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Remediation of Contaminated Rice Farmlands Soil and *Oryza sativa Rice* Product by Apple Pomace as Adsorbent

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To manage waste agricultural and food industries biomass and to convert it into a material resource this research was carried out. The current study deals with the utilization of Apple pomace as agricultural and food waste materials as bio-sorbents for removal of toxic heavy metal ions: Nickel, Cadmium and Lead from studied *Oryza Sativa* rice cultivated in Babol paddies' rice in Mazandaran province in the north of Iran. Fresh experimental Apple Pomace samples were collected from several main factories (such as Sanich) in Tehran county and Saveh city, Iran. Nickel, Lead and Cadmium concentrations in treated rice by Apple Pomace and conventional rice products were determined by wet digestion method and samples were analyzed according to standardized international protocols by wet digestion method and Flame Emission Spectrophotometer. The content of Ni, Pb, and Cd in the samples were analyzed by ANOVA, followed by Student's t-test (P<0.0). Our data revealed that mean Pb concentration in studied paddies which treated by AP significantely decreased (*p* d" 0.005) . The mean level of lead (mg/kg DW) for all studied rice samples in studied paddies without treatment was 2.7171 ± 0.011(mg/kg DW± SE) but for studied smples from paddies by AP which treated 10 days before the transplanting rice stems decreased to 0.0101 ± 0.001(mg/kg DW± SE).

Key words: Apple Pomace, Remediation Soil, Oryza Sativa Rice, Adsorbent, Rice Paddy.

The traditional method for cultivating rice is flooding the fields while, or after, setting the young seedlings. This simple method requires sound planning and servicing of the water damming and channeling, but reduces the growth of less robust weed and pest plants that have no submerged growth state, and deters any rodents and pests. Consistent water depth has been shown to improve the rice plants' ability to compete against weeds for nutrients and sunlight, reducing the need for herbicides. Rice crops are grown in 5–25 cm of water depending on growing conditions. While with rice growing and cultivation the flooding is not mandatory, all other methods of irrigation require higher effort in weed and pest control during growth periods and a different approach for fertilizing the soil. Methods of growing differ greatly in different localities, but in most Asian countries the traditional hand methods of cultivating and harvesting rice are still practiced. The fields are allowed to drain before cutting. Manual harvesting makes use of sharp knives or sickles, traditional threshing tools such as threshing racks, simple treadle threshers and animals for trampling. Since rice is predominantly grown under wetland conditions, it is important to understand the unique properties of flooded soils

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for better management of fertilizers for this crop[1]. When a soil is flooded, the following major chemical and electrochemical changes take place:

a) Depletion of molecular oxygen
b) Chemical reduction of soil
c) Increase in pH of acid soils and decrease in pH of calcareous and sodic soils
d) Increase in specific conductance
e) Reduction of Fe^{3+} to Fe^{2+} and Mn^{4+} to Mn^{2+}
f) Reduction of NO_3- to NO_2^-, N_2 and N_2O g) Reduction of SO_4^{2-} to S_2^- ; h) Increase in supply and availability of N, P, Si and Mo
i) Decrease in concentrations of water-soluble Zn and Cu
j) Generation of CO_2, methane and toxic reduction products, such as: organic acids and hydrogen sulphide. These will have a profound influence on soil nutrient transformations and availability to rice plants[3,4].

Accumulation of chemical substances at the surface of a solid is called adsorption. The process of removal of an adsorbed substance from the surface is known as desorption. The substance adsorbed on the surface of another substance is called an adsorbate. A substance which adsorbs another substance on its surface is called an adsorbent. Adsorption is one of the most convenient techniques for the removal of heavy metals from wastewater. Due to regeneration of adsorbent, minimization of chemical and or biological sludge, high efficiency, possibility of metal recovery[5], flexibility and simplicity of design, the process is suitable even when the metal ions are present in concentration as low as 1mg/L , [6], insensitivity to toxic pollutants, low cost, easy to operate adsorption has been found to be superior technique as compared to the other methods for the removal of heavy metals from the wastewater. Halnor and Ubale in 2013 first presented the use of activated carbon for the adsorption of heavy metals[7].

Types of Adsorption

The attachment of atoms or molecules of adsorbate on the surface of solids and liquids may be through two types of forces, physical or chemical .Depending upon the types of forces involved in adsorption, it may be divided into two types, physical adsorption or physisorption and chemical adsorption or chemisorptions[8]. In physical adsorption the forces of attraction between the particles of the adsorbate and the adsorbent are weak Van der Waals' forces. Physical adsorption is relatively weak because Van der Waals' forces are weak. In chemical adsorption the forces of attraction between the adsorbate and the adsorbent are chemical bonds. It is slow process. Adsorbents for metal removal: Literature survey indicates that there are several chemical, biological and waste vegetable matters or substances that have been used by several researchers as adsorbents for the removal of heavy metals from the wastewater. But to make the adsorption process economic adsorbent should be readily available, inexpensive and environmental friendly. So most of the researchers have been used adsorbent having low cost and which were abundant in nature or the materials which required little processing or was byproduct or waste material from another industry or which has lost its economic or further processing values. Such adsorbents are seaweed, orange peel, peanut skins, bamboo-pulp, dyed sawdust, algae, clay, zeolite, sawdust, flyash, maize or corn cob, modified cotton and wool, tea waste, dyed jute, groundnut shells[8,9], coffee, green tea, date tree leaves, jambhool, potato husk, ashoka leaf powder, syzygium cumini, Jute and sun hemp, apple pomace, almond husk, prosopis spicegera, ratrani leaf powder, jute stick, cashew nut shells, cassia siamea, coconut husk, feathers, hairs, bagasse etc.[9].Agricultural materials particularly those containing cellulose shows potential metal biosorption capacity. The basic components of the agricultural waste materials biomass include hemicellulose, lignin, extractives, lipids, proteins, simple sugars, water hydrocarbons, starch containing variety of functional groups that facilitates metal[10]. Conventional and unconventional by-products from the food processing industry have been frequently included in livestock diets[11]. In recent years, because of economic considerations and waste technology, by-products are receiving increased attention by livestock producers and animal nutritionists[12]. Apple pomace its alternative by-product obtained from apple juice industries. This by-product is produced in huge amounts annually. The chemical composition of final pomace is linked to the morphology of the original feed stock and the extraction technique used. According to NRC , 2001[13], apple pomace (AP) is very low in protein (contains only 6.4% protein on DM basis) and it also serves as a useful energy source for ruminants[14] (Oltjen *et al*., 1977). Studies showed that AP supplemented with natural protein was comparable to protein enriched corn silage[15-18]. In contrast, Elloitt *et al*. in 1981[19] demonstrated that tomato pomace (TP) has the potential to be a good source of protein, but may be limited in energy due to the high fiber content.

To manage waste agricultural and food industries biomass and to convert it into a material resource this research was carried out. The current study deals with the utilization of Apple pomace as agricultural and food waste materials as bio-sorbents for removal of toxic heavy metal ions: Nickel, Cadmium and Lead from studied *Oryza Sativa* rice cultivated in Babol paddies' rice in Mazandaran province in the north of Iran due to acchivement of current study and project we will continue to assist the local governments to conduct the investigation works of the soil pollution of farmlands and rice paddies in the future, which will ultimately control the condition of food farmlands. In addition, we complete the improvement works of the contaminated farmland as soon as possible and protect the safety of environment for agricultural production to ensure public health.

MATERIALAND METHODS

Bio-sorbent & Study Area

The field experiment was carried out at two rice fields (each one more than 15 hectares), in Gavan Kola in Babol County, Mazandaran Province in the north of Iran (36°192 393 N 52°462 423 E) [20] and was initiated in 2016. Mazandaran is an Iranian Province located along the southern coast of the Caspian Sea and in the adjacent Central Alborz mountain range, in central-northern Iran. The name and description of all the sites in this study are provided in figure 1.

The soil samples from all parts of paddy fields with textures of silty clay, silty clay loam, clay loam, and sandy loam were air dried and crushed. Each soil was studied and the soil characteristic was shown in table 1.

The originally native rice paddies area was used for years under conventional management, and the soil was sampled twice (15 and 210 days after incorporating AP). In this study two paddy field areas from Gavan Kola , Babol county in Mazandaran province in the north of Iran which had different textures or different particle size distribution and bulk density were chosen. Two field experiments were carried out to evaluate rice (*Oryza sativa*) productivity in mostly silt loam to which 50 Mg ha (-1) of Apple Pomace were added as a control.

Fresh experimental Apple Pomace samples (approximately 50 Kg) were collected from several main factories (such as Sanich) in Tehran county and Saveh city, Iran. The pomace was air-dried in a large laboratory dryer at below 50°C for 7 days. Chemical composition of AP was determined using the method suggested by AOAC[20-23]. Neutral detergent fiber (NDF) and acid detergent fiber (ADF) were determined using the method of Van Soest et al.[24-27].

Dry matter (DM) was determined by drying the samples at 100 ^{o}C for 24 hrs and ash by igniting the samples in muffle furnace at 550 ^{o}C for 6h and Nitrogen (N) content was determined by the Kjeldahl method[21]. Crude protein (CP) was calculated as N × 6.25. Neutral detergent fiber (NDF) and Acid detergent fiber (ADF) were determined by procedures outlined by Georing and Van Soest[22]. The characteristics of studied Apple Pomace are mentioned in table 2.

Ash Content

One gram of the oven-dried samples in powder from was placed in acid washed crucible by known weight. They were ignited in a muffle furnace for 4-5 hours at 550 ºC. After cooling crucibles they were weighed and the ash contents were expressed in terms of the oven-dried weight of the sample[22,24].

Crude Protein

The protein nitrogen in one gram of the dried samples were converted to ammonium sulphate by digestion with concentrated H2SO4 (Merck 96.5%) and in the presence of CuSO4 and K2SO4. The solutions were heated and the ammonia evolved were steam distilled into Boric acid 2%. The nitrogen from ammonia were deduced from the titrations of the trapped ammonia with 0.1M HCl with Tashirus indicator (methyl red: methylene blue 2:1) until a purplish pink color were obtained. Crude proteins were calculated by multiplying the valve of the deduced nitrogen by the factor 6.25 mg[25].

Experiment

Nickel, Lead and Cadmium concentrations in treated rice by Apple Pomace and conventional rice products were determined by wet digestion method and using 2 g of each rice sample and 12 ml concentrated nitric acid (65% Merck) and 4 ml of Hydrochloric Acid (36.5%, Merck) was added and placed on a hot plate with gradual heat increase to insure full digestion and the disappearance of any residual and nickel, lead and cadmium contents were determined by using flame atomic absorption spectrophotometer (FAAS). Standardized international protocols were followed for the preparation of material and analysis of heavy metals contents by wet digestion method and atomic absorption spectrophotometer analysis based on annual book of ASTM standards and AOAC[19-21]. All digested sample flasks were firstly heated slowly and then vigorously till a white residue is obtained. The residue was dissolved and made up to 10 ml with 0.1 N HNO3 in a volumetric flask. All glassware and plastic containers used were washed with liquid soap, rinsed with water, soaked in 10% volume/volume nitric acid for 24hrs, cleaned thoroughly with distilled water and dried in such a manner to ensure that any contamination does not occur. Blanks and samples were also processed and analyzed simultaneously. All the chemicals used were of Analytical Grade (AR). For heavy metal analyses 5 gram of each rice sample in different states and stages of cooking method was weighed on electronic balance (Shimadzu LIBROR AEX 200G). The samples were analyzed according to standardized international protocols by wet digestion method, Using HNO_3 and HCl , analyzed by a Flame Emission Spectrophotometer Model AA-6200 (Shimadzu, Japan) using an air-acetylene flame for heavy metals in research Analytical Laboratory in Pharmaceutical Sciences Branch , Islamic Azad University, using six standard solutions for each metal. All necessary precautions were taken to avoid any possible contamination of the sample as per the AOAC guidelines[19-23].

Bio-removal Nickel, Cadmium & Lead from Rice Samples

According to the results of all experiments applied above, current investigation was designed to examine the capacity of Apple Pomace for the bio-removal of Nickel, cadmium and lead ions from contaminated soil of paddy rice samples after the determination of these metals in such rice samples in different states. In this experiment, 50 Mg ha (-1) of Apple Pomace were added as a control and rice crops after milling as white grain rice products ready for consumption were studied in both groups of survey: treated by RH and conventional rice .

Risk Assessment

To evaluate the potential risk of rice consumption containing the heavy metals, Provisional Tolerable Daily Intake (PTDI) for a 60kg adult person was calculated by the following equation in which C is the heavy metal concentration in rice, Cons is the average consumption of rice in country (110g per capita per day) and BW is body weight of an Iranian adult person (60kg). The output was compared with the WHO/FAO and Iranian standard level.

$$PTDI = C \times Cons\ BW$$

The Iran standard PTDI limits have been recommended for, Cd, Pb and As 0.001, 0.0036 and 0.0021mg/day/kg BW, respectively[22,24].

Statistical analysis

The values reported here are means of five values. Data were tested at different significant levels using student t-test to measure the variations between the concentrations of heavy metals with and without treated by Apple Pomace adsorbent. The content of Ni, Pb, and Cd in the samples were analyzed by ANOVA, followed by Student's t-test ($P<0.0$). One way analysis of variance (One-ANOVA) was used for data analysis to measure the variations of heavy metal concentrations using SPSS 22.0 software (SPSS Inc, IBM, Chicago, IL).

RESULTS AND DISCUSSION

The mean level of heavy metals was determined in a laboratory scale using 5 samples and for each sample 5 subsamples. All samples were analyzed three times. To clarify the status of the obtained concentration values better, the maximum allowable contents of metals in rice, we referred to the joint FAO/WHO and national standard. Expert Committee on Food Additives (JECFA) has proposed a maximum level of 0.2 mg/kg Cadmium in rice but the community warned that

Table 1. Particle Size, texture, organic matter content, FC and PWP of the studied soils

Soil texture	Sand (%)	Silt (%)	Clay(%)	Organic matter (%)	PWP(%W)	FC(%W)
Silty clay	7.5	43	50	1.52	23.4	44
Silty clay loam	15	45	40	1.96	24.2	39
Sandy loam	72	12	10	0.30	6.4	14

Table 2. Chemical compositions of studied Apple Pomace samples (on DM basis)

Composition	Apple Pomace
Ash (%)	1.1
Crude Protein (%)	22.1
Calcium (%)	0.45
Phosphor (%)	0.47
Neutral detergent fiber (NDF) (%)	57.2
Acid detergent fiber (ADF) (%)	50.5
Fat (Oil plant) (%)	0
Pectin (%)	12.5

Fig. 1. Description of Study Area

"people who eat a lot of rice from regions containing the higher levels of cadmium could be significantly exposed[25].

Iran Standard (No. 12968) has established the maximum limit of Cd in rice about 0.06 mg/kg and on the whole Institute of Standard and Industrial Research of Iran set limit of 0.15 mg/ kg as the maximum level for lead and arsenic and 0.06 mg/kg for cadmium in rice (Organization INS. Food & feed-maximum limit of heavy metals, in 2013[24] . Although the concentration of Pb and Cd varied among the samples, 68.3% of the untreated rice samples contained lower limit than the upper level of 0.15 and 0.06 mg/kg recommended by Iran Standard.

The physical appearance of untreated white raw rice and treated samples by AP in the paddies was seen in figures 2,3 and 4. After pretreatment in the contaminated soil of paddies , it was seen to be detoxified rice samples from Lead in figure 2 . Our data revealed that mean Pb concentration in studied paddies which treated by AP significantely decreased (*p* d" 0.005) . The mean level of lead (mg/kg DW) for all studied rice samples in studied paddies without treatment was 2.7171 ± 0.011(mg/kg DW± SE) but for studied smples from paddies by AP which treated 10 days before the transplanting rice stems decreased to 0.0101 ± 0.001(mg/kg DW± SE).

ANOVA analysis showed that there was a significant difference in Ni and Pb contents in conventional farms samples and white rice from treated paddies' soil samples ($p < 0.05$ and $p < 0.005$ respectively). There were no permitted values available for the other heavy metals such as Nickel to be compared with those of the rice sample contents. The permissible limit of Nickel in plants recommended by WHO is 10mg/k[35] .Nickel has been considered to be an essential trace element for human and animal health. In living systems, it is associated with DNA and RNA molecules and also a regulatory element for the various enzyme systems[25-30].

The mean content of Cadmium in untreated rice product in 150 studied samples were 0.2017 ± 0.0081(mg/kg DW± SE) while in treated rice samples by AP were 0.0106 ± 0.0022(mg/kg DW± SE) which means decreasing significantely ($p < 0.05$).

The removal of metal ions from aqueous streams using agricultural materials is based upon metal bio-sorption[31].

Agricultural waste materials are usually composed of lignin and cellulose as the main constituents. Other components are hemicellulose, extractives, lipids, proteins, simple sugars, starches, water, hydrocarbons, ash and many more compounds that contain a variety of functional groups present in the binding process[32].

A number of agricultural wastes like, hazelnut shells, orange peels, maize cobs, peanut shells, soya bean hulls, jack fruit, soya bean hulls in natural or modified forms has been explored and significant removal efficiency was reported[33] . Diverse plant parts such as coconut fiber pith, coconut shell fiber, plant bark (Acacia Arabica, Eucalyptus), pine needles, cactus leaves, neem leave powder have also been tried for chromium removal showing efficiency more than 90–100% at optimum pH[34-37]. The utilization of rice bran and wheat bran as an adsorbent are found to be less effective as only 50% removal efficiency was reported[35-38]. Cadmium and Cadmium compounds as compared to other heavy metals are relatively water soluble therefore mobile in soil and tends to bio-accumulate. The long life time PVC-window frames, plastics and plating on steel are the basic sources of cadmium in the environment. Cadmium accumulates in the human body especially in kidneys, thus leading to disfunction of the kidney[39].

Potential use of rice bran and wheat bran was tried for sequestering cadmium and significant removal efficiency was reported[40-41]. Studies were

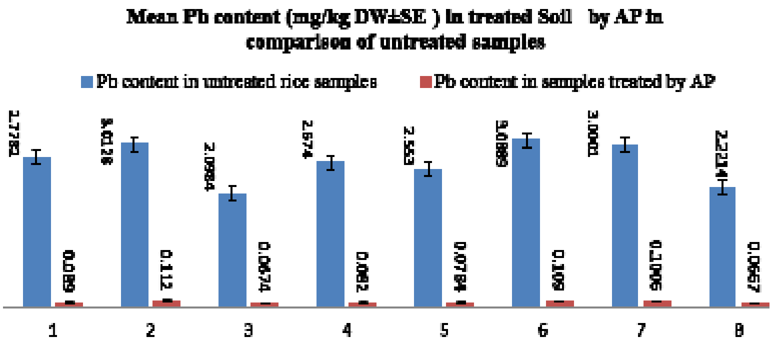

Fig. 2. The mean content of Lead (mg/kg DW ± SD) in white raw rice samples untreated in comparison of treated by AP

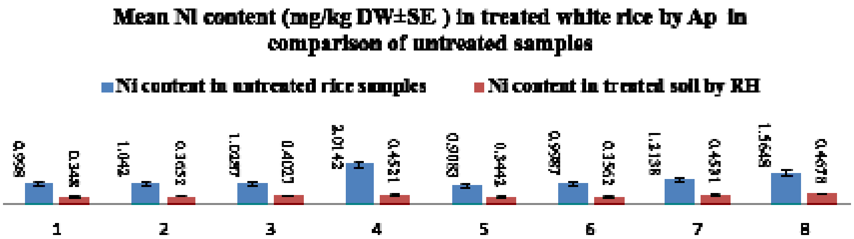

Fig. 3. The mean content of Nickel (mg/kg DW ± SE) in white raw rice samples untreated in comparison of treated by AP

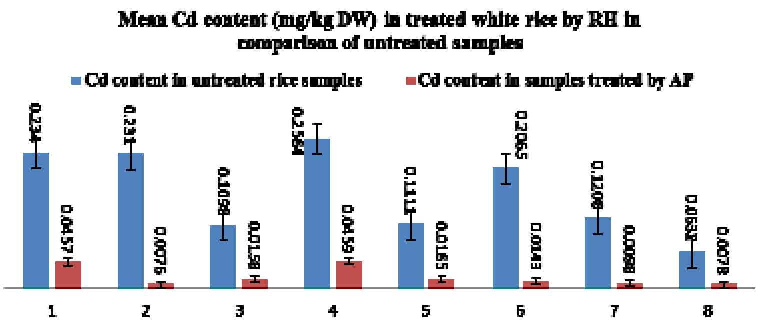

Fig. 4. The mean content of Cadmium (mg/kg DW ± SE) in white raw rice samples untreated in comparison of treated by AP

also conducted on use of rice polish, Apple Pomace and black gram husk in their natural as well as modified form for the removal of cadmium and their relative efficiency was reported[42]. Bark of the plants such as Pecia glehnii and Abies sachalinensis and dried plant biomass of parthenium was tried for the removal of cadmium[41,42]. Use of other parts of the plants such as peels of peas, fig leaves, broad beans, orange peels, medlar peels and jack fruits as adsorbents have been reported to show high removal efficiency at acidic pH[43]. Adsorption experiments conducted on hazelnut shells, peanut hulls, walnut shells, and green coconut shells gave significant results for removal of cadmium[32]. Studies were conducted on activated carbon of bagasse pith, coir pith, peanut shells and dates and their removal efficiency varies from 50 to 98%[40-43]. Research has also been carried out by using chemically treated agricultural waste materials like base treated Apple Pomace, treated juniper fibers, and corncob modified with citric acid, modified peanut shells, succinic anhydride treated sugarcane etc. [39-43]. Most of the studies showed that agricultural waste either in natural form or modified form is highly efficient for the removal of cadmium metal ions.

CONCLUSION

Most common methods for removing heavy metals from polluted environments including the use of physical and chemical methods in site and off site but these methods are complex, costly and time consuming. Therefore, bioremediation methods are useful due to the characteristics such as simplicity, low cost and lack of complexity. In current study the investigation work of farmland pollution went from taking samples from a large sampling area, following with investigation to determine and tracking the target area, to locking-up and remediate after adding "Apple Pomace into the Soil Pollution Remediation Act". The investigation has produced valuable results. Due to establishing the early warning system for the national farmland pollution control, the extensive investigation of the absorption difference of heavy metals between various crops and vegetables grown in different areas and assessing the hazard effects of different crops absorbing the contents of heavy metals in soil on human health, conducting field experiment on reducing the absorption of Cd on food crops, discussion on how to reduce the effects of absorption of heavy metals in soil on various food crops (including rice and vegetables), and seeking for an economical and effective solutions on reducing the risk of food crops and to build a database for the heavy metal background concentration in the soil of Mazandaran province ' farmlands.

Conflict of Interest

The authors have no affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this publication.

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