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Phytoremediation of nickel from the effluents of selected ghee industries of Khyber Pakhtunkhwa, Pakistan

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Abstract

Nickel is a known haemotoxic, hepatotoxic, pulmonary toxic, genotoxic, nephrotoxic, reproductive toxic, immunotoxic, neurotoxic and carcinogenic agent. To convert vegetable edible oil into ghee, nickel is used as a catalyst in hydrogenation process. The effluents flowing out from ghee industries contain nickel which contaminate environment. In the present study the effluent water, drains sediment and the plants which were growing along the drains carrying effluents of five ghee industries were analyzed. The concentration of Ni in mg/L in the ghee industries was in the order: Utman Ghee Industry, Gadoon, KPK (0.656) >Gulab Banaspathi, Jamroad Road, Peshawar (0.435) >Saqib Banaspathi, Jamroad Road, Peshawar (0.263) >TajPlus Ghee Industry, Skhakot, KPK (0.249) >Sher Banaspathi, Dargai, KPK (0.047). The highest concentration of nickel was present in the effluent water of Utman Ghee Industry, Gadoon, KPK. The concentration of Ni (mg/kg) in the drains carrying effluents of each industry was in the order: Taj Plus Ghee Industry, Skhakot, KPK (179.06) >Gulab Banaspathi, Jamroad Road, Peshawar (176.93) >Saqib Banaspathi, Jamroad Road, Peshawar (78.89) >Sher Banaspathi, Dargai, KPK (56.62) >Utman Ghee Industry, Gadoon, KPK (24. 38). The phytoextraction capacity of seventeen plants was studied which were growing along the drains carrying effluents of these industries. The calculation of bioconcentration factor (BCF) and translocation factor (TF) of the plants showed that six plants ((*Rumex nepalensis, Pimpinella saxifrage, Cyperus rotundus, Conyza Canadensis, Rumex hastatus* and *Saccharum spontaneum)* among these studied plants have feasibility for the phytoextraction of Ni metal.

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Introduction

Recently, in the entire cultural history, man has faced very unpleasant ecological crises, the problem of pollution of his environment which sometimes in past was undisturbed, virgin, pure, uncontaminated and quite suitable for him. Pollution is an undesirable alteration in the biological, physical or chemical characteristics of water, land and air that may harmfully affect living organisms. Every use to which water is put such as, irrigation, making paper, washing and cooling etc. adds pollutants to water. Lakes as well as rivers have been used as a site for depositing waste products and industrial effluents for centuries, most of them are highly poisonous. Solid waste products and chemicals are the main sources which contaminate soil (Verma *et al* 2005). In ghee industries, vegetable oil is converted into vegetable ghee by hydrogenation in the presence of nickel as a catalyst (Khan *et al* 2007). The effluents flowing out of ghee industries contain nickel metal. Its concentration reported in the effluents of Sohail vegetable ghee hayatabad peshawar was 0.88 mgL^{-1} (Tariq *et al* 2006). Natural sources of the atmospheric Ni are dusts from volcanic emission and weathering of rocks. In ambient air Ni level is small (approximately 6 to 20 $ng.m^{-3}$) but it could be present up to 150 $ng.m^{-3}$ in contaminated air. Uncontaminated water contains almost 300 ng $Ni.dm^{-3}$, farm soils contain about 3-1000 mg $Ni.kg^{-1}$, but the concentration of Ni metal can reach up to 24 000-53 000 $mg.kg^{-1}$ in soil located near metal refineries and in dried sludge (Denkhaus *et al* 2002). Nickel metal is carcinogenic to living organism (Smialowicz *et al* 1984). Nickel carcinogenicity depends on its chemical form, living organisms used, dose, route and period of exposure (USEPA 1980). Inhalation of nickel oxide and nickel sub-sulfide shows evidence of carcinogenicity in humans and other mammals (USEPA 1980). Metallic nickel and nickel carbonyl can cause cancer in experimental animals but their carcinogenicity in human beings is not leading to a firm conclusion (USPHS 1993). Some specific Ni compounds are weak mutagen but most of the evidence is negative (WHO 1991). The capacity of Ni compound to cause mutations is proportional to the cellular uptake of Ni (USPHS 1993). Ingestion or inhalation does not cause teratogenic effects in mammals except from nickel carbonyl (USEPA 1986).

The physico-chemical methods of soil remediation provide the land unsuitable for the growth of the plants because these methods seriously alter biological activities; they remove beneficial microbes i.e. fungi, useful bacteria, fauna in the process of decontamination and mycorrhiza (Burns *et al* 1996). The expenses of the conventional remediation techniques may be from $10 to $1000 per cubic meter while the expenses of Phytoextraction are estimated to be as less as $ 0.05 per cubic meter (Cunningham *et al* 1997). Phytoextraction is a best method for the removal of pollutants from the soil. In this method we can isolate the pollutants from the soil without destroying fertility and structure of the soil. It is also known as phytoaccumulation (USEPA 2000). Plant can absorb, concentrate and precipitate poisonous metals from polluted soils into its roots and shoots. Phytoaccumulation is suited best for the remediation of diffusely contaminated sites. In such sites contaminants occur merely superficially and at relatively low concentration (Rulkens 1998). In the present study the industrial effluents, industrial sediments as well as the plants growing along the drains carrying effluents of five ghee industries were analyzed for nickel metal and by calculating the bioconcentration factor and translocation factor of each plant deterymine their feasibility for phytoextraction.

Material and method

Ghee Industries

The selected ghee industries were,

1. Uthman Ghee Industry, GadonAmazai District Swabi
2. Sheer Ghee Industry, Dergai, District Malakand
3. Taj Ghee Industry, Sakhakot, District Malakand
4. Saqib Ghee Industry, Jamroad Road, Peshawar
5. Gulab Ghee Industry Jamroad road, Peshawar

Collection of Industrial Effluents and their analysis for Nickel

The collection of waste water at different points was made from each of the above five mentioned ghee industries. After that the collected waste water samples were filtered through filter paper and the obtained samples analyzed for nickel metal by Atomic Absorption Spectroscopy (AAS). Results are shown as mean ± SD.

Collection of Sediments and their Analysis for Nickel

Sediment were collected at three points (S1, S2 and S3) from drains carrying effluents of each of the above mentioned five ghee industries. Sediment samples were analyzed for the concentration of nickel metal according to Sharidah (1999) 5gram sample of the soil was taken in a 100 mL beaker. 3 mL of 30 % H_2O_2 was added to it. This was left undisturbed for 1 hour until the vigorous reaction was ceased. Then 75 mL of 0.5 M HCl solution were added to it and heated it on hot plate for 2 hours. The digested sample was then filtered through a Whatman filter paper. The filtrate was used for the determination of the concentration of heavy metal (Nickel) by atomic absorption spectrometry (AAS). The analysis was conducted in triplicate. Results are shown as mean ± SD.

Plant Collection, Identification and Drying

Various plant species growing inside or near Effluents were collected from each of the above mentioned ghee industries. The collected plants were dried in shade and mounted on herbarium sheets and then identified with the help of Flora of Pakistan or by matching with already identified specimens in the herbarium of department of Botany, Islamia College University Peshawar. The plant parts (root, stem and leaves) of each plant were separated. Samples were analyzed for nickel metal by Atomic absorption Spectroscopy (AAS).

Analysis of Accumulated Nickel Metal in Plant Samples

For this purpose, each plants part was thoroughly washed with tape water and then with distilled water in order to remove dust and soil particles. The clean plant parts were dried in an oven at 105°C for 24 hours. Then the samples were digested according to Awofolu (2005): 0.5 gram sample of the plant part was taken into a 100 mL beaker. 5 mL concentrated (65%) HNO_3 and 2 mL $HClO_4$ was added to it and heated on hot plate until the digest became clear. The digest was allowed to cool and then filtered through a Whatman filter paper. The filtrate was collected in a 50 mL volumetric (measuring) flask and diluted to the mark with distilled water. The filtrate obtained used for the analysis of heavy metal (Ni) by AAS (AAS-700, Perkin-Elmer, USA) using acetylene/air as gas mixture. The lamp wavelength (λ) for Ni was 232.0nm. As mentioned previously, each experiment was run in triplicate for each plant part. Results are shown as mean ± SD.

Bioconcentration and Translocation factor

Bioconcentration factor (BCF) indicates the efficiency of a plant in up-taking heavy metals from soil and accumulating them into its tissues. "It is a ratio of the heavy metal concentration in the plant tissue (root, stem or leaves) to that in soil." It is calculated as follows (Zhuang 2007)

$$\text{BCF}=\frac{\text{Harvested tissue}}{\text{C soil}}$$

where C harvested tissue is the concentration of nickel metal in the plant harvested tissue (roots, stem or leaves) and C *soil* is the concentration of the same metal in soil.

Translocation factor (TF) shows the efficiency of the plant in translocating the accumulated heavy metals from roots to shoots. "It is a ratio of the concentration of the heavy metal in shoots (stem or leaves) to that in its roots." It is calculated as follows (Padmavathiamm 2007 and Adesodun 2010)

$$\text{TF}=\frac{\text{C shoots}}{\text{C roots}}$$

Where as C shoots is the concentration of nickel metal in shoots (Stem and leaves) and *C roots* is the concentration of nickel metal in Roots.

Both bioconcentration factor and translocation factor of the studied plants for Ni metal was calculated according to the above two formulas. From these calculations the feasibility of the plants for the phytoextraction of nickel metal was analyzed. Experimental data were analyzed using SPSS 16.0. Results were compared using T Test and One-Way ANOVA (Tukey test).

Results and discussion

Concentration of Nickel Metal in Gee industries Effluents

Concentration of nickel metal found in the effluents of selected ghee Industries is given in Table 1. From Table.1, it is clear that the concentration of nickel metal in the Effluents of selected ghee industries in mg L^{-1} is in the order of: Utman Ghee Industry, (0.656) >Gulab Banaspathi, (0.435) >Saqib Banaspathi, (0.263) >TajPlus Ghee Industry, (0.249) >Sher Banaspathi, (0.047). Table 1 indicates that among the five studied ghee industries the highest concentration of Ni is present in the effluents of Utman Ghee Industry that is 0.656 mg L^{-1}. These effluents if continuously flowing out from ghee industries will increase the concentration of Ni in aquatic ecosystem. Cempel and Nikel (Cempel 2006) stated that, drinking water generally contains nickel at concentrations less than 10µg/l. The present results shows that the industrial Effluent water contain high concentration of Ni as compare to the normal level in drinking water. These Effluents will cause damage to aquatic life.

Table 1. Ni concentration in ghee industries' effluents.

S.No	Industry Name	Ni concentration (mg L^{-1})
1	Taj Plus Ghee Industry, Skhakot, KP	0.249±0.099495
2	SherBanaspathi, Dargai, KP	0.047±0.178627
3	SaqibBanaspathi, Jamroad Road, Peshawar	0.263±0.129822
4	GulabBanaspathi, Jamroad Road, Peshawar	0.435±0.194844
5	Utman Ghee Industry, Gadoon, KP	0.656±0.109087

Results are mean of five independent experiments ± SD.

Concentration of Nickel in Ghee Industries' Drains sediments

Concentration of nickel metal found in the drains' sediments of selected ghee industries is given in Table 2. The valves in table 3.2 indicates that nickel metal in the ghee industries' drains sediments in mg kg^{-1} is in the order of: Taj Plus Ghee Industry, (179.06) >Gulab Banaspathi, (176.93) >Saqib Banaspathi, (78.89) >Sher Banaspathi, (56.62) >Utman Ghee Industry, (24. 38). Cempel and Nikel (14) stated that Ni content in soil varies in a wide range from 3 to 1000 mg/kg. The present data shows that the drains sediments of Taj Plus Ghee Industry, Skhakot, KPK have high concentration of Ni metal among five selected Ghee industries and that value is in between 3 and 1000 mg/kg.

Table 2. Ni concentration in ghee industries' drains sediments.

S.No	Industry Name	Ni concentration (mg kg^{-1})
1	Taj Plus Ghee Industry, Skhakot, KP	179.06±18.4267
2	SherBanaspathi, Dargai, KP	56.62±13.08849
3	SaqibBanaspathi, Jamroad Road, Peshawar	78.89±6.801296
4	GulabBanaspathi, Jamroad Road, Peshawar	176.93±21.90533
5	Utman Ghee Industry, Gadoon, KP	24. 38±2.855422

Results are mean of three independent experiments ± SD.

Phytoextraction of Nickel by the Plants Growing along Drains carrying Effluents of Taj Plus Ghee Industry

The accumulation of nickel metal in different parts of the plants growing along the drains carrying effluents of Taj Plus ghee industry is shown in Table 3. The Table 3 data shows that three plant species were growing dominantly along the drains carrying effluent of Taj Plus ghee industry. Nickel concentration in different parts of these plants showed that the phytoextraction capacity of these three plant species for nickel metal in mg/kg dry biomass is in the order of: *Scrophularia robusta* > *Euphorbia helioscopia*> *Salvia plebeian*. In these three plants the concentration of nickel metal is higher in their roots except *Salvia plebeian*, where nickel concentration is higher in shoots.

Table 3. Ni accumulation by plants growing along drains carrying effluents of Taj Plus Ghee Industry, Skhakot, KP.

S.No	Plant Species	Ni concentration in biomass (mg kg^{-1})		
		Root	Stem	Leaves
1	*Euphorbia helioscopia*	144.456±63.522	78.933 ^{C} ±2.995	87.8±3.269
2	*Salvia plebeia*	90.066±1.258	90.866 ^{BC} ±3.066	105.7±2.330
3	*Scrophulariarobusta*	167.94±43.284	104.5 ^{AB} ±13.524	150.38±50.135

Results are mean of three independent experiments ± SD. Means having different letters in the same column are significantly different at $p<0.05$ according to One-Way Anova (Tukey Test).

Phytoextraction of Nickel by the Plants Growing along Drains carrying Effluents of Sher Banaspathi, Dargai

The accumulation of nickel metal in different parts of the plants growing along the drains carrying effluents of Sher Banaspathi is given in Table 4. From Table 4, it is clear that four plant species were growing mostly along the drains carrying effluent of Sher Banaspathi. Nickel concentration in different parts of these plants showed that the phytoextraction capacity of these four plant species for nickel metal in mg/kg dry biomass is in the order of *Rumex nepalensis>Polygonum hydropiper>Cirsiumarvense>Pimpinella saxifrage*. Among these four plants, the data shows that *Rumex nepalensis* posses the high concentration of nickel.

Table 4. Ni accumulation by plants growing along drains carrying effluents of Sher Banaspathi, Dargai, KP.

S.No	Plant Species	Ni concentration in biomass (mg kg^{-1})		
		Root	Stem	Leaves
1	*Pimpinella saxifraga*	172.033±2.501	176.433±4.452	177.933 ^{B} ±0.461
2	*Rumex nepalensis*	417.363±207.178	308.743±146.225	634.47 ^{A} ±224.608
3	*Polygonum hydropiper*	453.933±306.536	396.366±228.633	344.156 ^{AB} ±35.685
4	*Cirsium arvense*	348.873±95.221	201±2.98161	205.166 ^{B} ±0.850

Results are mean of three independent experiments ± SD. Means having different letters in the same column are significantly different at $p<0.05$ according to One-Way Anova(Tukey Test).

Phytoextraction of Nickel by the Plants Growing along Drains carrying Effluents of Saqib Banaspathi, Peshawar

The accumulation of nickel metal in different parts of the plants growing along the drains carrying effluents of Saqib Banaspathi is given in Table 5. From Table 5, it is clear that two plant species were collected from Saqib Banaspathi. Various parts of these plants were analyzed for nickel metal which showed the phytoextraction capacity of *Cynodon dactylon>Cyperus rotundus*.

Table 5. Ni accumulation by plants growing along drains carrying effluents of Saqib Banaspathi, Jamroad Road, Peshawar.

S.No	Plant Species	Ni concentration in biomass (mg kg⁻¹)		
		Root	Stem	Leaves
1	*Cyperusrotundus*	105.533 ^{A} ±15.14508	98.933 ^{A} ±2.60832	115.066^{A}±0.152753
2	*Cynodondactylon*	230.063 ^{A} ±86.07762	138.293 ^{A} ±29.44707	167.71 ^{A} ±67.73287

Results are mean of three independent experiments ± SD. Mean having same letters in the same column are significantly not different (Paired-Samples T Test).

Phytoextraction of Nickel by the Plants Growing along Drains carrying Effluents of Gulab Ghee Industry, Peshawar

The accumulation of nickel metal in different parts of the plants growing along the drains carrying effluents of Gulab ghee industry, Jamroad Road, Peshawar is given in Table 6.

Table 6 shows that four plant species were collected from drains carrying effluents of Gulab Ghee Industry. Analysis of nickel in various parts of these plant species showed that concentration of nickel was in the order:

Chenopodium ambrosioides>Xanthium stramonium>Rumex halepensis>Scrophularia nodosa.

Table 6. Ni accumulation by plants growing along drains carrying effluents of Gulab Ghee Industry, Jamroad Road, Peshawar.

S.No	Plant Species	Ni concentration in biomass (mg kg⁻¹)		
		Root	Stem	Leaves
1	*Scrophularianodosa*	233.226 ^{B} ±52.180	138.533 ^{B} ±0.7505	260.286 ^{A} ±35.7907
2	*Rumexchalepensis*	270.926 ^{B} ±75.389	189.066 ^{B} ±31.884	188.603^{AB}±43.5542
3	*Xanthium stramonium*	397.66 ^{B} ±109.526	287.94 ^{AB} ±46.433	159.7 ^{B} ±1.752142
4	*Chenopodiumambrosioides*	762.296 ^{A} ±233.10	345.806 ^{A} ±85.676	168.133 ^{B} ±2.77368

Results are mean of three independent experiments ± SD. Means having different letters in the same column are significantly different at $p<0.05$ according to One-Way Anova(Tukey Test).

Phytoextraction of Nickel by the Plants Growing along Drains carrying Effluents of Utman Ghee Industry

The accumulation of nickel metal in different parts of the plants growing along the drains carrying effluents of Utman Ghee Industry, Gadoon, KP is given in Table 7. The data of the Table 7 shows that four plant species were collected from the drains carrying effluents of Utman Ghee Industry. Root, shoot and leaves of these plants were analyzed for nickel metal by atomic absorption spectroscopy (AAS). Analysis in these plant parts indicate that the concentration of nickel was in the order: *Datura stramonium>Saccharum spontaneum>Rumex hastatus>Conyza canadensis*. Mellem *et al*., (2011) stated that Ni metal is stored in the roots mainly. In most cases the concentration of nickel was higher in the roots of the analyzed plants.

Bioconcentration factor and Translocation

The values of bioconcentration factor and translocation factor of the seventeen plants of different ghee industries are given in Table 8. It is clear from Table 8 that, the bioconcentration factor of all the plants of Taj Plus ghee industry is less than one while the BCF values of all four plant of Sher Banaspathi, Dargai, is greater than one. Both the plants of Saqib banaspathi shows BCF valve greater than one and among the plants of Gulab ghee industry only *Scrophularia nodosa* shows BCF value less than one while the rest of the plants of this industry have BCF value greater than one. All the plants of Utman ghee industry shows BCF value greater than one. Sheoran *et al.*, (2001) stated that phytoextraction is not feasible if bioconcentration factor is less than one. Among the seventeen plants, *Rumex nepalensis* shows highest BCF valve (8.329).

Table 7. Ni accumulation by plants growing along drains carrying effluents of Utman Ghee Industry, Gadoon, KP.

S.No	Plant Species	Ni concentration in biomass (mg kg^{-1})		
		Root	Stem	Leaves
1	*Conyza canadensis*	33.866 ^{B} ±0.802081	35.833 ^{C} ±2.400694	37.066^{C} ±2.31804
2	*Rumex hastatus*	60 ^{B} ±1.058301	64.466 ^{B} ±1.209683	56.633^{B} ±1.91398
3	*Saccharum spontaneum*	60.5 ^{B} ±7.040597	74.266 ^{B} ±2.857155	60.4 ^{B} ±4.812484
4	*Datura stramonium*	211.864 ^{A} ±93.9148	164.212 ^{A} ±19.6026	87.903^{A} ±4.58009

Results are mean of three independent experiments ± SD. Means having different letters in the same column are significantly different at $p<0.05$ according to One-Way Anova(Tukey Test).

Table 8. TF of plants growing along drains carrying effluents of different Ghee Industries.

Name of industry	Plant species	Bioconcentration factor (BCF) ^{a}	Translocation factor (TF) ^{b}
Taj Plus Ghee Industry, Skhakot, KPK	*Euphorbia helioscopia*	0.465	0.577
	Salvia plebeian	0.548	1.09
	Scrophularia robusta	0.711	0.758
Sher Banaspathi, Dargai, KPK	*Pimpinella saxifraga*	3.129	1.029
	Rumex nepalensis	8.329	1.129
	Polygonum hydropiper	6.539	0.815
	Cirsium arvense	3.586	0.582
Saqib Banaspathi, peshawar	*Cyperus rotundus*	1.356	1.013
	Cynodon dactylon	1.939	0.665
Gulab Ghee Industry, Peshawar	*Scrophularia nodosa*	0.943	0.715
	Rumex halepensis	1.067	0.696
	Xanthium stramonium	1.095	0.487
	Chenopodium ambrosioides	1.452	0.337
Utman Ghee Industry, Gadoon, KPK	*Conyza canadensis*	1.495	1.076
	Rumex hastatus	2.483	1.009
	Saccharum spontaneum	2.761	1.112
	Datura stramonium	5.170	0.594

It is clear from the data of table 8 that among the plants of Taj Plus ghee industry, *Salvia plebeian* shows TF value greater than one while the rest of the two plants of this industry show TF less than one. Among the plants of sher banaspathi, the TF value of *Pimpinella saxifrage* and *Rumex nepalensis* is greater than one while the rest of the two plants show TF valve less than one. Among the plants of Saqib Banaspathi, Peshawar, *Cyperus rotundus* shows TF value greater than one while the TF value of *Cynodon dactylon* is less than one. All the plants of Gulab ghee industry shows TF value less than one while among the plants of utman ghee industry, the TF value of *Datura stramonium* is less than one and the rest of the plants of this industry shows TF value greater than one. Translocation factor value greater than one indicates the translocation of the metal from root to above ground part Jamil *et al* (2009) and Yoon *et al*

(2006) reported that, only plant species with both BCF and TF greater than one have the potential to be used for phytoextraction

Conclusions

The present study shows that the effluents of Utman Ghee Industry, Gadoon, KP have higher concentration of nickel metal while highest concentration of nickel found in the drains sediment of Taj plus Ghee Industry. The concentration of Ni metal in the effluent water and industrial sediments may be depending on the number of hydrogenation process of oil into ghee of each industry. It is concluded that among all seventeen studied plants, only six plants (*Rumex nepalensis*, *Pimpinella saxifrage, Cyperus rotundus, Conyza canadensis, Rumex hastatus* and *Saccharum spontaneum)* showed feasibility for the phytoextraction of Ni metal. The calculated bioconcentration factor as well as translocation factor of these six plants for nickel metal is greater than one.

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