



Physicochemical characterisation of nickel electroplating effluent before and after treatment with dead *Aspergillus niger*

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Article info

Article history:
Received 24 NOV 2015
Accepted 09 DEC 2015

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Abstract

Nickel electroplating effluent is of large scale environmental concern because the nickel diminishes the quality of water bodies into which they are released. The ability of microorganisms found in natural habitat constantly exposed to electroplating effluent can be recognized and exploited in biotreatment process. The physicochemical parameters viz., colour, odour, pH, electrical conductivity, TDS, TSS, TH, BOD, COD, calcium, magnesium, chloride, sulphate, phosphate, oil and grease and nickel were evaluated before and after treatment with the heavy metal tolerant *Aspergillus niger*. The results revealed that the level of physicochemical parameters in untreated nickel electroplating effluent was found to be above the permissible limits prescribed by BIS. The amount of nickel present in untreated electroplating effluent exceeded the limit prescribed by BIS (3 mg/l) whereas in the effluent inoculated with *Aspergillus niger* the level of nickel decreased. Thus the present study provides an environment clean up technology in such a way that the treated nickel electroplating effluent meets the permissible limits so that it can be reused for agricultural purposes.

Keywords: Nickel electroplating effluent, *Aspergillus niger*, physicochemical parameters

INTRODUCTION

Heavy metal contamination of waste water is an environmental enigma and removal of these toxic and persistent contaminants is highly imperative as they get biomagnified along the trophic level [1]. Electroplating industry is one of the major contributors of heavy metal pollution in surface water and this process involves metals such as cadmium, chromium, nickel, zinc and their compounds [2]. Nickel is one of the most important essential elements and it occurs most abundantly in the earth's crust. It is used in the manufacturing processes of stainless steel, ore refining, pigments, batteries, petroleum, food processing, plumbing, alloys and in electroplating [3].

Though nickel is an essential element required for the healthy growth of plants, animals and soil microbes, its excess affects the photosynthetic functions of higher plants, causes acute and chronic diseases in humans and reduces the soil fertility [4]. In recent years, the extent of nickel pollution has been recognized evoking the attention of many researchers on its removal from the environment through efficient means [5].

Various physicochemical processes such as precipitation, sludge separation, oxidation, reduction, ion exchange, reverse osmosis, electrochemical treatment and evaporation were used in the removal of metals from aqueous solution before they are disposed off. The major disadvantage is the production of sludge, expensive and not ecofriendly [6].

Bioremediation is an emerging technology which is gaining more attention among the environmentalists, for the removal of heavy metals using microorganisms. Further, it is cost effective and economical to the environment [7]. Hence, an attempt has been made in the present study to analyse the physicochemical characteristics of the nickel electroplating effluent treated with *Aspergillus niger*.

MATERIALS AND METHODS

Sample Collection

Fifty litres of the raw nickel electroplating effluent sample was collected in clean plastic cans from nickel electroplating industry located at Siddhapudur in Coimbatore district, Tamil Nadu, for physicochemical analysis. The effluent collected was stored at 4°C for further studies.

Physicochemical analysis

The nickel electroplating effluent was subjected to various physicochemical analyses. The physical and chemical parameters such as colour, odour, turbidity, pH, electrical conductivity, total suspended solids, total dissolved solids, chemical oxygen demand, total hardness, total alkalinity, sulphates, phosphates, ammoniacal nitrogen, calcium, magnesium, nickel, oil and grease [8], biological oxygen demand [9], sodium and potassium [10] and chlorides [11] were analysed in the untreated and treated effluent.

Metal analysis

To 50 ml of the effluent, 25 ml of 3:2:1 triple acid mixture (conc. nitric acid - conc. perchloric acid - conc. sulphuric acid) was added and kept aside for 3 - 4 hours in a fume cupboard. The contents were heated for 30 minutes until vigorous reaction had subsided and heated more strongly for 4 hours until the nitrous fumes are removed and white fumes of perchloric acid are evolved. The contents were allowed to cool and transferred with 3 - 4 washings of deionized water to 50 ml volumetric flask and made up to the mark with water. Aliquot of the samples were taken for the estimation of heavy metal [12].

Source of organism and culture

The fungus *Aspergillus niger* was isolated from the effluent contaminated soil sample and cultured in Rose Bengal Chloramphenicol medium in Erlenmeyer flasks at pH 5, at 30°C for 7 days. The fungus was obtained in mats and maintained for further analysis on the effluent samples. The obtained fungal biomass was autoclaved at 121°C for 20 minutes. Excess water was drained off after sterilization and the wet biomass was dried at 37 - 40°C for 4 - 5 days until moisture content was removed. Flakes of dry fungal biomass were crushed in a mortar and pestle and the powdered biomass was considered as "dead biomass" for the present study [13]. 10 g of the dead fungal biomass was inoculated into 1000ml of nickel electroplating effluent and incubated at room temperature for 5 days. At the end of the incubation period, the samples were removed, centrifuged at 5000 rpm for 10 minutes at 4°C and the supernatants was taken for physicochemical analysis [14].

RESULTS AND DISCUSSION

Physical characteristics of raw and microbially treated nickel electroplating effluent

The results of the physical parameters analysed in raw and microbially treated nickel electroplating effluent are shown in Table I.

Colour and odour - It was observed from the Table I that the colour of the raw effluent was appeared to be green with an unpleasant odour and that of microbially treated nickel electroplating effluent was colourless and odourless. The presence of colour is aesthetically undesirable and it increases the BOD and COD which leads to insufficient availability of oxygen to sustain aquatic life [15]. The colour intensity of the effluent may depend on the pollutants that enter into it [16]. Industrial wastes usually have their characteristic odour due to the presence of a large variety of contaminants or chemicals. Chlorine, added for disinfection of waters, may combine with certain impurities like phenolic compounds to produce high unpleasant odour [17]. The results of the present study is in accordance with the findings of [18] who observed a maximum colour removal in the dye factory effluent treated with the species of *Aspergillus*, *Phanerochaete* and *Trametes*.

Turbidity - The raw nickel electroplating effluent was observed to be turbid whereas the treated nickel electroplating effluent was clear. The turbidity of the raw effluent might be due to the discharge of large amounts of solids such as carbonates, bicarbonates, chlorides, sulphates, calcium and magnesium which are extensively used in the electroplating process.

pH - The pH of the raw nickel electroplating effluent examined was 9.5 which exceeded the tolerance limits of 5.5-9.0 prescribed by the Bureau of Indian Standards. The pH of the treated nickel electroplating effluent was found to be 7.9 which fall within the limits specified by BIS. Higher pH was also reported by [19] when they analysed zinc electroplating effluent and their findings are in accordance with the present study. High pH in untreated fertilizer effluent was reported by [20] which after treatment with *Aspergillus niger* and *Phanerochaete chrysosporium* showed a decrease. Similar such decrease was also observed in the present study in microbially treated nickel electroplating effluent.

Electrical Conductivity (EC) - The electrical conductivity of the raw nickel electroplating effluent recorded a maximum of 5.32 mmhos / cm and that recorded in microbially treated nickel electroplating effluent was a minimum of 1.2 mmhos / cm. Higher EC in raw effluent indicates the presence of high amount of ionic substances.

A high EC value was recorded in the zinc electroplating effluent which is a supportive evidence for the present study [19]. A reduction in the electrical conductivity was observed by treating the raw textile dyeing effluent with fungal systems [21]. Similar reduction was also recorded in the present study in microbially treated nickel electroplating effluent.

Total Suspended Solids (TSS) - TSS recorded in the raw nickel electroplating effluent of the present study was 600 mg / l which is six times greater than the tolerance limits prescribed by the Bureau of Indian Standards (100 mg / l) whereas it was 87 mg / l in the microbially treated nickel electroplating effluent which satisfies the specified limits of BIS. While analysing the metal finishing and plating industry waste waters [22] also reported a high amount of total suspended solids. Higher amount of total suspended solids may elevate the density and turbidity of water, which in turn may affect the osmoregulation. Higher levels of TSS may also interfere with the photosynthesis by preventing sunlight [23]. Total suspended solids when exceeding the limits are aesthetically unsatisfactory and may cause distress among human beings and livestock [24]. High TSS level found in the raw nickel electroplating effluent in the present study was reduced after treatment with *A. niger*. Similar reduction in TSS was also reported [25] in sugar factory effluent which was treated with *A. niger*.

Total Dissolved Solids (TDS) - The amount of total dissolved salts present in the raw nickel electroplating effluent was recorded as 3200 mg / l which exceeded the tolerance limits (2100 mg / l) prescribed by the Bureau of Indian Standards (BIS) and that of microbially treated nickel electroplating effluent was only 1610 mg / l which was within the tolerance limits prescribed by BIS. Higher value of total dissolved solids is attributed to the presence of colloidal or finely divided suspended matter which does not readily settle. The presence of

colloidal or finely divided suspended matter may be due to the direct discharge of solid wastes and construction activities around the catchment areas [26].

TABLE I. PHYSICAL CHARACTERISTICS OF THE RAW AND MICROBIAALLY TREATED NICKEL ELECTROPLATING EFFLUENT

Parameters	Nickel electroplating effluent		Tolerance limits 2490 – 1981 #
	Raw	Microbially Treated	
Colour	Green	Pale green to colourless	-
Odour	Unpleasant odour	Odourless	Odourless
Turbidity	Turbid	Clear	-
pH	9.5	7.9	5.5 to 9.0
Electrical conductivity (mmhos/cm)	5.32	1.2	-
Total Suspended Solids (mg / l)	600	87	100
Total Dissolved Solids (mg / l)	3200	1610	2100

Tolerance limits for industrial effluents discharged into in land surface waters prescribed by the Bureau of Indian standards (BIS).

High amount of TDS was also reported in zinc electroplating industrial effluent [27] which was in agreement with the present study. The reduction of TDS in the effluent treated with *A. niger* in the present investigation is in accordance with the study conducted by [28] who reported a maximum reduction of TDS in the textile effluent treated with the dead biomass of *Saccharomyces cerevisiae*, *Aspergillus terreus* and *Rhizopus oligosporus*.

Chemical characteristics of raw and microbially treated nickel electroplating effluent

Table II presents the results of chemical parameters analysed in the raw and microbially treated nickel electroplating effluent.

Biochemical Oxygen Demand (BOD) -The biochemical oxygen demand in the raw nickel electroplating effluent was nil whereas in microbially treated effluent, it was found to be 24 mg / l which falls within the tolerance limits (30 mg / l) set by Bureau of Indian Standards

for the discharge of effluents in inland surface waters. The reduction in BOD was also reported in fertilizer effluent treated with *A. niger* and *Phanerochaete chrysosporium* [20] and dye effluent treated with the species of *Aspergillus*, *Rhizopus* and *Geotrichum* [29]. The results of the present study were found to be in accordance with these reports.

TABLE II. CHEMICAL CHARACTERISTICS OF RAW AND MICROBIALLY TREATED NICKEL ELECTROPLATING EFFLUENT

Parameters	Nickel electroplating effluent		Tolerance limits 2490 – 1981 #
	Raw	Microbially treated	
Biochemical Oxygen Demand (BOD)	-	24	30
Chemical Oxygen Demand (COD)	1502	203	250
Total hardness	2729	196	-
Anions			
Total alkalinity	672	185	-
Chlorides	2749	543	600
Sulphates	1449	833	1000
Phosphates	11	3	-
Ammoniacal nitrogen	81	31	50
Cations			
Calcium	273	56	-
Magnesium	255	34	-
Sodium	98	16	-
Potassium	43	7	-
Nickel	126	2	3
Oil and grease	28	7	10

All the values are expressed in mg / l

Tolerance limits for industrial effluents discharged into in land surface waters prescribed by the Bureau of Indian standards (BIS).

Chemical Oxygen Demand (COD) - The chemical oxygen demand estimated in the raw nickel electroplating effluent was 1502 mg / l and this was found to be about six times greater than the tolerance limit (250mg / l) prescribed by the Bureau of Indian Standards. The value of COD in microbially treated nickel electroplating effluent was 203 mg / l which was within the permissible limits of BIS. Increase in COD was also reported by [30] in river samples where the electroplating effluent was discharged. When the water with high level of COD percolates into the ground they may affect the ecosystem. The reduction in COD was also

reported in paper mill effluent treated with *A.niger* [31] and *Trichoderma versicolor* [32] which support the findings of the present investigation.

Total Hardness - Hardness of water is mainly due to the presence of calcium and magnesium ions, and is an important indicator of the toxic effect of poisonous elements [33]. The total hardness recorded in raw nickel electroplating effluent was 2729 mg/l whereas it was recorded as 196 mg/l in microbially treated nickel electroplating effluent. Studies conducted by [34] in sugarcane industrial effluent also showed high total hardness which may support the present investigation. Hardness may be due to the presence of multivalent metal ions and the minerals dissolved in water. It has no hazardous effect but it increases the boiling point of water and inhibits lather formation with soap and causes scale formation in utensils [35]. The results of the nickel electroplating effluent treated with *A. niger* is in accordance with the findings of [36] who reported the reduction of total hardness in the textile dyeing effluent treated with water hyacinth.

Anions {total alkalinity, chlorides, sulphates, phosphates and ammoniacal nitrogen}

Table II shows that the level of anions tested was greater in raw nickel electroplating effluent when compared to microbially treated nickel electroplating effluent.

The level of total alkalinity estimated in the raw nickel electroplating effluent was 672 mg/l whereas the value recorded in microbially treated nickel electroplating effluent was 185 mg/l. A higher level of total alkalinity was recorded in the dye factory effluent [21] which may support the results of the present study. Alkaline cleaning to remove oil and grease is a common practice prior to plating process. The cleaners contain carbonates, silicates, bicarbonates and phosphates which could have accounted for the increased level of total alkalinity in the effluent.

The concentration of chlorides in raw nickel electroplating effluent was 2749 mg/l which is almost three times higher than the prescribed limit (600 mg/l) of BIS whereas that estimated in microbially treated nickel electroplating effluent was only 543 mg/l. Higher amount of chlorides was also reported in distillery effluent [37]. Large amounts of chlorides in the water leads to corrosiveness and may adversely affect water quality [38]. Excess amount of chlorides in the effluent when discharged into the soil, may not be absorbed by the soil but they may move readily with soil water and are taken up by the crops and move in transpiration stream. When they get accumulated in the leaves, they may develop burns or drying off leaf tissue or even cause damages in the crops [39].

Sulphate is yet another parameter that has shown its contamination reporting 1449 mg/l in raw nickel electroplating effluent as against 1000 mg/l given by BIS. The amount of sulphates estimated in microbially treated nickel electroplating effluent was 833 mg/l which falls within the tolerance limits. High level of sulphates were also reported by [40] in electroplating industry effluent. High concentration of sulphates may be harmful

to seedling stage and maturity of the plant [41]. High amount of sulphates may cause laxative effect, diarrhoea and disorders of alimentary canal in human beings [42]. Less amount of sulphates present in the microbially treated effluent may corroborate with the results of [43] who observed the removal of sulphate in higher level from the paper mill effluent using *Oscillatoria perornata* and *Scenedesmus quadricauda*.

The phosphate content in the raw nickel electroplating effluent was recorded as 11 mg/l whereas it was estimated as 3 mg/l in microbially treated nickel electroplating effluent. An increase in phosphate content was also reported in distillery effluent [44] which may be a supporting evidence for the present investigation. Removal of maximum amount of phosphates from domestic sewage was reported [45] using the fungi *Trichothecium roseum*, *Cladosporium cladosporioides* and *Fusarium oxysporum* which supports the results of present study.

Ammoniacal nitrogen estimated in the raw nickel electroplating effluent was found to be 81 mg/l. The amount recorded in microbially treated nickel electroplating effluent was 31 mg/l which was within the tolerance limits (50 mg/l) prescribed by BIS. It was also reported by [46] that in polluted waters, ammonia generally arises from the aerobic and anaerobic decomposition of the nitrogenous organic matter.

Higher levels of total alkalinity, chlorides, sulphates, phosphates and ammoniacal nitrates in dye effluent were found to be lower when treated with species of *Aspergillus*, *Rhizopus* and *Geotrichum* species [29]. Studies conducted by [47] on the removal of excess amount of ammoniacal nitrogen and phosphate present in the aquaculture waste water by using an alga *Enteromorpha flexuosa* may also support the present study.

Cations (calcium, magnesium, sodium, potassium and nickel)

The levels of calcium, magnesium, sodium, potassium and nickel estimated in the raw and microbially treated nickel electroplating effluent are presented in Table III.

The level of calcium, magnesium, sodium and potassium recorded in the raw nickel electroplating effluent were 273 mg/l, 255 mg/l, 98 mg/l and 43 mg/l respectively, whereas in microbially treated nickel electroplating effluent, the levels decreased. High levels of calcium and magnesium were also reported in tannery effluent [48] and in chromium electroplating effluent [49]. Excessive amount of calcium may cause problems related to urinary tract in human beings [50]. Higher concentration of magnesium results into encrustation of water supply structures and has an adverse effect on domestic use [51]. Higher amount of sodium and potassium were also reported in tannery effluent [52] and in zinc electroplating industrial effluent [27]. Plating baths contain metal salts, acids, alkalis, ammonia, sodium and potassium as common cationic constituents which brighten the plating surface. This might be the reason for the increased levels of sodium, potassium and other cations in the electroplating industry effluents.

A significant reduction in the level of sodium, potassium, calcium and magnesium was observed in the paper mill effluent treated with *Westiellopsis prolifica* [53] and this may be in accordance with the present study.

The level of nickel recorded in the effluent was 126 mg/l which exceeded the tolerance limit of 3 mg/l stipulated by the Bureau of Indian Standards. The nickel content in the microbially treated nickel electroplating effluent was estimated as 2 mg/l which was within the permissible limits prescribed by BIS. Higher level of nickel in the effluent may be due to the usage of nickel in the electroplating process which might have been let out in the spent water. Higher nickel content was also reported [54] in the industrial effluent of Kalyan-Dombivali (Maharashtra) and in nickel electroplating industrial effluent [55]. Excess quantities of nickel thrown into the biosphere might result in pollution hazards to the habitat in that area. Similar to the present investigation removal of excess amount of copper and nickel from the electroplating effluent using *A.niger* was also reported by [56]. Higher amount of copper and zinc was reduced by *A. niger* in metal bearing effluent [57].

Oil and grease

The amount of oil and grease estimated in the raw nickel electroplating effluent was 28 mg/l which was higher than the permissible limits of Bureau of Indian Standards (10 mg/l). In the microbially treated nickel electroplating effluent, the amount of oil and grease was found to be 7 mg/l which was within the tolerance limits. Oil is applied as lubricating medium in the machineries and also present as a surface active agent. [58] observed a high level of oil and grease in automobile waste water. The amount of oil and grease in the dye effluent was reduced to a great extent when treated with species of *Aspergillus*, *Rhizopus* and *Geotrichum* [29] which may support the results of the present study.

Thus it can be concluded that *Aspergillus niger* can be used in removal of nickel from the electroplating effluent and thereby promotes a pollution free environment.

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