Application of agricultural wastes for removal of heavy metals from industrial wastewater by adsorption process

SUMMARY
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Summary

The present work has been done to explore the potential of naturally available bio-wastes for treatment of wastewaters with special focus on removal of heavy metals. The wastewaters were collected from two important industries; tannery and flashlight manufacturing. These industries discharge their partially treated or untreated wastewater directly into receiving water bodies. The discharged wastewaters are usually dark colored, concentrated or thick, foul smelling wastewater with high concentrations of dissolved and suspended physicochemical pollutants e.g. nitrates, phosphate, sulphate, cations, anions, heavy metals etc. Among all pollutants, contamination of water resources with toxic heavy metals like As, Cu, Ni, Cd, Cr, Pb etc. is a severe global problem and serious concern because of their highly toxic nature, non-biodegradability, persistency and continuous deposition into the vicinity of receiving water body pertaining to bio-accumulation in living being. These toxic metals may also be transmitted form one trophic level to next trophic level through food chain and ultimately reach to the highest level that includes human beings. Such conditions may be very dangerous for the health of humans and other living beings as heavy metals cause different ill effects onto different vital organs and systems (e.g. digestive, circulatory, excretory, neural systems). Therefore, it is essential to treat metal contaminated waste water prior to its discharge to any of the environmental systems mainly in aquatic bodies.

Over a few decades a number of conventional techniques have been identified by different scientists and researchers for the removal of heavy metals from different industrial effluents. These techniques include chemical precipitation, ion exchange, electrochemical removal, membrane filtration, reverse osmosis, electro dialysis etc. But, among all these, adsorption (biosorption) is recognized as highly effective, eco-friendly and efficient technology being flexible in design, simple operation and relatively less toxic sludge is produced as by product. Biosorption involves naturally occurring substances and agricultural product viz. bark, stem, leaves, roots, peels, sand and clay etc. and animal wastes like skin, hull, shells etc. to decontaminate aquatic environment. These biological substances contain heterogeneous functional groups e.g. carbonyl, alcoholic, phenolic, amino, amides, etc. which have the tendency to form different metallic complexes and chelates onto their surfaces. The

decontamination involves amalgam of mechanisms like chemisorption, complexation, ion-exchange, diffusion etc. The present work was aimed to remove heavy metals present in industrial wastewater by application of different adsorbents in an ecofriendly and cost effective manner. More precisely, following specific objectives were drawn for this study –

- Estimation of physicochemical properties and heavy metals present in the industrial wastewater.
- Removal of heavy metals from wastewater using various combinations of agricultural wastes.
- Optimization of control techniques for the removal of heavy metals from the wastewater using agricultural wastes.
- Risk assessment of heavy metals to the environment.

In order to designated objectives, four naturally available agricultural wastes namely peels of sweet lemon (*Citrus limetta*), lemon (*Citrus limon*) & orange (*Citrus sinensis*) and bagasse were selected to treat heavy metals present in tannery and flashlight manufacturing wastewaters which were primarily chromium (Cr) and lead (Pb). All of these agricultural wastes were converted into biochar namely sweet lemon peel biochar (SLPB), lemon peel biochar (LPB), orange peel biochar(LPB) and bagasse biochar (BB) to increase the surface area for enhancing the adsorption capacities. Effects of adsorbent dosage, contact time, pH, temperature and initial metal ion concentration were observed onto the adsorptive removal of selected heavy metals. Initially the experiments were run with known concentration for both heavy metals (5, 10, 20 and 40 ppm) for optimization of saturation point for maximum removal. After optimization, optimized dosage and contact time were utilized to explore removal efficiencies of selected biosorbents for removal of heavy metals and its effect on to the physicochemical properties (pH, EC, BOD and COD) of wastewaters were also observed. Initially, the physicochemical properties of wastewaters were examined which showed that most parameters viz. TDS, TSS, alkalinity, sulphate, nitrate, total hardness, magnesium, calcium, chromium and lead, exceeded recommended limits given by Central Pollution Control Board (CPCB 2013) and Indian Standard Institute(ISI 2000) and Inland Surface Water-Bangladesh (ISWB).

Further, screening of adsorbents was done on the basis of ease in availability, low cost of processing and abundance of functional groups for adsorption. After screening, physicochemical properties of all four biosorbents were affirmed by moisture content & ash content (%), pH, CHNS (%), H/C ratio, C/N ratio, biochar yield (%), pore volume(cc g^{-1}), pore diameter (nm), surface area (m^2 g^{-1}), tot. surface acidic groups i.e. carboxylic, lactonic & phenolic groups (mol gm^{-1}). The results demonstrated that the highest surface area was of SLPB (30.62 m^2 g^{-1}) followed by LPB (24.89 m^2 g^{-1}), OPB (15.21 m^2 g^{-1}) and BB (12.628 m^2 g^{-1}). The maximum biochar yield i.e. 86.67 % was obtained with SLPB followed by lemon peel (84.47%), orange peel (79.20%) and bagasse (73.33%). Total concentration of surface acidic groups in SLPB, LPB, OPB and BB was 7.382, 7.480, 7.408 and 7.033 mol gm^{-1}, respectively. Results revealed that all adsorbents had important acid functional groups i.e. carboxylic groups, phenolic groups, lactonic groups that aided in adsorption of heavy metals. Furthermore, CHNS study concluded that SLPB and LPB showed higher C and H content with lower H/C ratio which suggest it to be more efficient adsorbents than OPB and LPB with lesser C and H content with higher H/C ratio. Whereas, SEM studies supported successful adsorption of heavy metals as changes in the surface morphology of all the selected biosorbents were observed after adsorption of heavy metals from wastewaters. Likewise, EDX analysis also confirmed adsorption of heavy metals as changes in peaks of biochar before adsorption and after adsorption of heavy metals were recognized by absence and presence of peaks of Cr and Pb spectrums, respectively through EDX. Likewise, chemical structure and major surface functional groups involved in adsorption of Cr and Pb present in tannery and flashlight wastewaters were determined by FTIR studies. The spectra demonstrated that adsorbents were rich in different functional and chemical groups. The strongest peaks were found between 3846.8 and 3352.9 cm^{-1} probably due to -OH stretching vibrations of biopolymers and poly saccharides (lignin, pectin, cellulose etc.). The shift in position of peaks of biochars before and after adsorption of Cr and Pb proposes that the process was smoothened by chemisorption due to binding of heavy metals by nucleophilic functional groups. Moreover, some functional groups were lost after adsorption which suggested that these groups were spent in the binding of heavy metals by formation and dissociation of bonds and groups through different processes like complexation, chelation, ion-exchange etc. Further, alterations in structural crystallites of adsorbents were studied by XRD. The existence of sharp crystalline peak for SLPB at 24.37º (2θ), LPB at 26.59º (2θ), OPB at 24.35º (2θ) and BB at 26.41º (2θ) indicated presence of natural cellulose, lignin and non-crystalline hemicelluloses materials. After adsorption, slight changes in position of peaks were recorded that demonstrated no change in the crystallinity of biochars. Thus, treatment of the wastewaters did not cause any structural change in the adsorbents as the crystallinity remained same as that of before adsorption of heavy metals.

The optimized adsorbent dosage and contact time for successful adsorption of heavy metals were 5.0 to 10 g and 160 to 180 minutes for Cr and 3.5 to 5.0 g and 140 to 180 minutes for Pb, respectively. Whereas, optimized pH for the maximum removal of Cr (95.47 %) and Pb (97.42 %) were recorded at pH 3 and 5 by SLPB. The optimum temperature for removal of Cr and Pb were recorded as 65 and 55 ºC, respectively. In addition to this, the optimum initial metal ion concentration was 40 mg L^{-1} on the basis of concentration of the medium and if the maximum removal rate would be considered then will be 5 mg L^{-1} for both heavy metals. The effect of initial metal concentration on removal efficiencies of all selected adsorbents was lowest, that may be due to dependence of adsorption mainly onto adsorbent dosage, contact time, pH and temperature of the medium. Further, the removal percentages of BOD for tannery effluent by SLPB, LPB, OPB and BB increased from 12.12, 12.12, 11.13 and 10.39 to 53.85, 41.50, 37.31 and 28.34 % respectively, until the optimum dosage and contact time. Likewise, BOD removal percentage was also increased from 18.23, 16.71, 12.05 and 11.29 to 33.74, 29.91, 24.85 and 22.00 %, respectively for flashlight wastewater. In addition to this, application of SLPB, LPB, OPB and BB reduced COD concentration of tannery effluent from 22.75, 24.31, 5.94 and 3.59 % to 67.76, 65.52, 29.66 and 4.51 % respectively, until optimum dosage and contact time. Likewise, the COD of flashlight wastewater was reduced from 29.63, 10.97, 6.02 and 6.15 to 42.64, 17.35, 19.44 and 13.85 % respectively, by the application of SLPB, LPB, OPB and BB. However changes in pH and EC were not much distinct.

As adsorbent dosage, contact time and pH parameters showed high removal percentage during optimization process and also did not require any special supervision or technical acquaintance during operation. So, these three were selected for removal of heavy metals form real industrial wastewaters of tannery and flashlight. The maximum removal of Cr and Pb were attained by SLPB (97.82 & 97.11 %) followed by LPB (91.50 & 87.80 %), OPB (86.64 & 86.07%) and BB (74.23 & 75.38

%) at the end. The best results were obtained at relatively acidic pH (between 3-5). However, treatment with BB recorded maximum removal of Pb at pH 5. At saturation point only 0.08, 0.33, 0.51 and 0.99 mg L^{-1} of Cr and 0.07, 0.29, 0.333 and 0.59 mg L^{-1} of Pb were left in tannery and flashlight wastewater, respectively which fell under recommended limits of CPCB (2013), ISI (2000) and ISWB. Further, the kinetics involved in the adsorption of Cr and Pb present in tannery and flashlight wastewaters were studied for pseudo first and pseudo second order models. The assumption was based on higher value of R^2 which was recorded for pseudo second order kinetic model. Thus, adsorption of Cr and Pb followed pseudo second order which assumes that the rate of adsorption is directly proportional to the number of active surface sites resulting in chemisorption more appropriately than physisorption. Freundlich and Langmuir equations were used to describe the relationship between equilibrium metal biosorption q_e (mg L^{-1}) and final concentrations C_e (mg L^{-1}) at equilibrium. The R^2 values of Langmuir & Freundlich isothermic model for adsorption of Cr and Pb onto the surface of SLPB were nearby 1. It was found to be higher for Freundlich isothermic model which better fitted for adsorption of Cr and Pb in comparison to Langmuir. Thus, it could be concluded that adsorbent surfaces were heterogeneous and availed multi-layer adsorption with interactions between adsorbate and absorbent. In addition to this, the monolayer adsorption capacity (q_{max}) of SLPB, LPB, OPB and BB for the removal of Cr and Pb were found to be 2872.5 and 2840.91, 874.96 and 940.69, 116.75 and 512.53, 2.745 and 12.741 mg g^{-1}, respectively. These capacities were enough to adsorb Cr and Pb successfully from real wastewaters. In addition to this, the thermodynamic parameters (ΔG°, ΔH^{o} and ΔS^{o}) were also to evaluate the effect of temperature onto the adsorption of 5, 10, 20 and 40 ppm aqueous solution of Cr and Pb at optimum dosage and contact time. The results indicated that the adsorptive removal of Cr and Pb were endothermic, spontaneous and increase in randomness with increased temperature was recorded as values of ΔH^{o}, ΔG° & ΔS^{o} were positive, negative and positive. In addition to this, the desorption study showed that about 45.63, 45.75, 55.38 and 54.43 % of Cr and 88.15, 88.98, 86.82 and 90.05 % of Pb were desorbed by SLPB, LPB, OPB and BB, respectively. The maximum desorption for Cr and Pb were attained by 0.1 M HNO_3 for SLPB and 0.1 M HCl for remaining three adsorbents and 0.1 M HCl for SLPB, LPB and OPB, and 0.1 M HNO_3 for BB, respectively. The orders of desorption for Cr and Pb were found be in the order of OPB>BB>LPB>SLPB and BB>LPB>OPB>SLPB, respectively.

Green moong and tomato among legumes, fruit and oil yielding plants, and lady's finger among vegetables were selected to assess the risk of treated wastewater on the environment. All three selected economic plants were grown in the greenhouse conditions to explore the effect of residue Cr and Pb onto the growth parameters and its bioaccumulation into the plants. The maximum growth parameters were recorded with sweet lemon followed by lemon and orange biochars in all of the plants irrigated by both of the treated wastewaters. The concentrations of heavy metals bio-accumulated in plant species were very low for almost all of the selected adsorbents but the best one was reported observed with SLPB and the concentrations were under the limit of CPCB i.e. 0.05 mg L^{-1} for both heavy metals, and also under the limit of WHO i.e. 0.1-0.2 mg kg^{-1} for Cr & 0.1 mg kg^{-1} for Pb. Such concentrations may be considered as negligible, but the development of fruits was also found to be very low in comparison to control due to higher concentrations of salts present in the treated wastewaters. These may be removed by various other eco-friendly techniques e.g. coagulation, electro dialysis etc. This would aid in enhancement of growth and development of plants as well as might reduce concentrations of heavy metals with combination of adsorption technique. Moreover, the bioaccumulation of HMs in selected plants irrigated with biosorbent treated wastewater will not cause any severe effect onto the health of human and other animals feeding on it as translocation of such a little concentration into fruits will hardly be noticeable.

Thus, it may be summarized that the best adsorbents for treating tannery and flashlight industrial wastewater among selected adsorbents at optimized conditions was found to be by SLPB followed by LPB, PB and BB. All biosorbents followed Freundlich isotherm for removal of both toxic metals. All of the selected adsorbents followed pseudo second order kinetics for both heavy metals from respective industrial wastewater. In addition to this, the best eluant for extraction of Cr and Pb was 0.1 M HNO_3 and 0.1 M HCl for SLPB. Moreover, the irrigation of these plants with the biosorbent treated wastewater will not cause any threat or risk to the lives of humans as the concentration of both of the heavy metals were very low to be translocated to other trophic level.