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Cadmium removal from aqueous phase using some vegetables derived low-cost biosorbents

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ABSTRACT

The objective of present study was to identify the potential cadmium (Cd) detoxifying low-cost bio-sorbent by assessing Cd uptaking efficiency. Eight low-cost biosorbents - tap root of *Daucus carota* and *Beta vulgaris*, leaves of *Hygrophila spinosa*, *Ipomea aquatica*, *Trigonella foenum-graecum* and *Spinacia oleracea* and fruit of *Cucumis sativus and Musa paradisiaca* were collected and employed in sorption study to evaluate their comparative Cd removal efficiencies. The Cd removal efficiency varied from 61.32 to 96.33% and results revealed that the highest efficiency was observed in *Daucus carota* and lowest in *Beta vulgaris*. The tap root of *Daucus carota* could be recommended as a well efficient low-cost and easily accessible biosorbent in removal of Cd from contaminated water without posing any negative hazardous impacts in environmental.

1. Introduction

Cadmium (Cd) is a non-biodegradable and highly toxic trace heavy metal and gets concentrated in kidney. It acts as an inhibitor of sulphydryl enzymes and hydroxyl, carboxyl, phosphatyl, cysteinyl and histidyl protein, purine and porphyrin molecules in cell. Cd decreases ATP generation by diverting proton flux from oxidative phosphorylation reaction to the proton leak reaction. It also competes with Cu, Fe and Zn metal and causes essential metal deficiency within body. All these causes hypertension, respiratory disorders, damage of kidney and liver, aminoaciduria, hypercalciuria, glucosauria, proteinuria, osteoporosis, formation of renal calculi etc. Carcinogenic as well as teratogenic effects are also reported in other animals.

Human body is contaminated with Cd through inhalation, drinking and ingestion of food from steel utensils, paint, plastics, silver-cadmium and nickel-cadmium batteries, PVC articles, aluminium solder, engraving, lithography, iridescent porcelain and potteries, photography, colouring glass, ceramic alloy, amalgam dentistry, photoelectric cell, photoconductors, rectifiers, phosphors, soaps, paper, rubber, textiles, printing inks, ceramic glazes, fireworks etc and their manufacturing industries, tobacco smoking, leafy vegetables, soybeans, peanuts, sunflower seed, potato, rice, wheat, maize, meat and fishes etc.

Cd abundance in earth crust is 0.1 – 0.5 mg l^{-1} (Wikipedia, 2017). Global annual production of cadmium was 23000 tonnes (USGS, 2016). It has been accumulated 0.1 – 5 ng m^{-3} in rural atmosphere, 2.0 – 15 ng m^{-3} in urban atmosphere and 15 – 150 ng m^{-3} in industrialized atmosphere (ICdA, 2011), 0.01 – 0.11mg l^{-1} in drinking water (Mohod and Dhote, 2013), 0.076 – 0.245 mg l^{-1} in surface water (Parera et al, 2016), 0.01 – 3.2 mg l^{-1} in wastewater (Kulkarni and Kaware, 2013), 1.7 – 1.97 mg kg^{-1} dw in river sediments (Akhand et al, 2016), 33.22 – 49.39 mg kg^{-1} dw in pond sediment (Wojtkowska et al, 2015), 0.1 – 2.4 mg kg^{-1} dw in lake sediment (Pradit et al, 2010), 0.01 – 152.95 mg kg^{-1} in agricultural soil (Zhang et al, 2014), 3.26 – 3.63 µg g^{-1} in freshwater fish (Nandi et al, 2012), 0.12 – 3.7 mg kg^{-1} dw (Liu et al, 2016) and 0.11 – 83.9 µg g^{-1} ww in human body Satarug et al, 2010).

Technological progress is accompanied with environmental pollution proportionately. Pollutants like Cd enter into ecosystem undesirably and becomes arrested and concentrated in biotic components of different trophic level. As, Cd is a non-biodegradable element then the pollutant in magnified in higher trophic level through food chain.

Several eco-technologies have now been implemented successfully to prevent the mobility of Cd into different biotic component and ultimately into human body. Most of tools have been designed for Cd removal from drinking water, surface water and wastewater. Different bio-sorbent derived from plant and animal biomass are being utilized as low cost, eco-friendly and well efficient component. The biomass of soil bacteria *Exiguobacterium sp.* is a good Cd sorbent utilized for removal of Cd from solution. The cell wall of the bacteria can concentrate Cd maximum as much as 15.6 mg g-1 at pH 7.0 (Park and Chon, 2016). The highest Cd adsorption capacity of *Saccaromyces cerevisiae* was recorded as 110 mg g-1 at pH 6.0 in a suspension of 0.30 g l-1(Tálos et al, 2012). The biosorbent Opuntia albicarpa L. Scheinvar accumulated Cd highest as per 0.155 mg g-1 at pH 4.0 after thermal treatment (Beltrán-Hernández et al, 2015).

The objective of the study was to investigate the Cd removal efficiency of eight low-cost and eco-friendly biosorbents – tap roots of *Daucus carota and Beta vulgaris*, leaves of *Hygrophila spinosa*, *Ipomea aquatica*, *Trigonella foenum-graecum* and *Spinacia oleracea*, fruit of *Cucumis sativus and Musa paradisiaca* from synthetic Cd solution in order to identify potential Cd detoxifying biosorbent.

2. Materials and methods

2.1. Preparation of biosorbent

Biosorbents - tap roots of *Daucus carota* (carrot) *and Beta vulgaris* (beet), leaves of *Hygrophila spinosa*, (Kokilakṣa) *Ipomea aquatic* (water spinach), *Trigonella foenum-graecum* (Fenugreek) and *Spinacia oleracea (*Spinach), fruit of *Cucumis sativus* (Cucumber) *and Musa paradisiaca* (Banana) procured from local sources, were cleansed under running tap water and then washed with distilled water. These are then sun-dried and chopped into small pieces, then oven dried at 60°C for 48 hours till obtaining a stable weight. About 50 gm of each sample was ground to powder in an electrically automated mixer grinder machine (Classic 750, Bajaj Electricals Ltd., India). It was passed through a metal sieve having mesh size of 2 mm. Powders were stored in a sealed glass container for successive experiment.

2.2. Preparation of synthetic solution of Cd

A 100 ml standard stock solution of 0.1M $CdCl_2$ was prepared dissolving $CdCl_2$ in distilled water. A Solution of 100 µg l^{-1} $CdCl_2$ solution was prepared dissolving stock solution in distilled water and used for experimental purposes.

2.3. Batch sorption experiment

The sorption experiment was carried out in three batch experiments considering three parameters namely – contact time, pH and sorbent dose in triplicate capped glass bottles (50 ml) using eight biosorbents. All bottles were filled with 50 ml of 100 µg l^{-1} solution of $CdCl_2$. The contact time experiment was conducted using sorbent dose 0.05 gL^{-1} (i.e, 2.5 mg in 50 ml) for 30 hours at pH 7. The batch study of pH was performed with pH 4.5, 5.5, 6.5, 7.5 and 9.5 using dose 0.05gL^{-1} for 24 hours. The sorbent dose experiment was carried out using 0.05, 0.1, 0.15, 0.2 and 0.25 gL^{-1} with pH 7 for 48 hours period. All bottles were capped and shaken by mechanical shaker at the rate of 150 excursion min^{-1} at 25^0C.

2.4. Sampling and analysis

Water samples (1 ml) from each glass bottle were collected in 2 ml centrifuge tubes, centrifuged and then filtrated through 0.5µm filter (Advantec, Tokyo, Japan). These samples were used for quantification of Cd using the atomic absorption spectrophotometer (ASS, Analyst 200, Perkin Elmer). The efficiency of removal was calculated in the following formula:

$$R_e = \{(C_0 – C_t) / C_0\} \text{ x } 100$$

Where, C_0 and C_t are the concentrations of $CdCl_2$ in the solution at time 0 and t respectively.

Fig. 1 Removal efficiency of Cd from synthetic aqueous solution (100 µg l^{-1}) using different biosorbents. Bar (T) indicates standard error of mean (±SE) of three samples (n =3). Super scripts – a, b, c, d, e, f, g and h, indicate significant difference (p<0.05) among efficiencies in different bio-sorbents

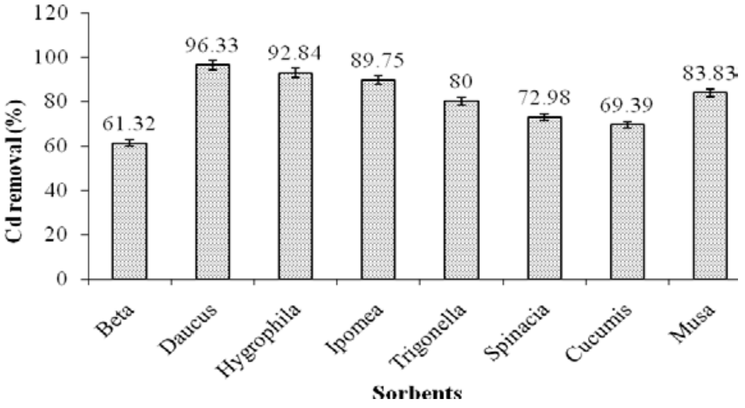
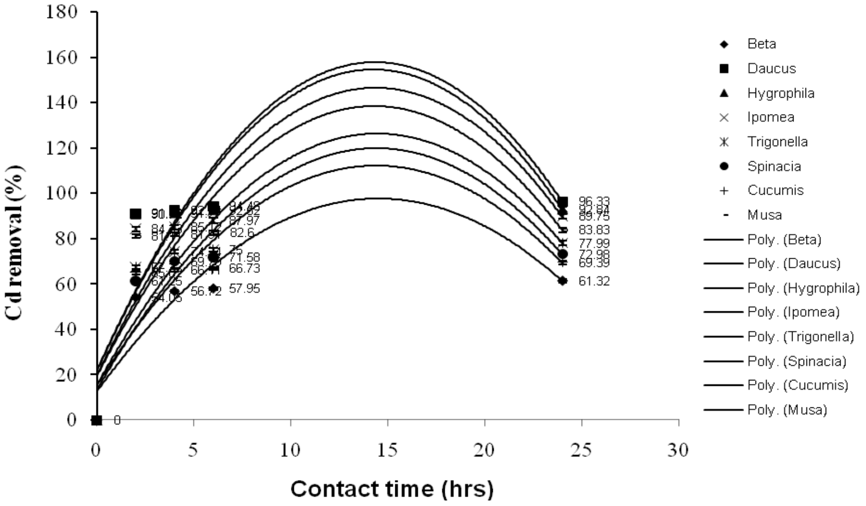


Fig. 2 Removal efficiency of Cd from synthetic aqueous solution (100 µg l^{-1}) using different bio-sorbent in different contact time. Bar (T) indicates standard error of mean (±SE) of three samples (n = 3). Curves show trend of removal efficiencies. Poly. – polynomial curve



2.5. Statistical analysis

Values of concentration and sorption capacity were presented as arithmetic mean of three samples (n = 3). The deviations among replicated values were calculated as standard error of mean (±SE). The mean variations among treatments were calculated by one way ANOVA (Duncan test) and values were significant when $p < 0.05$.

3. Results and discussion

3.1. Removal efficiency

The quantity of Cd was removed by different bio-adsorbent from synthetic aqueous solution (100 µg l^{-1}) was 61.32 – 96.33% (Fig. 1) at pH 7 and 25^0C. The highest removal efficiency was observed in *Daucus carota* and lowest in *Beta vulgaris*. The removal efficiency of biosorbent was following order variation: *Daucus* > *Hygrophila* > *Ipomea* > *Musa* > *Trigonella* > *Spinacia* > *Cucumis* > *Beta.*

These bio-sorbents are made-up of cellulose, hemicellulose, pectin, lignin and cutin which contains –COOH and –OH as functional groups (Gönen and Serin, 2012) for binding with Cd^{2+} co-ordinately and forming a stable complex resulting in sorption (Rana and Bhakta, 2017). The amount of –COOH plus –OH groups in these bio-sorbents caused to vary in their sorption capacity and removal efficiency for Cd. Though surface area was an influencing factor for sorption capacity (Bhakta et al., 2014) yet the uniform size of sobent particle (2 mm) of all these sorbent could not influence the removal efficiency.

In case of *Daucus,* β-carotene ($C_{40}H_{56}$) had no any contribution in removal of Cd because it lacked of any functional groups (–OH or –COOH). But it was enriched with retinol ($C_{20}H_{30}O$) which provided numerous –OH (Uzoekwe and Uzoekwe, 2017). They also reported that *Daucus* possessed other functional groups like >C=O and ≡C-H. The highest removal efficiency was achieved due to presence of higher number of functional groups.

In case of *Beta*, the quantity of functional groups might be less though the phytochrome β- cyanin (betanin, isobetanin, probetanin, and neobetanin) provided many functional groups – OH, –COOH, ≡N-H and >C=O. Since, Cd had no affinity to N-H and CO groups.

3.2. Efficiency and contract time

The Cd removal was increased with increasing contact time for 24 h of interaction with all sorbent by 61.32 - 96.33 % at pH 7 (Fig. 2). The efficiency was observed highest in *Daucus* (96.33%) and lowest in *Beta* (61.32%). The efficiency followed the order - *Daucus* > *Hygrophila* > *Ipomea* > *Musa* > *Trigonella* > *Spinacia* > *Cucumis* > *Beta* at 26 h period. The highest efficiency by each sorbent was not achieved in 24 h because the efficiency tended to follow a 2nd order polynomial curve (Figure 2). So, it was expected to obtain maximum efficiency at approximately half of their contact time of 24 h. In case of *Daucus* and *Hygrophila,* > 90% sorption was achieved within 2 h period of interaction and this trend was observed in other sorbents but the efficiency was slow after 2 h period of contact.

Contact time is also an influential factor. Initially the efficiency was rapid due to availability of adequate free functional groups (-OH,-COOH, etc.). The competition of numerous Cd^{++} for limited functional groups declined the sorption efficiency. The quantity of available free functional groups in sorbent caused their varying removal efficiencies.

3.3. Efficiency and pH

In case of *Daucus carota*, the removal efficiency was observed 87.43 – 97.06% in different pH (4.5 – 9.5), but the highest removal was recorded at pH – 6.5 (Fig. 3). One way ANOVA analysis showed that all efficiencies values at different pH were significant at 5% level. The efficiency increased with increasing pH up to pH-6.5 and thereafter it is decreased with increasing pH. The efficiency trend followed a polynomial path (Fig. 3). Therefore, the optimum pH was 6.5 in removing the maximum Cd from aqueous phase.

pH played a vital role in Cd sorption process. It governed ionization of Cd and activation of functional groups (-OH, -COOH and ≡C-H) (Azouaoua et al, 2010) within this pH range (pH: 4.5 – 9.5). At low pH (pH 6.5), the interaction between Cd^{++} and functional groups and complex formation was highest. At low pH, the competition between proton and Cd^{++} for functional groups of sorbent was weak that favoured Cd^{++} for more complex formation.

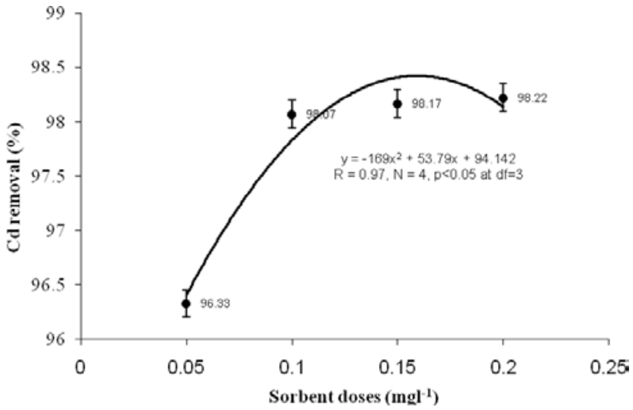


Fig. 3 Removal efficiency of Cd from synthetic aqueous solution (100 µg l^{-1}) using *Daucus carota* as bio-sorbent in different doses. Bar (T) indicates standard error of mean ($\pm SE_{x^-}$) of three samples (n = 3). Super scripts – a and b, indicate significant difference ($p<0.05$) among efficiency in different doses. Curve indicates the trend of Cd removal efficiency and the trend follows the equation where N – number of mean data, R – correlation coefficient. P – probability value at 5% level of significance and df – degree of freedom

3.4. Efficiency and sorbent dose

In case of *Daucus carota*, Cd removal was maximum (96.33 – 98.22 %) and increased with increasing doses of sorbent (0.05 – 0.20 mg l^{-1}) (Fig. 4). The efficiency was increased significantly ($P<0.05$) up to dose 0.1 mg l^{-1} and the efficiencies values at >0.1 mg l^{-1} were statistically insignificant ($P>0.05$). It indicated that Cd removal was not increased with increasing dose of sorbent. The efficiency trend was characterized by a polynomial path which revealed a decreasing efficiency with increasing doses (Fig. 4).

At pH < 7, the sorbent provided more binding sites for Cd^{++} with increasing sorbent doses that resulted in more Cd removal from aqueous solution. At the dose 0.1 mg l^{-1}, almost all binding sites remained saturated with the concentration of Cd^{++}s (100 µg l^{-1}). Higher doses though provided more binding sites but the concentration of Cd^{++} was not increased proportionately. Therefore, the removal was not increased significantly.

5. Conclusions

The study clearly revealed that employed biosorbents have significant properties in detoxifying the Cd of aqueous phase. Common vegetables have significant sorbent capacity for heavy metals and these can be applied for heavy metal removal from contaminated water. The efficiency of the tap root of *Daucus carota* is excellent (>96%) biosorbent in Cd detoxification in contaminated water. Matrix of pH, contact time and sorbent doses are the vital influencing factors in d removal study. Removal efficiency can also be influenced by the concentration of heavy metal in contaminated water. Weak acidic media (pH 6.5) favours removal efficiency. Further study is needed to investigate more efficient as well as low-cost biosorbent in this regard.

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References

Akhand A, Chanda A, Das S, Sanyal P and Hazra S, 2016. High cadmium contamination at the gateway to Sundarban ecosystem driven by Kolkata metropolitan sewage in India. Current Science 110 (3): 386–391.

Azouaoua N, Sadaouia Z, Djaafrib A and Mokaddem H, 2010. Adsorption of cadmium from aqueous solution onto untreated coffee grounds: Equilibrium, kinetics and thermodynamics, Journal of Hazardous Materials 184: 126–134.

Beltrán-Hernández RI, Vázquez-Rodríguez GA, Felipe Juárez-Santillán L, Martínez-Ugalde I, Coronel-Olivares C and Lucho-Constantino CA, 2015. Cadmium Removal from Aqueous Systems Using Opuntia albicarpa L. Scheinvar as Biosorbent, BioMed Research International 2015 : 6 pages. http://dx.doi.org/10.1155/2015/832571

Bhakta JN, Munekage Y, Ohnishi K, Jana, BB, Balcazar JL, 2014. Isolation and characterization of cadmium and arsenic absorbing bacteria for bioremediation. *Water, Air & Soil pollution*, 225(10):2151. DOI: 10.1007/s11270-014-2151-2

Gönen F and Serin DS, 2012. Adsorption study on orange peel : Removal of Ni (II) ions from aqueous solution. African Journal of Biotechnology 11 (5) : 1250–1258.

International Cadmium Association (ICdA), 2011. http://www.cadmium.org/index.php. Accessed 8 Oct 2011.

Kulkarni SJ and Kaware JP, 2013, A Review on Research for Cadmium Removal from Effluent, International Journal of Engineering Science and Innovative Technology 2 (4): 465–469.

Liu Y, Liu K, Li Y, Yang W, Wu F, Zhu P, Zhang J, Chen L, Gao S and Zhang L, 2016. Cadmium contamination of soil and crops is affected by intercropping and rotation systems in the lower reaches of the Minjiang River in South-Western China. Environmental Geochemistry and Health 38(3): 811–820.

Mohod CV and Dhote J, 2013. Review of Heavy Metals in Drinking Water and Their Effect on Human Health, International Journal of Innovative Research in Science, Engineering and Technology 2 (7): 2992–2996.

Nandi S, Srivastava RC and Agarwal K M, 2012. Lead and Cadmium accumulation in freshwater fishes Labeo rohita and Catla catla, Journal of Environmental Research And Development 6(3A): 748–752.

Park J H and Chon Hyo-T, 2016. Characterization of cadmium biosorption by Exiguobacterium sp. isolated from farmland soil near Cu-Pb-Zn mine, Environmental Science and Pollution Research 23 (12): 11814–11822.

Perera PA, Chintaka T, Sundarabarathy Thenmoli V, Sivananthawerl T, Kodithuwakku Suranga P and Edirisinghe U, 2016. Arsenic and Cadmium Contamination in Water, Sediments and Fish is a Consequence of Paddy Cultivation: Evidence of River Pollution in Sri Lanka. Achievements in the Life Sciences 10(2): 144–160.

Pradit S, Wattayakorn G, Angsupanich S, Leemaker M and Baeyens W, 2010. Distribution of trace elements in sediments and biota of Songkhla Lake, southern Thailand. Water Air Soil Pollution 206: 155–174.

Rana S and Bhakta J N, 2017. Heavy Metal (loid) Remediation Using Bio-waste : A Potential Low-Cost Green Technology for Cleaning Environment. In : Handbook of Research on Inventive Bioremediation Techniques. Bhakta J N (Ed.), IGI Global, USA, pp.

Satarug S, Garrett S H, Sens M A and Sens D A, 2010. Environ Health Perspect 118:182–190. doi:10.1289/ehp.0901234

Tálos K, Pernyeszi T, Majdik C, Hegedüsova A and Páger C. 2012. Cadmium biosorption by baker's yeast in aqueous suspensions, Journal of the Serbian Chemical Society 77 (4): 549–561.

USGS (United States Geological Survey), 2016. Commodity Statistics and Information. https://en.wikipedia.org/wiki/Abundance_of_elements_in_Earth%27s_crust.

Uzoekwe N M and Uzoekwe S A, 2017. Molecular Spectroscopic Analysis of Daucus carota

Plant Pigment Extracts. Annual Research & Review in Biology 15(3): 1–5.

Wojtkowska M , Karwowska E, Chmielewska I , Bekenova K and Wanot , 2015. Copper and cadmium in bottom sediments dredged from Wyścigi Pond, Warsaw, Poland—contamination and bioaccumulation study. Environment Monitoring and Assessment 187:737. doi: 10.1007/s10661-015-4945-0

Wikipedia, 2017, Cadmium. Wikimedia Foundation Inc., USA. https://en.wikipedia.org/wiki/Cadmium

Zhang X, Chen D, Zhong T, Zhang X, Cheng M and Li X, 2014. Assessment of cadmium (Cd) concentration in arable soil in China, Environmental Science Pollution Research. doi: 10.1007/s11356-014-3892-6