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Removal of toxic metallic ions Cr(VI), Cu(II), Ni(II), Co(II) and Cd(II) from waste water effluents of tanneries by using *Punica granatum* (pomgranate) membrane

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A B S T R A C T

The biosorption of toxic metal ions from tannery wastewater effluents was studied with the aid of adsorbent prepared by physicochemical treatment of pomegranate's membrane (inner whitish material). The results showed that the physicochemical treated *Punica granatum* (pomegranate) membranes/ peels absorb higher concentration of metallic ions from tannery wastewater as compared to heat treated *Punica granatum* membranes/peels. The contact time of wastewater effluent with pomegranate membrane has also been studied. The biosorption of metallic ions are observed to be more effective by increasing contact time of physicochemical modified adsorbent *i.e.* heterogeneous mixture of H_3PO_4.$ZnCl_2$ modified pomegranate membranes/peels. It has also been observed that maximum adsorption of toxic metallic ions from tannery wastewater can be obtained by using *P. granatum* membranes/peels treated with heterogeneous mixture of H_3PO_4.$ZnCl_2$ at a temperature of 873K. A comparison of heat treated *P. granatum* membranes and acid treatment treated *P. granatum* membranes (with conc. HNO_3) is conducted. The maximum adsorption was observed by a heterogeneous mixture of H_3PO_4.$ZnCl_2$ treated pomegranate membranes/peels. It was also observed that heterogeneous mixture of H_3PO_4.$ZnCl_2$ treated *P. granatum* membranes/peels, activated at 873K provide best absorption of toxic metallic ions from tannery waste water.

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INTRODUCTION

Heavy metal pollution became a global issue affecting on existence and development of human society due to industrializations. As toxic and potential carcinogenic metals, like Cr (VI), Cu (II), Ni(II), Co(II) and Cd(II) pollutions are found from leather industries. These heavy metals may vary in concentration from one industry to other. The other metals can also be present in tanneries and leather industrial wastes; like Ca, K, Mg, Fe, Mn, Pb and Zn [1]. The presence of heavy metallic ions like Cr [2], Cu, Cd, Ni, Co [3] can have negative impact on human health [4]. These heavy metallic pollutants can enter in to seed, fruits easily if heavy metals contaminated soils are used for the production of crops [5]. Furthermore the heavy metals are biodegradable and tend to accumulate in living organisms.

Pakistan is one of the major supplier of leather products to Europe and rest of the world market. Pakistan has a large leather shoe manufacturing base (the eighth largest in the world) [٦]

Although many common methods are used for the removal of theses toxic metallic ions but most innovative method for removal of toxic metallic ions from tannery effluent including biosorption has been investigated. A search for a low cost and easily available adsorbent has led to the investigation of materials of agricultural products as well as industrial byproducts which are

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considered as potential metal sorbents. The utilization of these low cost adsorbent for the treatment of wastewater make it more valuable [7]. For this purpose variety of materials are tested which includes streptomyces sp. [8] Arthrobacter sp. and a Bacillus sp. Coal [9] , palm kernel shell crushed shell [10], maize (Zea mays) leaf [11], straws, Water hyacinth (Eichhornia crassipes) [12], oil palm fruit fibers [13], chitosan [14],[15], Eucalyptus barks [16], Rice husk [17],[18], saw dust [19, 20], different fruit's peels like banana peel [21] pomegranate peel [22] etc. Some adsorbents were passed through different physical and chemical treatment to enhance their efficiency. Phosphoric acid modified rice husk was enhanced the efficiency of rice husk for the removal Chromium [23]. The adsorption of hexavalent chromium from aqueous solution onto formaldehyde treated sawdust and charcoal of sugarcane begasses was also studied at different pH values [24]. Chemically modified pomegranate peels are used for removing lead (II) and copper (II) from aqueous solutions [25]. In the present study, the biosorption of toxic metallic ions from tannery waste water was investigated by using physiochemical modified pomegranate membranes/ peels as well. The adsorption capacity of these adsorbents was carried out using batch experiments. The influence of contact time was also investigated and the experimental data obtained were evaluated.

METHODS

Potassium dichromate, copper sulphate, nickel carbonate, cobalt chloride and cadmium chloride were used for the preparation of stock solutions of 60 ppm for Cr (VI) and 50 ppm for other metals i.e. Cu (II), Ni(II), Co(II) and Cd(II) in distilled water separately. 1:1 ratio of Phosphoric acid and zinc chloride solution and 0.1 M nitric acid were also used for the chemical treatments of *Punica granatum* membranes. All experiments were carried out to investigate the parameters for the extraction of toxic metallic ion from the sample solution by using Analytical Balance ER-120A, Air Drying Oven 108 L., Orbital Shaker OS-1/02, Muffle Furnace-1473K HTMF-1/07, U.V. Spectrophotometer Beckman Model DB-GT and Atomic Absorption Spectrometer (Aanalyst 100).

Preparation of Biosorbents

The *P. granatum* (Pomegranate) membranous peels were washed with distilled water and dried in open air. The final drying was carried out in air dryer at 333 K. The whole material was then ignited in muffle furnace for 4 hours at 873K. Temperature is the factor which can increase or decrease the adsorption capacity of adsorbents. When the whole material was carbonized then divided into three portions. One portion was kept untreated and labeled as "raw". The second portion was soaked in the solution prepared from 1:1 ratio of heterogeneous mixture of zinc chloride and phosphoric acid (CP-1) and third portion was soaked in 0.1 M nitric acid for 24 hours (CP-2). The given materials were then dried before further use.

Experiments of Biosorbents

Untreated and treated adsorbent (*P. granatum* membranes) were used for the removal of toxic metallic ions *i.e.*, Cr (VI), Cu (II), Ni (II), Co (II) and Cd (II) commonly found in tannery effluents by making their standard solutions *i.e.* 60 ppm $K_2Cr_2O_7$, 50 ppm $CuSO_4$, 50 ppm $NiCO_3$, 50 ppm $CoCl_2$ and 50 ppm $CdCl_2$, respectively. A 50 ml of standard solution of $K_2Cr_2O_7/CuSO_4/NiCO_3/CoCl_2/CdCl_2$ and sample of biosorbent were taken in six different 100ml of conical flasks and agitated them on orbital shaker for homogenization at 150 rpm for one hour. The samples then filtered and kept safe for further use. The particle size and weight of the sample/biosorbent were measured and reported in Table 1. The best selected adsorbent i.e. CP1, was then mixed with the tannery effluents. The percentage removal of toxic metallic ions was calculated with the help of following formula

$$\%\,Removal = \frac{C_o - C_i}{C_i} \times 100 \qquad (1)$$

Where C0 is initial concentration of toxic metallic ions and Ci is the final concentration of toxic metallic ions.

TABLE 1. Particle size and weight of biosorbent taken for treatment

Sample No.	Particle Size	Weight of the samples taken for 50ml of standard solutions 50ppm 60ppm $K_2Cr_2O_7$ at 549nm wavelength	50ppm $CuSO_4$ at 324nm wavelength	50ppm $NiCO_3$ at 487nm wavelength	50ppm $CoCl_2$ at 416nm wavelength	50ppm $CdCl_2$ at 375nm wavelength
1	260nm-300nm	3.0410g	3.0956g	3.0345g	3.0541g	3.0784g
2	260nm-300nm	3.0543g	3.0671g	3.0256g	3.0873g	3.0458g
3	260nm-300nm	3.0823g	3.0447g	3.0693g	3.0747g	3.0765g

Preparation of working standards

The working standards were made by taking 5ml of K2Cr2O7 filtrate in 50 ml of measuring flasks. A 1ml of DPC solution and 1ml of O-phosphoric acid were added to the mixture. Pink color was developed in case of K2Cr2O7. The solutions were level by adding distilled water mixed the solutions gently all flasks were shaken carefully for a max period of 5 minutes. Pink color that formed as a result of the reaction between Chromium (VI) and 1, 5-diphenyl carbazide in acidic medium, was

measured by using UV- Spectrophotometer at fix wavelength i.e. 549nm. The same procedure was repeated for tannery effluents at the same wavelength i.e. 549nm and their absorbance were measured with the help of U.V. Spectrophotometer (Beckman Model) which was then converted into concentration by following Beer Lambert Law. As a result, different color complexes were formed as shown in the Figure 1. A 10ml volume of each filtrate of other metallic ions [Cu (II), Ni (II), Co (II) and Cd (II)] was placed in 50 ml of different measuring flasks. All flasks were shaken gently and were subjected to atomic absorption spectrometer (Aanalyst 100) to measure the absorbance of Cu (II), Ni (II), Co (II) and Cd (II) at wavelengths of 324nm, 487nm, 416nm, 375nm respectively. Same Law (Beer Lambert Law) was used for the conversion of absorbance into concentration and percentage adsorption were calculated by the same method as discussed above.

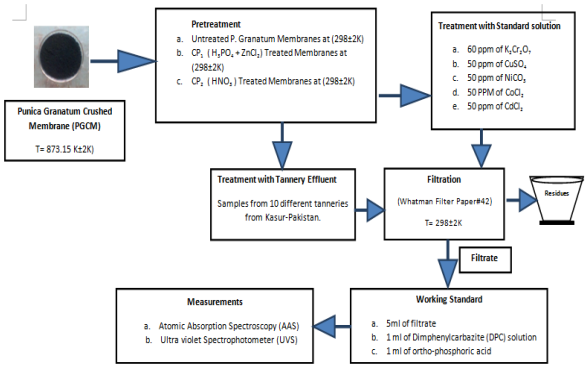

Figure 1. A schematic representation of different steps for the removal of toxic metallic ions Cr (VI), Cu (II), Ni (II), Co (II) and Cd (II) from waste water effluents of tanneries by using *Punica granatum* (pomgranate) membrane

RESULTS AND DISCUSSION

The study showed that *P. granatum* (Pomegranate) membranes was a good biosorbents for adsorbing large quantity of Cr (VI), Cu (II), Ni (II), Co (II) and Cd (II) ions. The result shows that *P. granatum* membranes have an influence on the absorbance of relative metals. The activated *P. granatum* membranes were used for absorption purposes. Then it was passed through different level of treatments to check changes in efficiency. It was observed that activated pomegranate peels showed maximum absorption *i.e.* 99.54 - 99.65% for selected metals *i.e.* Cr (VI), Cu (II), Ni (II), Co (II) and Cd (II). There was an appreciable increase in absorption capacity when given at different treatments *i.e.* H_3PO_4.$ZnCl_2$ and HNO_3. For Cr (VI), the absorption capacity was increased from 99.64 to 99.81% with a mixture of H_3PO_4 and $ZnCl_2$ while with HNO_3, it increased from 99.64 to 99.69% (Figure 2). The H_3PO_4 and $ZnCl_2$ mixture treated pomegranate peels > HNO_3 treated pomegranate peels > untreated activated pomegranate peels.

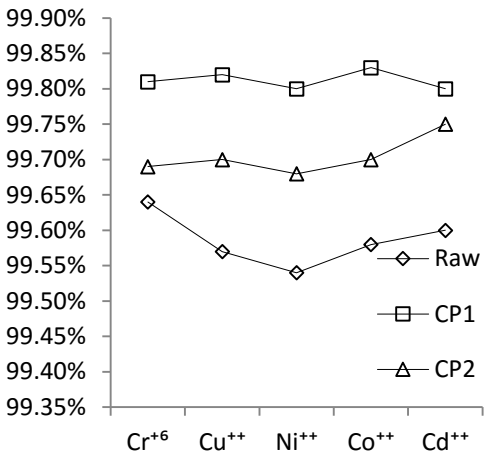

Figure 2. Percentage absorption of metals on physico chemically treated *P. granatum* membranes

The second metal *i.e.* Cu (II) was passed through untreated activated pomegranate peels. The percentage absorption was then 99.57%. This percentage was increased when the same concentration of standard solution of Cu (II) was treated with HNO_3 treated pomegranate peels *i.e.* 99.70. 99.82% absorption was observed when the same concentration of standard solution of Cu (II) was treated with $H_3PO_4$and $ZnCl_2$ solution treated pomegranate peels. When 50 ppm standard solution of Ni (II) was treated with activated pomegranate peel, 99.54% absorption was observed. This percentage absorption increased to 99.68% by using HNO_3 treated pomegranate peels and to 99.80% by using H_3PO_4 and $ZnCl_2$ mixture treated pomegranate peels. Same pattern was observed for Co (II) and Cd (II).

Effect of Temperature on biosorbent

One of the purposes of this research is to ascertain the effect of temperature on the surface of *Punica granatum* membranes. The effect of temperature on the removal of Cr^{+6}, Cu^{++}, Ni^{++}, Co^{++} and Cd^{++} in stock solutions by *P. granatum* was studied by varying the temperature between 273 and 1073K. The data presented in Figure 3 showed that adsorption of metal ion by *P. granatum* membranes increased with increase in temperature because as temperature increases, the attractive forces between biosorbent surface and metal ions are weakened and sorption decrease [26]. Careful examination of the Figure 3 revealed that the magnitude of such increase was continued between 273- 873K. After passing through this temperature % adsorption was started decreasing and the *P. granatum membranes* were converted into ash. So, the best temperature for adsorption was 873K.

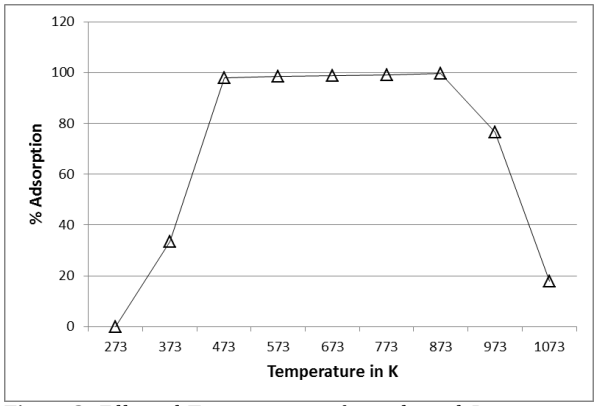

Figure 3. Effect of Temperature on the surface of *P. granatum* membranes for adsorption of all toxic metallic ions

Effect of Biosorption on Tannery Effluent

There are about 200 tanneries in Kasur and most of them are found in Niaz Nagar which is becoming the target area of creating pollution and causing different diseases in a particular area. As far as tanneries are concerned, they are generating thousands of hazardous substances per day and these substances are becoming the part of our environment. It is necessary to adopt such methods that can create less pollution over there and people will remain safe from different diseases. Use of toxic chemicals is the main source of pollution especially in drinking water. The water is basically used for the purpose of cleaning the hides or skin. Tannery waste water is highly polluted in terms of heavy metals like Cr (VI), Cu (II), Ni (II), Co (II) and Cd (II) [1,2,3,4] The selected samples were then treated with 10 samples of waste water which were collected from 10 different tanneries of Kasur. According to National Environmental Quality Standard (NEQS) the absorbance or concentration of heavy metals should be in the range of 0.008-0.05 or 0.015-0.09 ml/l. Absorbance if exceeds 0.05/0.09mg/l then it results a great damage to the environment [27]. In this study, best adsorbent was obtained by the treatment of *P. granatum* membranes with the H_3PO_4 and $ZnCl_2$ mixture. The absorbance before and after treatment of *P. granatum* membranes that was found in the tanneries of Kasur, is reported in Figure 4. Figure 5 shows the percentage of removal for the tremendous change before and after treatments with *P. granatum* membranes.

Effect of Contact Time

The removal of Cr (VI), Cu (II), Ni (II), Co (II) and Cd (II) ions increases with time and attains saturation in about 5 hours. Figure 6 (a, b, c) represents the percent removal of Cr (VI), Cu (II), Ni (II), Co (II), Cd (II). The five metals showed a fast rate of biosorption during first hour of the sorbate-sorbent contact and the rate of percent removal becomes almost insignificant due to a quick

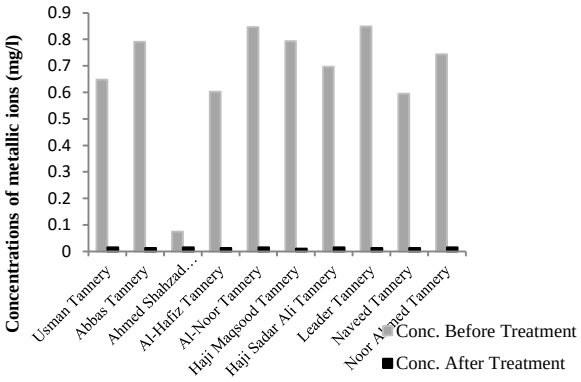

Figure 4. The absorbance of metals in effluent of tanneries of Kasur before and after treatment of biosorbent

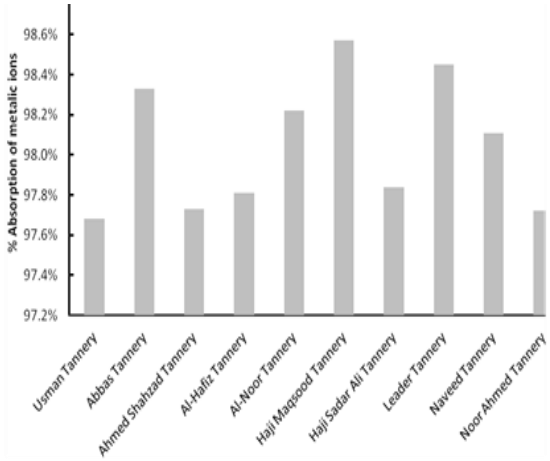

Figure 5. The Percentage Absorption of metals from the effluent of tanneries of Kasur

exhaustion of the adsorption site. The rate of percent removal of metal is more in the beginning on account of a greater surface area of the adsorbent being available for the adsorption of the metals. The tremendous change of adsorption for all other unknown metals that were found in tannery effluent with respect to contact time was also measured (Figure 7).

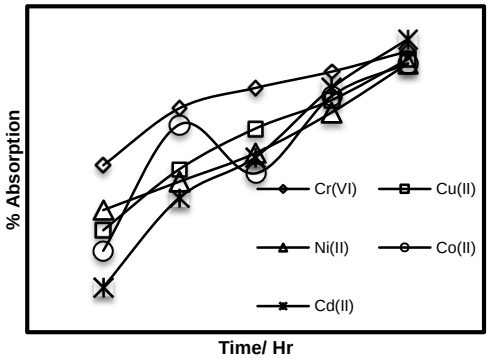

Figure 6a. The experimental data of percentage removal efficiency of heavy metals on raw biosorbent (raw) surface as a function of time.

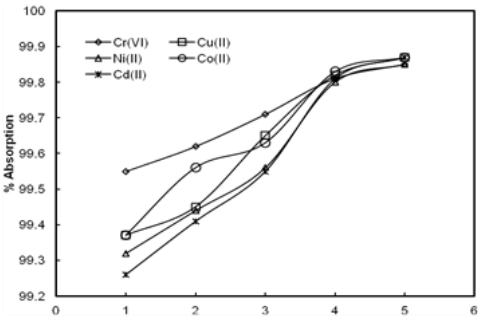

Figure 6b. The experimental data of percentage removal efficiency of heavy metals on CP1 biosorbent (CP_1) surface as a function of time.

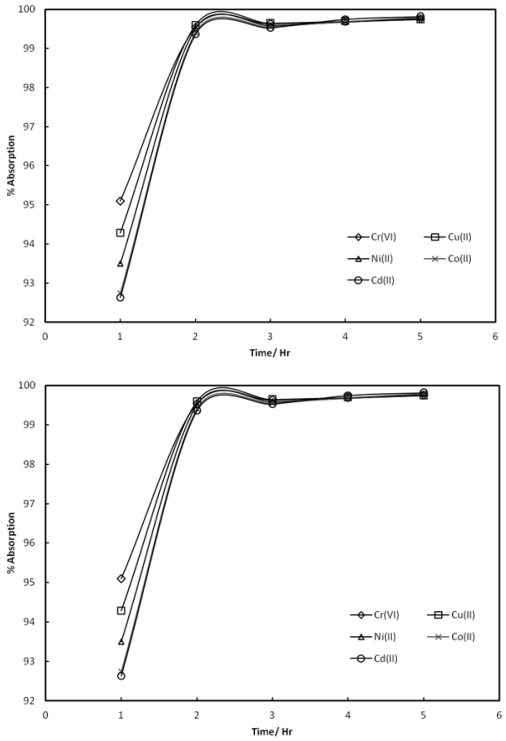

Figure 6 c. The experimental data of percentage removal efficiency of heavy metals on raw biosorbent (CP2) surface as a function of time.

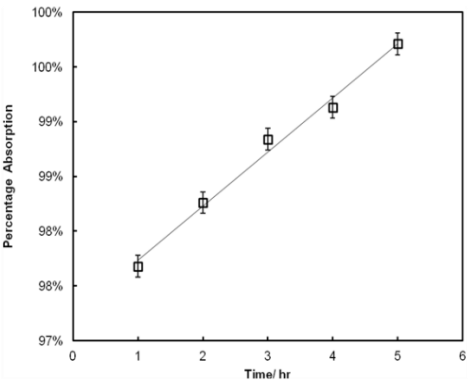

Figure 7. Effect of contact time on the removal of heavy metals of Tanneries

CONCLUSION

It is concluded that biosorption of metallic ions on chemically treated *P. granatum* membranes/peels with HNO_3 at 873K and chemically treated *P. granatum* membranes/peels with H_3PO_4 + $ZnCl_2$ mixture at 873K shows an increasing trend in case of Cr(VI) removal. The similar increasing trends were also observed for other metallic ions Cu (II), Ni(II), Co(II) and Cd(II). It is further concluded that biosorption of Cr(VI), Cu (II), Ni(II), Co(II) and Cd(II) with pomegranate membranes/peels follow the following trend in terms of removal efficiency : The H_3PO_4 + $ZnCl_2$ mixture treated pomegranate peels > HNO_3 treated pomegranate peels > untreated activated pomegranate peels. The percentage absorption has been found an increasing function of contact time.

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Persian Abstract

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چکیده

جذب بیولوژیکی یون های فلزی سمی از جریان های پساب دباغ خانه با کمک جاذب های آماده شده با تیمارفیزیکی شیمیایی غشای درخت انار مطالعه شد. نتایج نشان میدهد که غشا/پوست درخت انارتیمار شده با روش فیزیکی شیمیایی یون های فلزی بیشتری را ازجریان پساب در مقایسه با تیمارحرارتی نشان میدهند. زمان ماند جریان پساب با پوست انار بررسی گردید. جذب بیولوژیکی یون های فلزی با افزایش زمان ماندجاذب های تیمارشده با روش فیزیکی شیمیایی مثلا درمخلوط پوست انار اصلاح شده با $H_3PO_4.ZnCl_2$ افزایش میابد.همچنین بیشترین جذب یون های فلزی با استفاده ازپوست انار مخلوط ناهمگن $H_3PO_4.ZnCl_2$ در دمای ۸۷۳ کلوین مشاهده شد. مقایسه ی بین پوست انار تیمار شده با روش حرارتی و اسیدی (HNO_3با) انجام شد. بیشترین جذب با مخلوط ناهمگن $H_3PO_4.ZnCl_2$ مشاهده شد. همچنین تیمار پوست انار با مخلوط $H_3PO_4.ZnCl_2$ و فعال سازی در ۸۷۳ کلوین بهترین جذب یون های فلزی از جریان پساب را فراهم می کند.