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Preparation and Characterisation of Chemically Activated Almond Shells by Optimization of Adsorption Parameters for Removal of Chromium VI from Aqueous Solutions

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Abstract**—**Activated carbon was prepared from agricultural waste "almond (Prunus amygdalus) nut shells" by chemical activation with phosphoric acid as an activating agent at 450 °C for 24 hr soaking time. The physical and chemical properties were analyzed. The adsorption of chromium VI from aqueous solution on almond nut shell activated carbon (ASAC) was investigated. The adsorption process parameters pH, agitation speed, agitation time, adsorbent dose were optimized. 98% of Cr VI was sorbed at pH 2 and stirring speed 200 rpm.. Surface structure showed that ASAC has a spongy type structure showing large number of pores

Keywords**—**adsorption, sorbent ,sorbate and activation

I. INTRODUCTION

CHROMIUM and its compounds are toxic metals introduced into natural water from a variety of industrial wastewater.

The major sources are from Textile Dyeing, Leather Tanning, Electroplating and Metal Finishing industries which cause severe environmental and public health problems. The hexavalent form of chromium is considered to be a group "A' human carcinogen because of its mutagenic and carcinogenic properties [1]. It leads to liver damage, pulmonary congestion, oedma and causes skin irritation resulting in ulcer formation [2]. Its concentration in industrial wastewater ranges from 0.5 mg/l to 270000 mg/l [3]. The tolerance limit for the discharge of CrVI into inland surface water is 0.1mg/l and in potable water is 0.05 mg/l [4]. A wide range of physical and chemical processes is available for the removal of Cr (VI) from wastewater such as electro-chemical precipitation, ultra filtration, ion exchange and reverse osmosis [5, 6,]. The major drawbacks with these processes are high cost, toxic sludge generation or incomplete metal removal. The commercial activated carbon produced from coal can effectively remove chromium but these are also expensive as well as nonrenewable resources.

Many researchers have worked on production of activated carbon from renewable resources, using low cost methods and materials and also emphasis was also on to decontaminate water in an environmental friendly manner. Agricultural and industrial waste material is used as Activated carbons used by different researchers for the removal of chromium such as coconut husk and palm pressed fibers [7], coconut shell activated carbon [8], wood and dust coal activated carbons [9], saw dust and used rubber tyre carbon [10], cactus, olive stone/ cake, wool, charcoal and pine needles [11] rice husk carbon [12], Cequisetifolia leaf carbon [13] bagasse and fly ash [14] hazelnut shell [15] husk of Bengal gram [16] sugarcane bagasse [17] rice bran [18] rice husk [19] have been reported in the literature.

Almonds (Prunus amygdalus) is one of the important stone fruit grown in Pakistan. It is mainly grown in Balochistan and NWFP, and is widely used in the country throughout especially in winter season. Approximately 10000 Tones almond nutshells are being generated annually and are of no use at present [20]. These nutshells are waste materials and can be collected on community basis for reuse. Almond nutshells are abundant, inexpensive and readily available lignocellulosic material. In the present study these nutshells were used to prepare the activated carbon for the removal of chromium. . The present work describes the chemical activation process for the manufacturing of activated carbon. Its physical and chemical properties were determined by standard methods. The sorption characteristic of Cr (VI) on modified almond nut shells was also observed. The effect of various operational parameters such as pH, agitation speed, agitation time adsorbate concentration and adsorbent dose on the removal of Cr(VI) from aqueous solution was also analyzed.

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II. METHOD AND MATERIAL

A. Adsorbent Preparation

The raw material used was almond nutshells, which were obtained from the local market. Nutshells were ground by Pestle and Mortar. The ground material was sieved in "RO-Tap type electrical sieve shaker". Particles retained on Mesh 10, which is approximately equal to 1.68 mm, were chosen for sorbent preparation. 50 gm of nutshells were weighed by using "Direct Reading Balance LM-20" with precision ± 0.002 mg. The weighed nutshells were impregnated in phosphoric acid for 2 hr (1:1 wt %).

A reactor of 7.5 inch length and 2.5inch diameter was designed. The samples were placed in that horizontal reactor. These samples were pyrolysed at 170 °C for 0.5 hr in the "Table Top Furnace Model Soft Temp 2FC Tanaka Scientific instrument CO LTD TOKYO furnace". The pyrolyzed samples were activated at 450 °C for 1 hr in Nitrogenous atmosphere. The granules were cooled in the furnace at inert atmosphere for overnight. The carbon was washed for 24-30 hr in Soxhlet Extractor, until pH was neutral. The pH of the rinsed water was analyzed, which was found to be 7. The sample was dried in an Electric Oven at 110 °C for 3 hr. The granules were sieved on 12-40 Mesh. The carbon retained on the 40 Mesh sieve approximately equal to 380 μm was stored for further analysis [21].

B. Preparation of stock solution

All the reagents were of analytical grade. An aqueous solution of 1000 ppm of chromium was prepared using potassium dichromate in double distilled water. The samples of required concentration were prepared by diluting the stock solution of chromium. The buffers of pH (1-3) (4-6) and (7-10) were prepared by mixing an appropriate volume of 0.1M solution of HCl- KCl, CH3COOH-CH3COONa and H3BO3-NaOH respectively [22].

C. Procedure for metal ion sorption studies

All The sorption capacity was determined by contacting various concentration 60-100 mg/l of 50 ml chromium solution with 0.25-1.25 gm almond shell activated carbon. The mixture was shaken in the "Rotary Shaker" at 90-200 rpm for 5-40 mins. Aqueous solution of different pH 2-10 was used. The sample was then filtered through "Watman filter paper No 1". The solution was analyzed on "Spectronic 21 Milton Roy Company" at wavelength 460 nm.

Each experiment was repeated three times and the results were taken as average. The amount of adsorption at equilibrium (qe mg/g) and sorption efficiency (%) were calculated according to the expressions

$$qe\ (mg/g) = \{(Co-Ce)\ V\}/m$$

$$\text{Sorption efficiency } \% = (Co-C)/Co \times 100$$

Where Co and Ce are the initial and equilibrium concentration (mg/l), V the volume of solution (L), m the weight of almond shells (g) and C is the solution concentration at the end of the sorption process (mg/l) [23].

D. Adsorbent analysis

The Physical (carbon yield, density, hardness,), chemical (pH, conductivity, ash) were analyzed [24]. The results are produced in Table. 1

The "Particle size analyzer LA 300" was used for determining the surface area. The surface structure of activated carbon was determined by "Jeol JSM-6380LV Scanning Electron Microscope" as shown in Fig. 1.

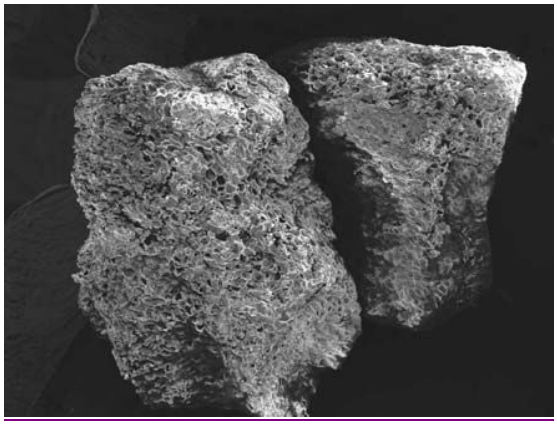

Fig. 1 SEM Image of Particle size

III. RESULTS AND DISCUSSION

A. Physical and Chemical characteristic of Activated sample

Bulk density is important parameter when carbon is removed by filtration because it determines how many pounds of carbons can be contained in a filter of a given solid capacity and how much treated liquid is retained by the filter cake. Carbons with adequate density also help to improve the filtration rate by forming an even cake on the filter surface. The American Water Work Association has set a lower limit on bulk density at 0.25 gm/ml for Granular Activated Carbon (GACs) to be of practical use [25]. The bulk density of prepared sample used for this work is within that limit, which is 0.52 gm/ml.

Carbons should possess sufficient mechanical strength to withstand the abrasion resulting from continued use. Hardness of currently commercial carbons are in the range of 70-90%.Where as the hardness of the activated sample was 98%.

The activated carbon considered in this work proved to be acidic, as presented in the Table No. 1. The acid or basic nature of an activated carbon depends on its preparation, inorganic matter and chemically active oxygen groups on its surface as well as the kind of treatment to which the activated carbon was submitted.

Water leachable minerals are generally not desirable in any

application because minerals may cause specific problems with catalysis of adverse reactions or interference by competitive adsorption. The conductivity of the chemically activated samples was reported to be 40 µs/cm.

The ash in activated carbon is not desirable and is

TABLE I
PHYSICAL AND CHEMICAL CHARACTERISTICS OF ASAC

S.NO	Characteristics	Values
1	Particle size	374µm
2	Density	.52gm/ml
3	pH	4.5
4	Conductivity	40µs/cm
5	Yield	37%
6	Hardness	98%
7	Ash	2.9%

considered as an impurity. The ash was found to be 2.9% in the activated samples.

The samples also exhibited a reasonable yield of 37%, which shows presence of carbon content. The by products and activation methods have an influence on the yield of samples.

B. *Optimization of adsorption Parameters for removal of chromium VI from aqueous solution*

Sorption is the collection of sorbed substances on the surface of sorbent. It is affected by the physical and chemical characteristics of the sorbent. Sorption studies were carried out by optimizing various parameters: pH, adsorbent dose, agitation time, agitation speed and sorbate concentration

C. *Effect of pH*

The adsorption of metal ion depends on solution pH which influences the electrostatic binding of ions to corresponding metal groups. The optimization of pH is necessary, so the effect of pH was studied in the range 2-10. Fig. 1 shows the effect of pH on % sorption. 0.5 gm of almond nutshells was agitated with 50 ml of 100 mg/l of sorbate. The sample was agitated at 100 rpm for 25 min at 303 k Temperature. It was observed at lower pH < 5 the sorption capacity was more. The functional group on the surface of the sorbent carry positive charge hence the negatively charged chromium species bind through electrostatic attraction to the surface of sorbent due to increase of electrostatic force of attraction. At pH greatar than five there is decrease in sorption due to increase of the negative charge on the adsorbent thus the electrostatic force of attraction between the sorbent surface and sorbate ion are decreased. The occupation of the adsorption sites by anionic species like HCrO4-, CrO42-, Cr2O2-7, which oppose the sorption of ion towards the sorbent surface. At pH 2 the maximum sorption of Cr was observed to be 97.77 % which indicates pH 2 optimum for sorption of chromium. At pH 2 to 3 the Cr (VI) removal was highest [26].

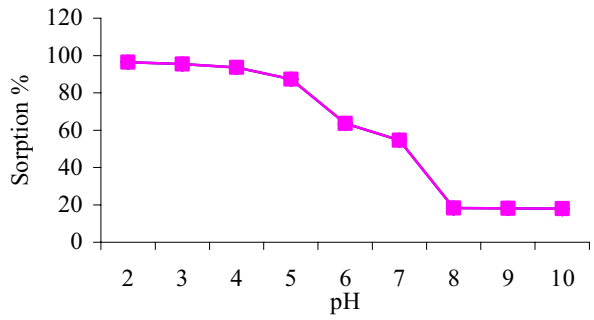

Fig. 1 Effect of pH on sorption of chromium on activated nuts

D. *Effect of shaking time*

The effect of shaking time on % sorption of chromium on ASAC was studied over an agitation time of 5-40 mins. 0.5 gm of ASAC, was shaked at 100 rpm with 50 ml of 100 mg/l sorbate concentration. At 303 k temperature the pH was maintained at 2. The Percent sorption increases from 66 % upto 75 %, the results are depicted in Fig. 2. The optimum equlibrium time was found to be 25 minute, which is quite less as reported i.e 120 min [27].

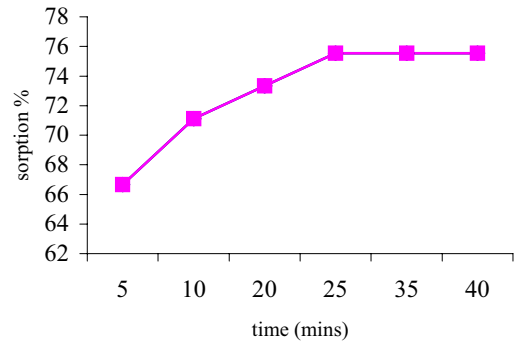

Fig. 2 Effect of agitation time for the sorption of chromium on activated nuts

E. *Effect of sorbent dosage*

In Fig. 3 the effect of adsorbent dose on percentage sorption of chromium is reported. For optimizing the adsorbent dose 0.25 to 1.25 gm of almond nutshells were agitated with 50 ml of 100 mg/l of chromium solution. The temperature was maintained at 303 k at pH 2 and 100 rpm shaking speed. The percentage sorption increased upto 84 % from 71 % and remained constant afterwards at 1 gm. Previous reports reveal that there should be a ratio between sorbent dose and sorbate concentration, which represents maximum percentage sorption.

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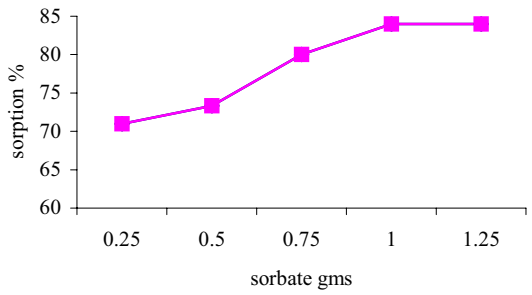

Fig. 3 Effect of sorbent for the sorption of chromium on activated nuts

F. *Effect of shaking speed*

The shaking speed was optimized as shown in Fig.4. The effect of the agitation of the sorbent/sorbate system in chromium adsorption was monitored at low, medium and high- agitation speeds (90, 100, 120, 150, 200 rpm). 0.5 gms of adsorbent and 50 ml of 100 mg/l chromium concentration at pH 2 was agitated for 25 minutes at 90-200 rpm. Maximum 97.77 % chromium sorption was achieved at 200 rpm. The effect of Cr sorption on low and high agitation speed was observed.

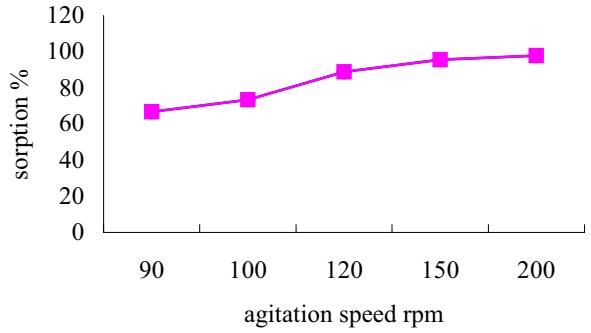

Fig. 4 Effect of agitation speed on sorption of chromium on activated nuts

An increase in sorption was observed from 66.66 % to 97.77 %, when the agitation speed was increased from 90 to 200 rpm. Due to agitation proper contact is developed between metal ion in solution and the binding sites, which promotes effective transfer of sorbate ions to the sorbent sites.

G. *Effect of adsorbate concentration*

Different adsorbate concentration ranging from 60 to 100 mg/l at pH 2 with adsorbent dose 0.5 gm, were agitated at 200 rpm for 25 min. At temperature 303 k the pH of sample was maintained at 2. The percentage sorption is given in Fig.5 which showed that % of Cr sorption increases with decreasing the concentration of sorbate. This is because in lower concentration there are sufficient active sites which the sorbent could easily occupy. However in higher concentration active sorption is not available for the sorbent to occupy, hence Cr ions are left unabsorbed in solution due to the saturation of binding sites.

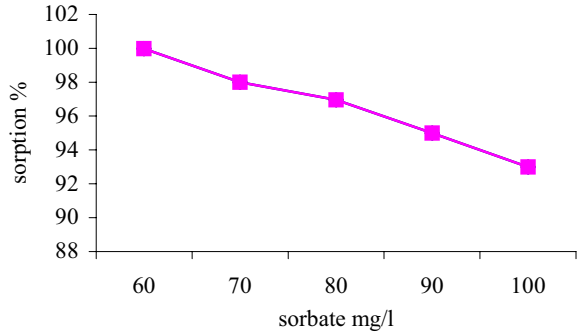

Fig. 5 Effect of sorbate concentration on sorption of chromium on activated nuts

H. *Almond nutshells characteristics*

The surface structure of almond nutshells was analyzed by "Scanning Electronic Microscope"(SEM) at 500X magnification. Untreated almond nutshells, activated almond nutshells and chromiuim sorbed activated almond nutshells were analyzed. It was observed that the pores of the untreated almond nutshells were closed Fig. 6(a). The activated nutshells had a porous structure showing large number of pores indicating large surface area Fig. 6 (b). The chromium sorbed activated sample has efficiently removed chromium because the pores are blocked showing the sorption phenomena Fig. 6(c).

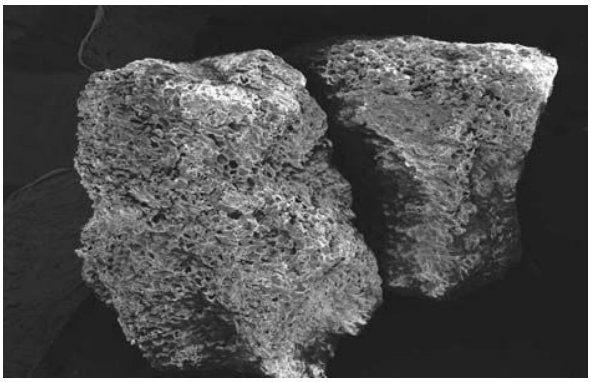

Fig. 6 (a) SEM activated nutshells showing porous structure

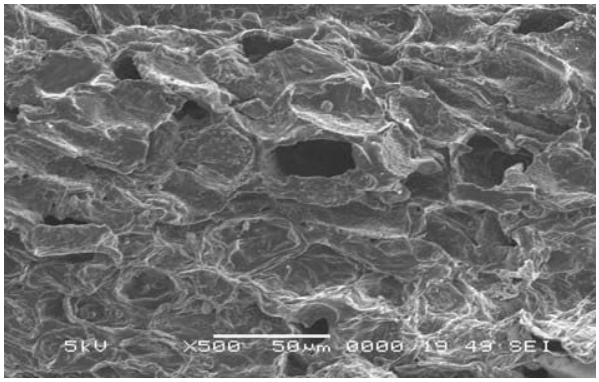

Fig. 6 (b) SEM of untreated almond nutshells

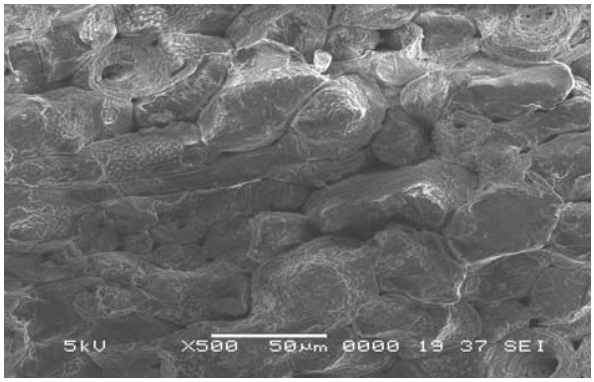

Fig. 6 (c) SEM of chromium sorbed activated almond nutshells

IV. CONCLUSION

The removal of Cr(VI) from aqueous solution is possible by using abundantly low cost adsorbents. Almond nut shells were chemically activated by Phosphoric acid. Activated nut shells are most effective for which the removal reached 94.73 % at 303 K.

Adsorption of Cr(VI) was highly pH dependent and the results showed that the optimum pH for the removal was 2.

Maximum sorption was achieved at 100 rpm shaking speed, while the optimum agitation time was 70 minutes.

The activated samples were acidic in nature having high hardness and low in mineral and ash content.

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