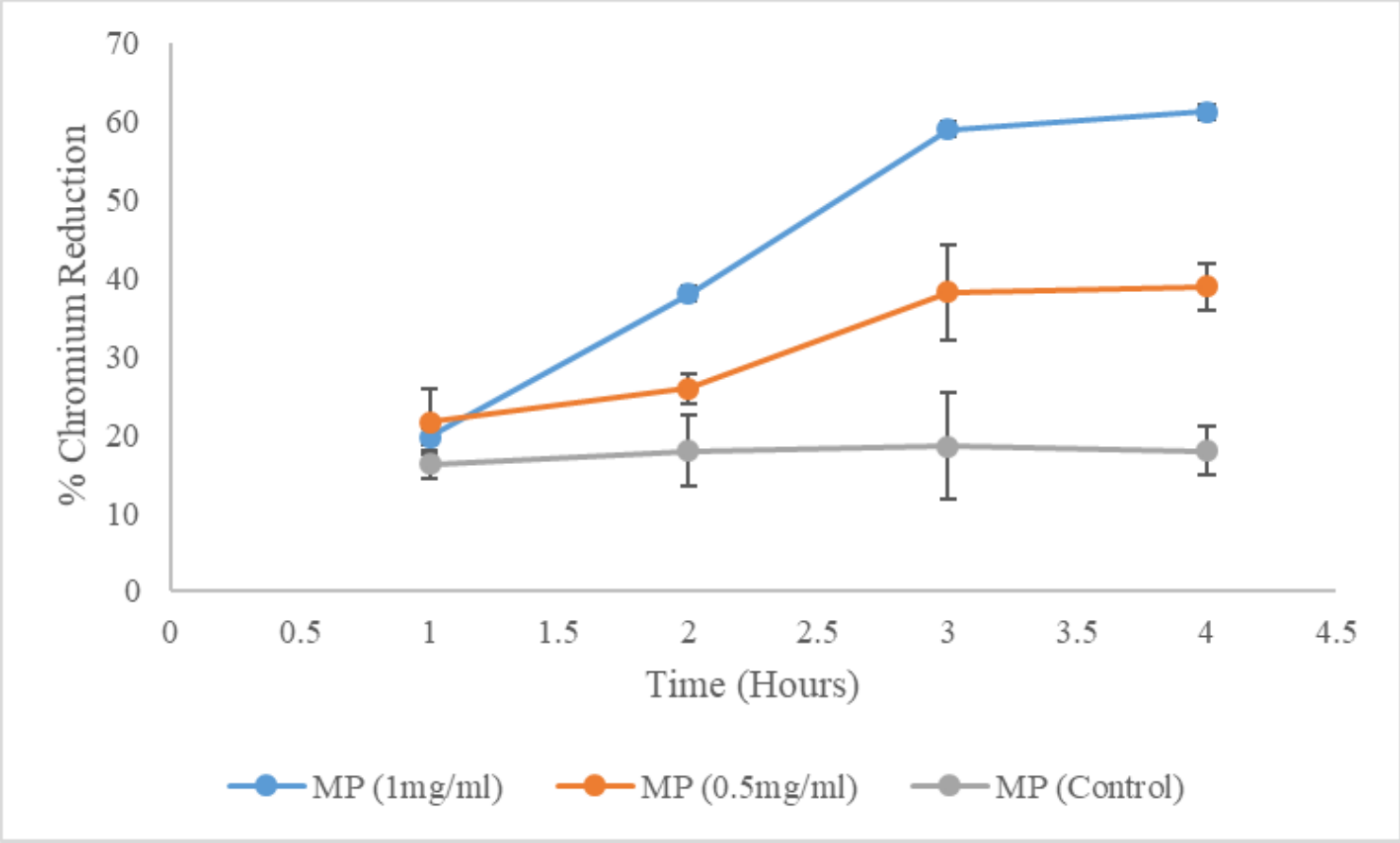

Figure 1

Cr (VI) Bioremediation Potential of Tamarindus indica Methanolic Leaves Extract Immobilized Microparticles in Cr (VI) contaminated Water model at pH 7, Temperature = 25oC, Cr (VI) Concentration = 5mg/L.

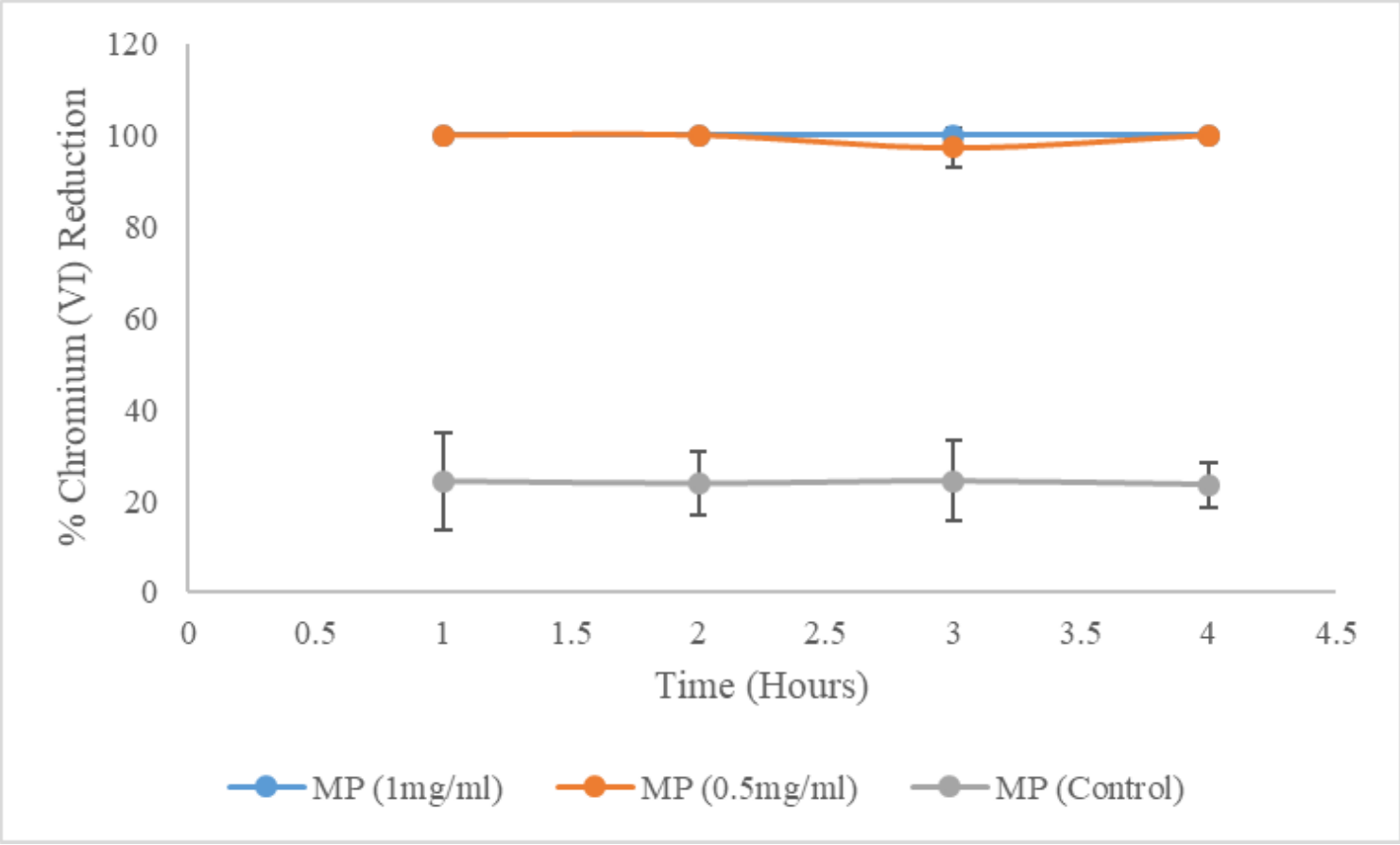

Figure 2

Cr (VI) Bioremediation Potential of Tamarindus indica Methanolic Leaves Extract Immobilized Microparticles in Cr (VI) contaminated Water model at pH 2, Temperature = 45oC, Cr (VI) Concentration = 5mg/L.

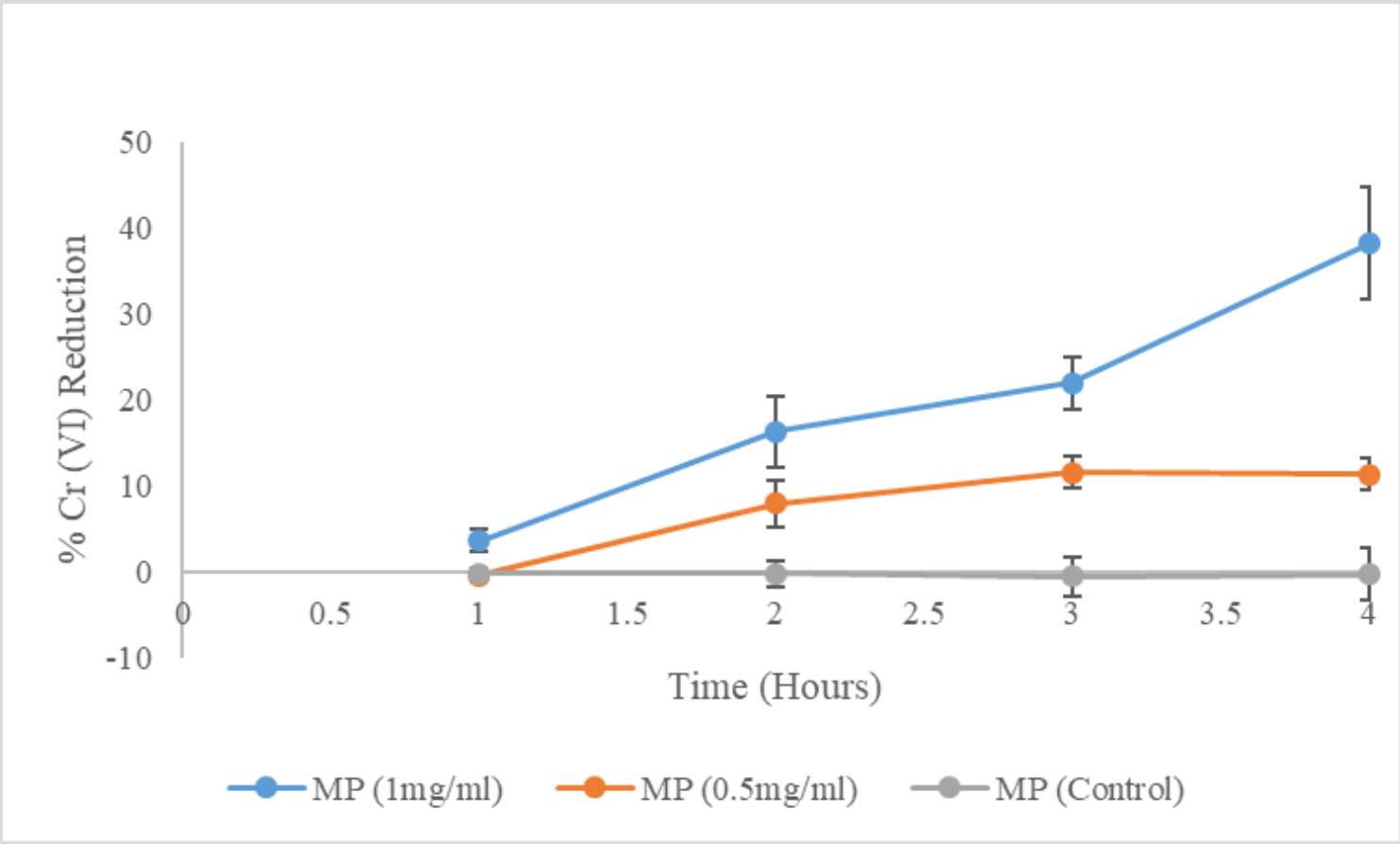

Figure 3

Cr (VI) Bioremediation Potential of Tamarindus indica Methanolic Leaves Extract Immobilized Microparticles in Cr (VI) contaminated Soil model at pH 7, Temperature = 25oC, Cr (VI) Concentration = 5mg/L.

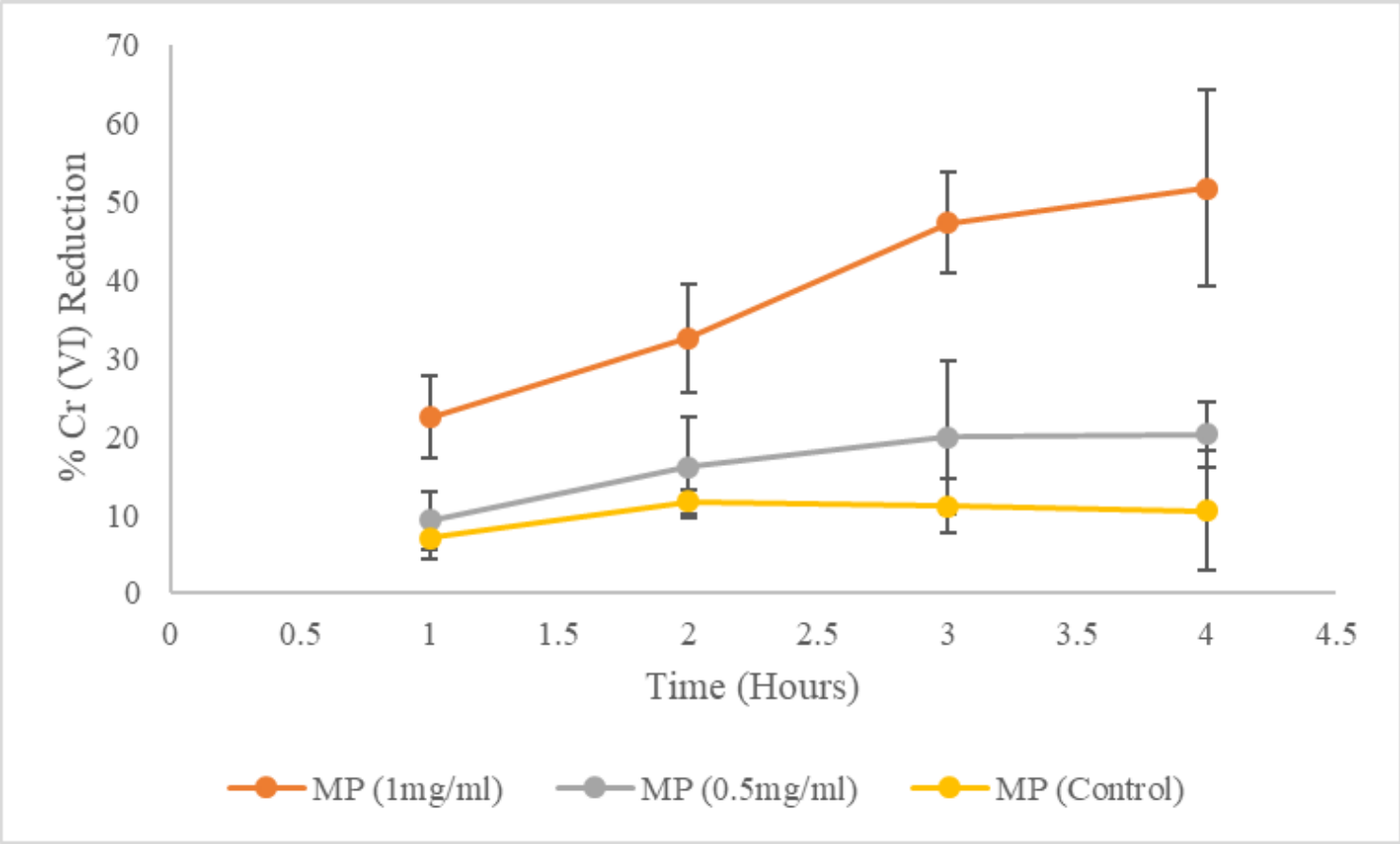

Figure 4

Cr (VI) Bioremediation Potential of Tamarindus indica Methanolic Leaves Extract Immobilized Microparticles in Cr (VI) contaminated Soil model at pH 2, Temperature = 45oC, Cr (VI) Concentration = 5mg/L.

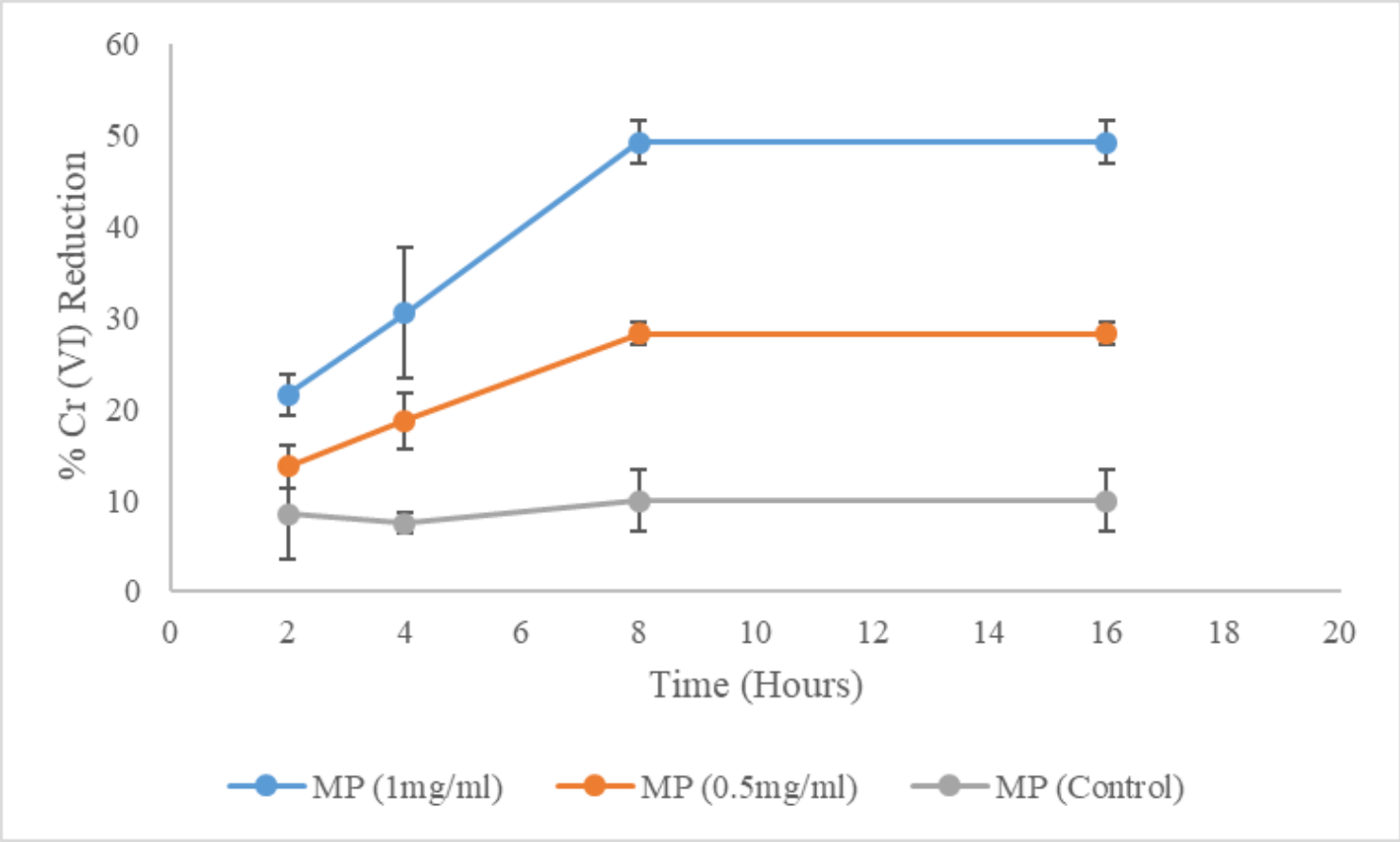

Figure 5

Cr (VI) Bioremediation Potential of Tamarindus indica Methanolic Leaves Extract Immobilized Microparticles on Tannery Effluent at pH 6.7, Temperature = 25oC, Cr (VI) Concentration = 23.1mg/L.

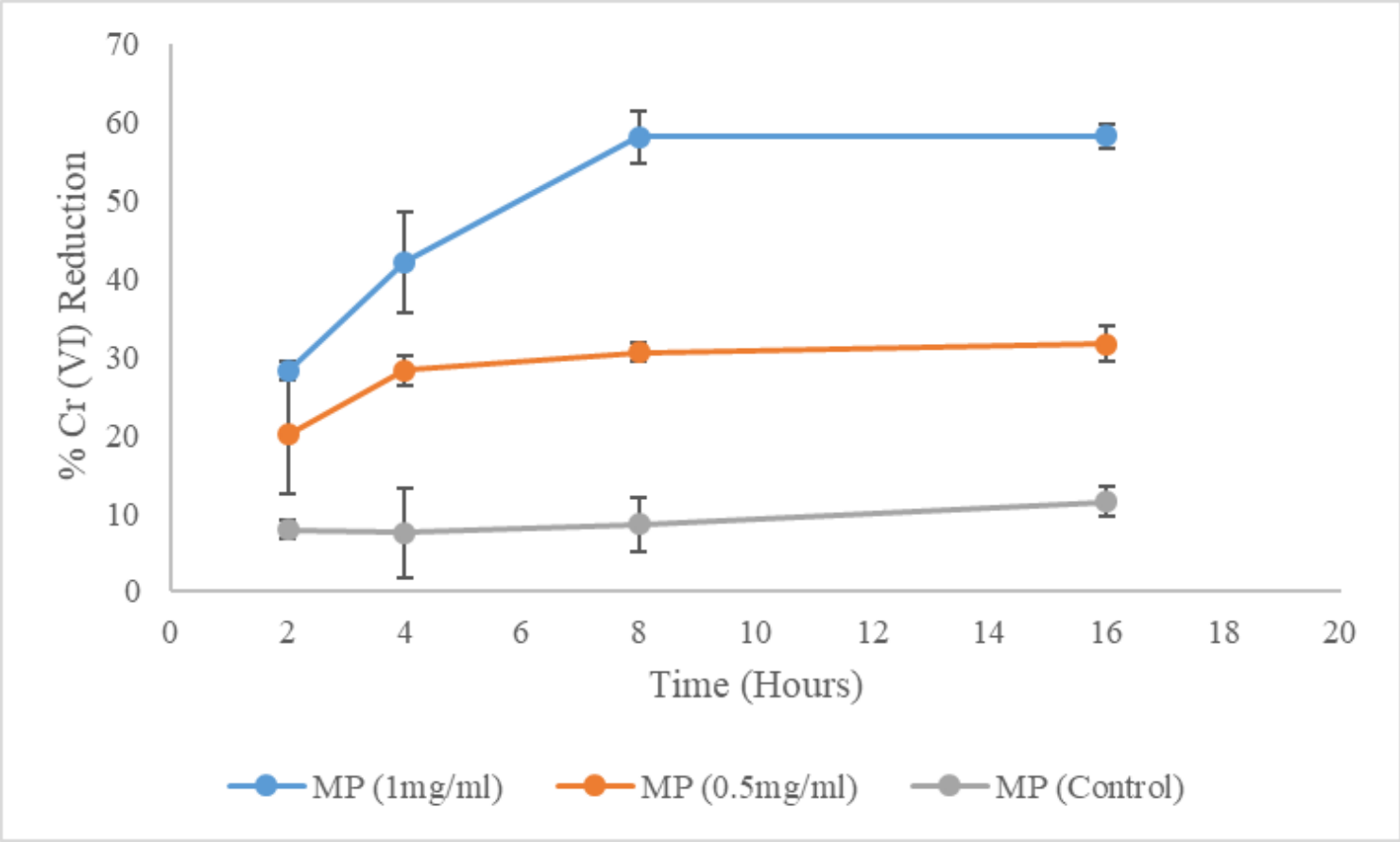

Figure 6

Cr (VI) Bioremediation Potential of Tamarindus indica Methanolic Leaves Extract Immobilized Microparticles on Tannery Effluent at pH 2.0, Temperature = 45oC, Cr (VI) Concentration = 23.1mg/L.

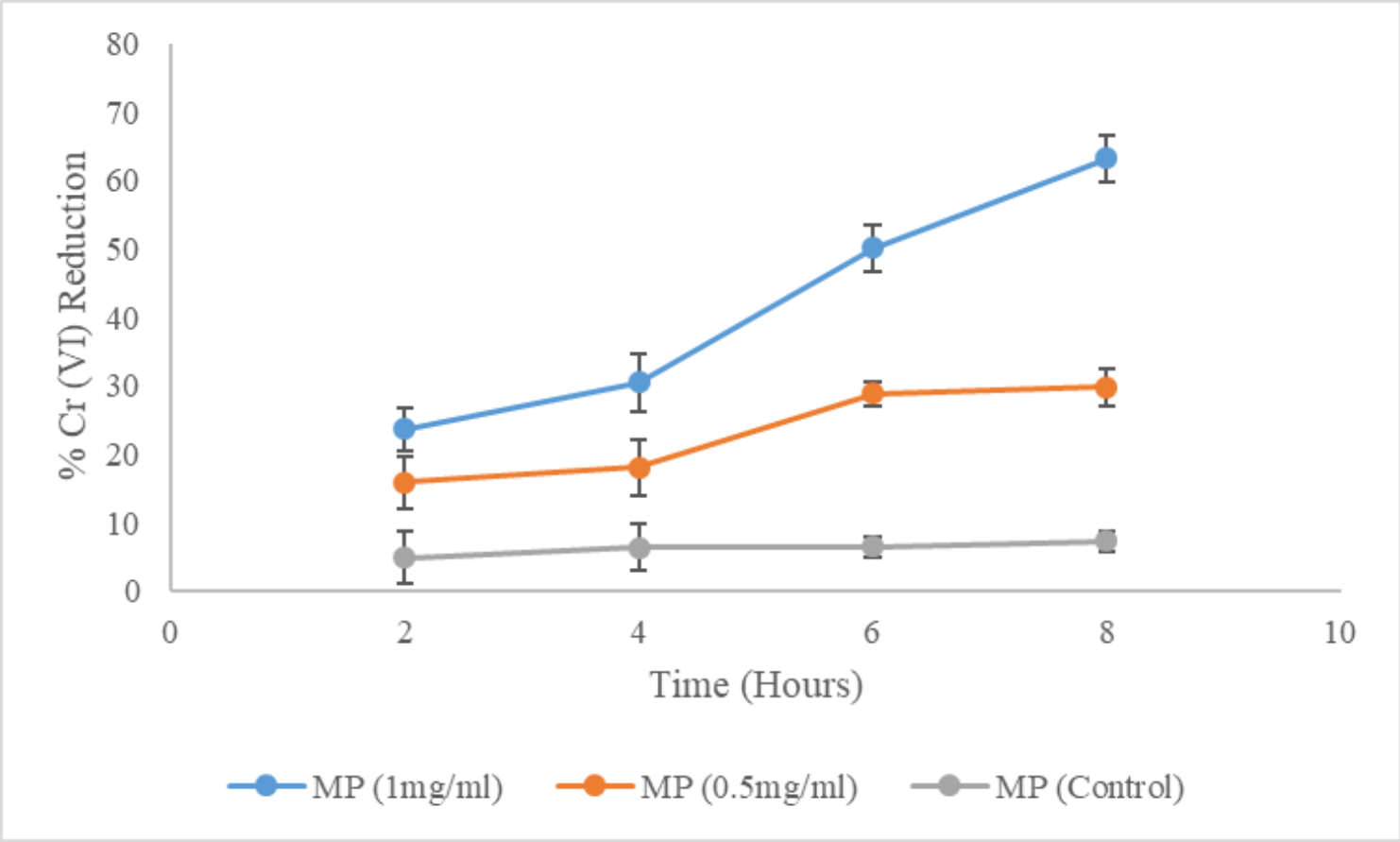

Figure 7

Cr (VI) Bioremediation Potential of Tamarindus indica Methanolic Leaves Extract Immobilized Microparticles on Contaminated Soil at pH 6.7, Temperature = 25oC, Cr (VI) Concentration = 14.6mg/L.

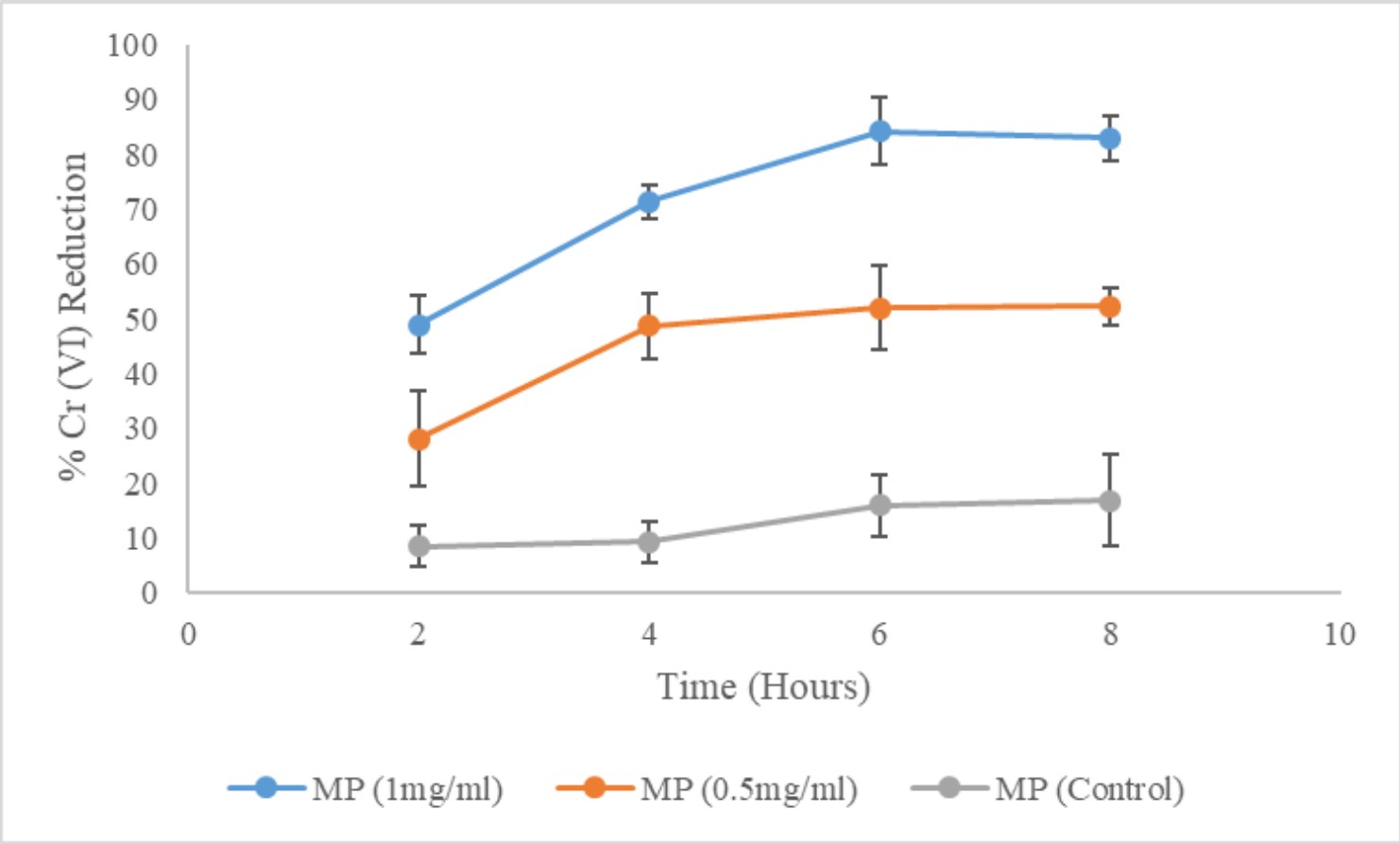

Figure 8

Cr (VI) Bioremediation Potential of Tamarindus indica Methanolic Leaves Extract immobilized Microparticles on Contaminated Soil at pH 2.0, Temperature = 45oC, Cr (VI) Concentration = 14.6mg/L.

Supplementary Files

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