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Adsorption of Cr(VI) Ions using Activated Carbon Produced from Indian Water Chestnut (*Trapa natans*) Peel Powder

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The indiscriminate discharge of heavy metals into water and soil from anthropogenic practices is becoming prominent threat to the environment. Heavy metals like chromium, cadmium, lead, arsenic, nickel *etc*. are heavily toxic and carcinogenic in nature. This study emphasizes the adequacy of activated water chest nut (*Trapa natans*) peel powder as a new adsorbent material for removal of chromium(VI) metal ions. Adsorption experiments were performed in batch process. Various process parameters like contact time, temperature, solution pH, dose of adsorbent, metal ion concentration *etc*. were optimized. The physico-chemical properties of adsorbent material were characterized by FTIR and XRD. The morphology, topology of adsorbent surface was characterized by scanning electron microscopy (SEM) and Brunauer, Emmett and Teller (BET) which revealed a highly porous structure and available specific surface area. The adsorption capacity (maximum) was counted as 59.17 mg/g and specific surface area was found 23.467 m^2/g at a pH 7. The adsorption process for Cr(VI) ions was in a good agreement with Langmuir isotherm. The process also followed pseudo second order kinetics. The obtained result shows that activated water chest nut (*Trapa natans*) peel powder (AWCPP) can be a hopeful low-cost and eco-friendly bio-adsorbent for removal of Cr(VI) metal ions and also better adsorbent than other various reported adsorbents.

Keywords: Adsorption, Wastewater, Water chestnut, Cr(VI), Adsorption isotherms, Activated water chest nut peel powder.

INTRODUCTION

Heavy metal contamination in water is becoming a severe issue owing to serious toxicities and carcinogenic nature of the pollutants. The presence of heavy metals such as arsenic, chromium, cadmium, nickel and zinc in the aqueous environment endangered the human health and safety [1]. Heavy metals are non-biodegradable, carcinogenic and toxic for living organisms. The biomagnifications of heavy metals in the food chain is adversely affecting the ecosystem [2]. Chromium and its compounds are toxic metals introduced into the environment through a variety of sources like textile, dyeing, metal finishing industries, leather tanning and electroplating [3]. Chromium(VI) contains +6 oxidation state which is considered as a carcinogenic agent for human being [4]. Heavy metal toxicity leads to edema, liver damage and pulmonary congestion [5]. Therefore, the treatment of contaminated water is essential before its release into the surroundings. Various techniques such as adsorption [6], precipitation [7], ultra filtration [8], flocculation [9] and ion-exchange [10] have been used to remove metal pollutants from wastewater [11]. Though, adsorption process being very simple, versatile, economical and efficient for the removal of heavy metals and dyes from polluted waters [12]. It is becoming a popular technique, because the removal efficiency of metal ions is high as well as reusability of adsorbent [13,14]. Major types of adsorbents such as molecular sieve, zeolites, silica gel, clay, polymers and carbon based materials (activated carbon) are used as adsorbent material for adsorption process [15]. The activated carbon is a graphite based amorphous material with large surface area that is used for removal of heavy metals [16]. They are non-polar and highly porous micro crystallites with a graphite lattice, usually prepared in small pellets [17]. Water chestnut (*Trapa natans*) locally called singhara is very common food for Asian people keeping to its sole taste. Indian water chestnut or caltrop is an aquatic plant belonging to the genus *Trapa*. In this study, we used Indian water chestnut peel powder for the fabrication of activated carbon and as an adsorbent for removal of Cr(VI) ions from its effluents.

EXPERIMENTAL

Water chest nuts (*Trapa natans*) were locally collected. All chemicals used in this study were of analytical grade which includes potassium dichromate, conc. sulphuric acid, hydrochloric acid and sodium hydroxide.

Preparation of adsorbent: Water chestnut peels were washed with double distilled water to remove of dirt, acid contents and coloured compounds. Peels were sun dried for 4 days. Further dried at 50 °C using hot air oven for 6 h. After drying, the material was grounded into powder form using domestic mixer and sieve analysis was performed. The particle size of 0.147 mm (100 mesh number) was selected. Powdered material was stored in air tight glass bottle to protect it from moisture. It was further treated with conc. H_2SO_4 [1:1 (w/v)] at room temperature for 1 h. Afterward it was placed in muffle furnace at 160 °C for 0.5 h to remove volatile impurities. The heat treatment converts powered material into activated carbon form. Then washing with double distilled water was given to remove any residues.

Experimental procedure: 2.827 g of $K_2Cr_2O_7$ (analytical grade) was mixed in 1 L of double distilled water to prepare 1000 mg/L of chromium(VI) stock solution. The pH of the aqueous solution is varied (2-12) by adding the required amount of 1 N HCl and 1 N NaOH. Samples of different concentration (10-100 mg/L) of chromium(VI) were prepared by appropriate dilution of chromium(VI) stock solution. It was treated with different concentrations of activated carbon (2-20 mg per 20 mL of chromium(VI) solution) using magnetic stirring. The stirred solution was allowed to stand for 20 min and supernatant was taken and analyzed for Cr(VI) content through AAS. The percentage removal of Cr(VI)was estimated by the following formula [18]:

$$\text{Removal (\%)} = \frac{A - B}{A} \times 100$$

where, A = initial concentration of chromium(VI); B = concentration of chromium(VI) after removal.

Numerous constraints including contact time, solution pH, reaction temperature, adsorbate concentration in addition to adsorbent dose were evaluated for best removal efficiency of Cr(VI). Various isotherm and kinetic models were fabricated for study of adsorption [19].

Characterization: The physico-chemical properties of adsorbent were analyzed (scan rate 2°/s, 2θ angle from 10° to 50°) through XRD (Rigaku Ultima IV, USA) and FTIR (Perkin Elmer Frontier FTIR, USA). The sample was analyzed within the frequency range of 4000-400 cm^{-1}. The morphological characteristics were investigated through scanning electron microscope (SEM). Before analysis, samples need to be made conductive by Au coating for scanning by a SEM (JEOL, JSM 6100, Japan). The specific surface area of adsorbent was investigated through Brunauer, Emmett and Teller (BET) method and AAS (Agilent Technologies, 200 Series AA) used for determining the concentration of chromium(VI) within a sample.

RESULTS AND DISCUSSION

XRD and FTIR: Physico-chemical properties of dried and well-powdered adsorbent were evaluated through X-ray diffraction (XRD) pattern. The broad peak in XRD spectra revealed the amorphous nature of activated water chestnut peel powder (Fig. 1). The strong diffraction peaks emerged at 2θ = 22.46° and 25.25° indicates the existence of graphite crystallite of carbon in water chestnut active carbon [20]. The FTIR spectrum of the activated water chestnut peel powder (Fig. 2). The bands 3100-2850 cm^{-1} region indicated the presence of aliphatic -CH group stretching [21]. The broad band at 3748 cm^{-1} associated with -OH stretching vibration and peak at 1574 cm^{-1} matches to C=C stretching of the aromatic rings. Two peaks at 1710 and 1029 cm^{-1} were attributed to the vibration absorption of C–O [20].

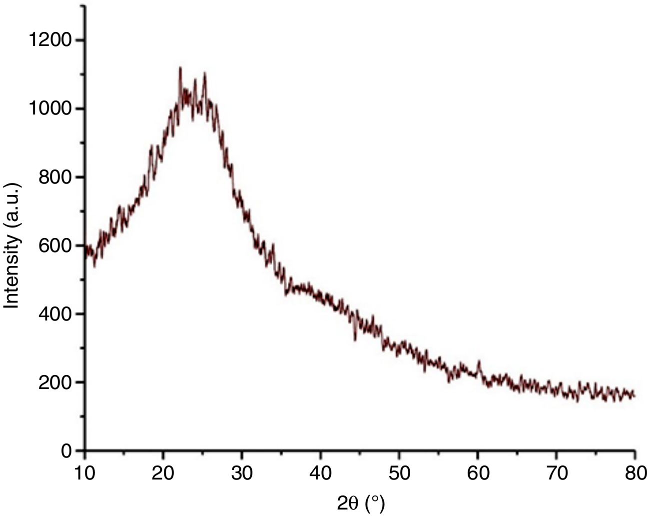

Fig. 1. X-ray diffraction pattern of AWCPP

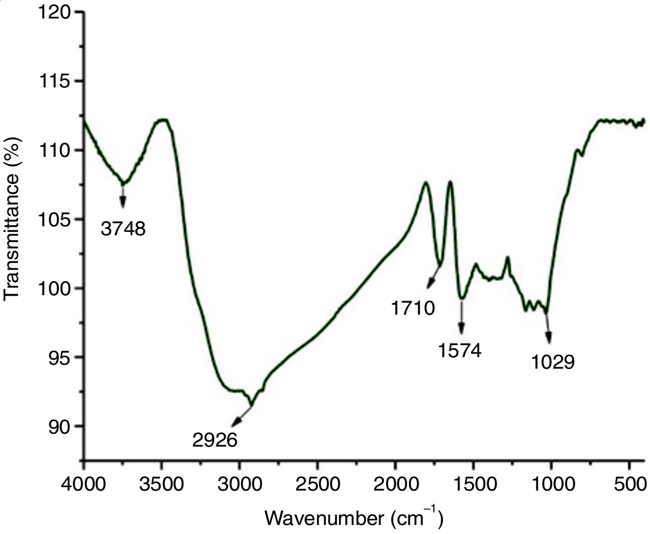

Fig. 2. FTIR spectra of AWCPP

SEM: The metal interaction with adsorbent was investigated through SEM. The synthesized activated carbon skeleton defines the pore configuration. Lower the crystalline, larger the specific surface area [20]. The porous structures of adsorbent are useful for attachment of organic and inorganic contaminants. The porous structure of the adsorbent will become beneficial point for the adsorption of chromium(VI). The interconnected pores provide an adsorption sites for chromium(VI) adsorption [22]. The porosity of a sample is directly affected

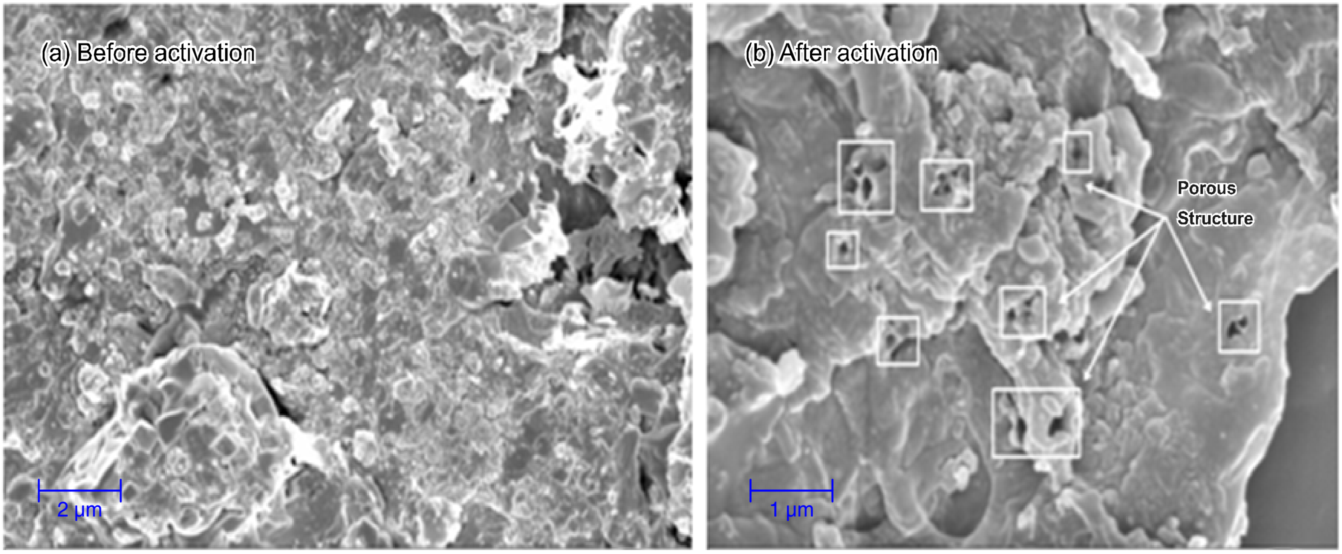

Fig. 3. SEM image of adsorbent

by the conditions present during the processing of activated carbon, inherent cellular structure and composition of solid [23]. The results clearly show (Fig. 3) that after activation the adsorbent attained more irregular and porous surface site for adsorption.

BET: Brunauer, Emmett and Teller (BET) method was used to determine the specific surface area of the adsorbent [24]. The specific surface area found is 23.467 m^2/g, while the pore volume and pore diameter 0.039 cc/g and 1.556 nm respectively (Fig. 4).

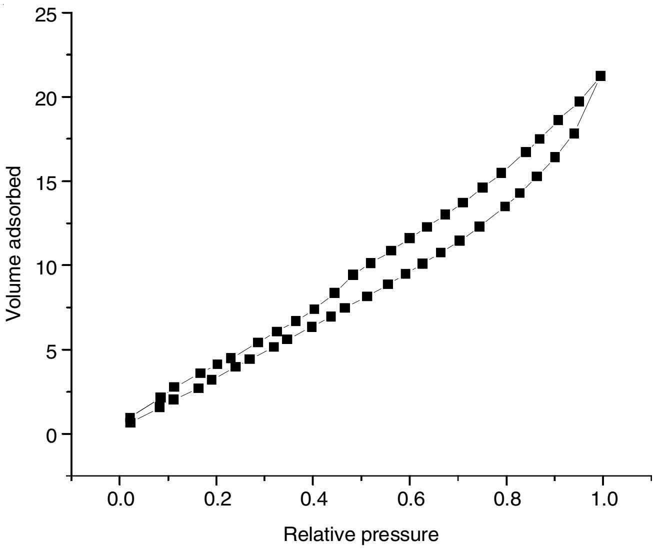

Fig. 4. BET analysis of AWCPP

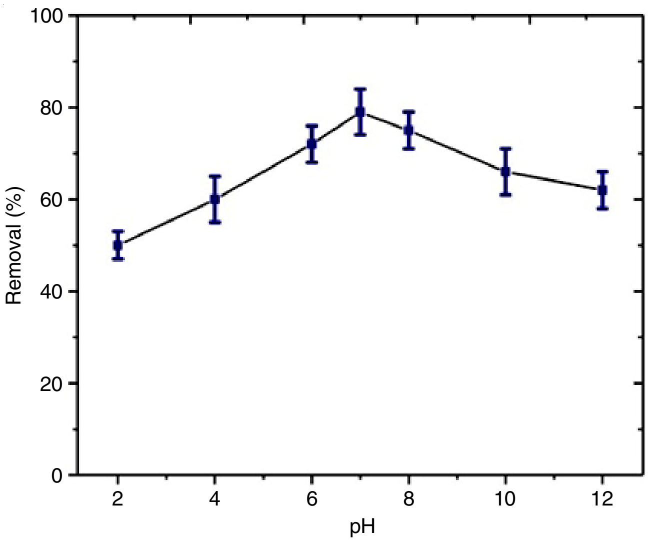

Fig. 5. Percentage removal of Cr(VI) at different pH

Effect of pH: pH is a factor that affects surface charge and ionization degree of a material. Hence, pH can alter the removal process of contaminant [25]. The value of optimum pH was established for Cr(VI) ion (0.5 g of adsorbent in 50 mL solution) of 50 mg/L Cr(VI) concentration (pH values from 2 to 12). The acidic solution and basic solution was maintained by 1 N HCl and 1 N NaOH respectively. pH effect on the removal efficiency of adsorbent is shown in Fig. 5. It is evident that the maximum removal is around 78 % observed at neutral pH value 7. It may be happened because at low pH hydrogen ion competes with Cr(VI) ions and occupied adsorption sites. But at neutral pH 7, there is negligible competition of hydrogen ions due to which availability of sites for binding with Cr(VI) ions to the adsorbent is more. Attraction between the adsorbate and the adsorbent is because of the electrostatic interaction which is the main driving force for the adsorption of the metal ions that is stronger the interaction higher the adsorption.

Effects of adsorbent dosage: The dependence of adsorbent dose on Cr(VI) ions adsorption was studied by changing the dose amount of activated water chest nut (*Trapa natans*) peel powder (AWCPP) from 0.2 to 1.0 g at 7 pH, concentration of Cr(VI) ions in solution is 50 mg/L, volume 50 mL and a contact time of 240 min. The removal of Cr(VI) metal ions increased from 60 to 79 % with an increase in dose of absorbent from 0.2 to 1 g (Fig. 6) and finally a steady value was obtained might be due to less contact of adsorbent with adsorbate present in bulk. The increase in uptake of Cr(VI) ions as adsorbent dosage increased can be attributed to the availability of more surface area and active sites on the surface of adsorbent.

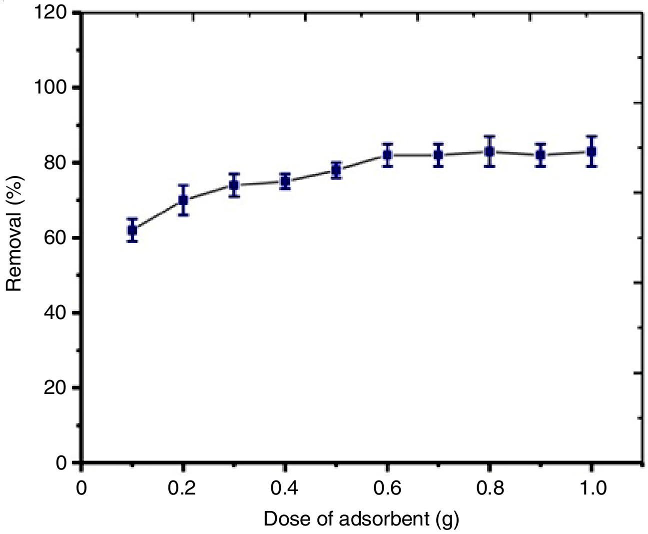

Fig. 6. Removal efficiency of Cr(VI) at different adsorbent concentration

Effect of chromium concentration: Effect of adsorbate concentration (20-100 mg/L) on adsorption efficiency of AWCPP was studied at room temperature and pH 7. The change in percentage removal by changing the Cr(VI) concentration (Fig. 7). A linear increase in adsorption efficiency was observed with increase in Cr(VI) ions concentration to 50 mg/L afterwards there was saturation in percentage removal at higher concentrations of Cr(VI) ions and no significant change occurred. This saturation was due to occupancy of all adsorption sites with increasing concentration of Cr(VI).The adsorption decreases at higher concentration levels as the adsorption sites get occupied and there is no availability of vacant sites for adsorption.

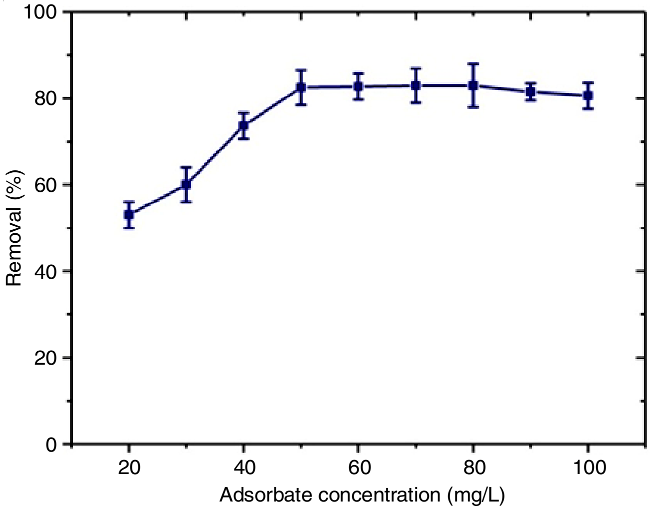

Fig. 7. Percentage removal of Cr(VI) at different adsorbate concentration

Effect of contact time: The adsorption capacity was studied with effect of contact time for the favourable use and practical application of AWCPP. An increase in adsorption was seen (from 10 to 78 %) at initial 60-300 min thereafter remained constant (Fig. 8). Initially rapid rate of adsorption is due to more surface area and vacant sites were available for Cr(VI) ions to get stuck on the surface of adsorbent. Later electrostatic hindrance caused slow adsorption rate might be owing to by already adsorbed ions and a slow pore diffusion of ions.

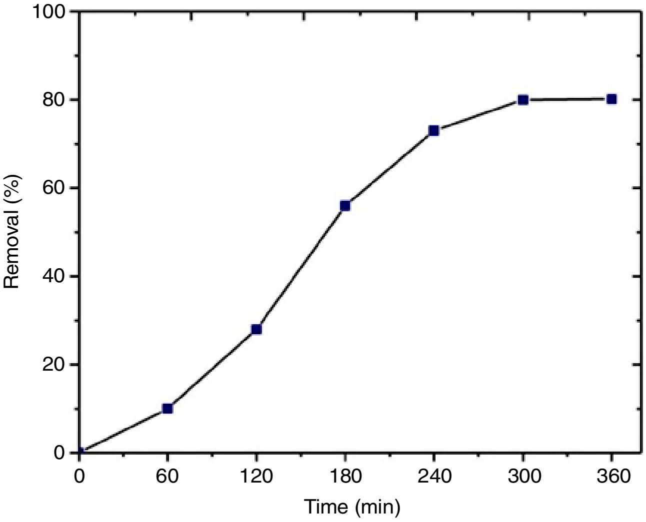

Fig. 8. Contact time effect on percentage removal of Cr(VI)

Effect of temperature: The effect of the temperature distress the percentage removal of Cr(VI) (Fig. 9). Experiments were carried out at different temperature (20, 30, 40, 50, 60 and 70 °C). It was observed that initially the percentage removal of Cr(VI) ions increased with temperature. This is due to increase in rate of reaction. Thus, there are strong intermolecular forces between adsorbate and adsorbent than those between adsorbate and solvent that causes adsorbate easier to be adsorbed. At higher temperature adsorption capacity decreased may be due to desorption of Cr(VI) ions from the surface of adsorbent.

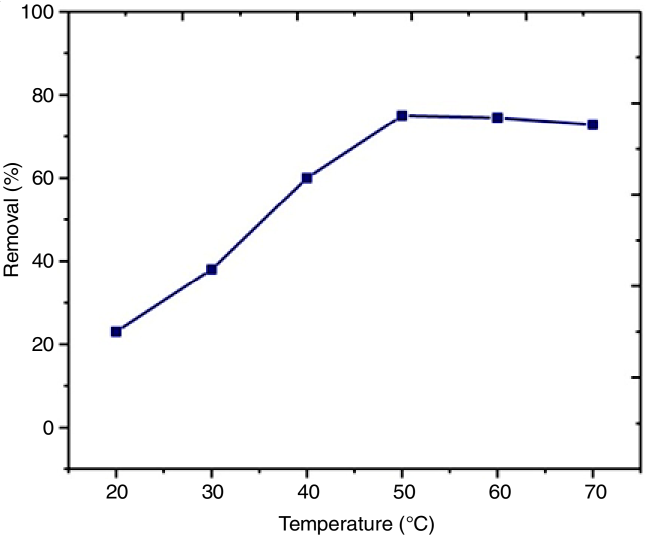

Fig. 9. Effect of temperature on removal of Cr(VI)

Adsorption isotherms: The mechanism of adsorption process was studied using isotherm and kinetic models. Various isotherm models were applied for best fit of data (figure not shown).

The adsorption process was best fitted in Langmuir adsorption isotherm. The given equation was used for calculation of Langmuir isotherm [26]:

$$\frac{C_e}{q_e} = \left(\frac{C_e}{q_{max}}\right) + \left(\frac{1}{q_{max}}\right) b$$

where, C_e = final concentration; q_e = constant concentration that found in the final solution of equilibrium concentrations of Cr(VI) mg/L; b and q_{max} are the isotherm constants. The maximum adsorption outcome using AWCPP was found to be 59.17 mg/g. The value of constant b was calculated as 5.02 with almost 80 % removal of Cr(VI).

Various kinetic models were applied for evaluation of chromium removal process and the present trend was found to be exact fitted in pseudo second order model (figure not shown).

Comparison of adsorption capacity of different adsorbents for the adsorption of chromium(VI): The adsorptive capacity of the adsorbent investigated in this work has been compared with other adsorbents that were reported in the literature and the values of adsorption capacity (Table-1). The experimental data of the present work were compared with reported values. Results of this research work revealed that the adsorbent AWCPP has higher adsorption capacity than rice straw, gulmohar fruit shell, sunflower, papaya peel and banana peel (Table-1).

TABLE-1
COMPARISON OF ADSORPTION CAPACITY OF DIFFERENT ADSORBENTS FOR THE ADSORPTION OF CHROMIUM(VI)

Adsorbents	Adsorbent capacity (mg g^{-1})	Ref.
Rice straw	3.15	[27]
Pre boiled sunflower stem	4.90	[28]
Gulmohar's fruit shell	12.28	[29]
Untreated *Juniperus procera* sawdust	16.03	[30]
Untreated avocado kernel seeds	10.08	[30]
Untreated papaya peels	7.16	[30]
Cranberry Kernel shell	6.81	[31]
Rosehip seed shell	15.17	[31]
Banana peel	10.42	[31]
Activated water chest nut peel powder	59.17	This work

Conclusion

Water chestnut (*Trapa natans)* peels (activated) was chosen as an adsorbent studying adsorption of chromium(VI) ions at pH 7. The adsorption rate increased with an increase in adsorbent dosage. Langmuir isotherm and second order kinetics were followed with maximum adsorption capacity of 59.17 mg/g. No interference of other metal cations was observed on adsorption potential of chromium(VI) ions. Physico-chemical properties and porous structure of activated water chestnut peel indicates that AWCPP is an excellent adsorbent for the removal of chromium(VI) ions from polluted water. This study shall be helpful in designing of new biosorbers used in industries for removal of chromium(VI) ions out of their effluents.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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