Biosorption of chromium(VI) ion from aqueous solutions using walnut, hazelnut and almond shell

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Abstract

The potential to remove Cr(VI) ion from aqueous solutions through biosorption using, the shells of Walnut (WNS) *(Juglans regia)*, Hazelnut (HNS) *(Corylus avellana)* and Almond (AS) *(Prunus dulcis)* was investigated in batch experiments. The equilibrium adsorption level was determined to be a function of the solution contact time and concentration. Kinetic experiments revealed that the dilute chromium solutions reached equilibrium within 100 min. The biosorptive capacity of the shells was dependent on the pH of the chromium solution, with pH 3.5 being optimal. Adsorption of Cr(VI) ion uptake is in all cases pH-dependent showing a maximum at equilibrium pH values between 2.0 and 3.5, depending on the biomaterial, that correspond to equilibrium pH values of 3.5 for (WNS), 3.5 for (HNS) and 3.2 for (AS). The adsorption data fit well with the Langmuir isotherm model. The sorption process conformed to the Langmuir isotherm with maximum Cr(VI) ion sorption capacities of 8.01, 8.28, and 3.40 mg/g for WNS, HNS and AS, respectively. Percentage removal by WNS, HNS and AS was 85.32, 88.46 and 55.00%, respectively at a concentration of 0.5 mM. HNS presented the highest adsorption capacities for the Cr(VI) ion.
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Keywords: Shell; Low-cost adsorbent; Batch model; Chromium; Adsorption; Walnut; Hazelnut; Almond

1. Introduction

The discharge of heavy metals into aquatic ecosystems has become a matter of concern over the last few decades. They are extremely toxic elements, which can seriously affect plants and animals and have been involved in causing a large number of afflictions. Increased knowledge about toxicological effects of heavy metals on the environment is well recognized and therefore, it is inevitable to search for different methods to reduce water pollution [1]. The major sources of heavy metal contaminations are the industrial effluents. Due to their persistence in nature, it becomes essential to remove them from wastewaters [2]. Inorganic micro-pollutants are of considerable concern because they are non-biodegradable, highly toxic and have a probable carcinogenic effect [3,4].

An alternative method for the removal of heavy metals is considered based on the biological methods of metal removal and recovery. The biosorption process involves a solid phase (sorbent or biosorbent; biological material) and a liquid phase containing a dissolved species to be sorbed (metal ions). Biosorption is a fast and reversible reaction of the heavy metals with biomass. The by-products obtained from biomaterial production are a cheap source of biosorbents. Several approaches have been studied and developed for the effective removal of heavy metals using biosorbents like peat, lignite and humic acids, treated activated carbons and coal-based natural adsorbents, chitosan-based polymeric surfactants, fly ash, microbial biomass and other agricultural by products, soya bean hulls, walnut hulls, cotton seed hulls and corn cobs, walnut skin, coconut fibre, cork biomass, defatted rice bran, rice hulls, soybean hulls and cotton seed hulls, wheat bran, cotton and mustard seed cakes, barks [5–34]. There are other systems for treating wastewaters containing toxic metal ions is today the use of micro-organisms such as bacteria, fungi and algae but as yet not suitable for applications on a large scale [35,36].

Conventional techniques have limitations [37] and often are neither effective nor economical especially for the removal of heavy metals at low concentrations. New separation methods are effective and environmentally acceptable at affordable cost [38]. Several methods are utilized to remove chromium from indus-

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trial wastewater. The commonly used procedures for removing metal ions from effluents include chemical precipitation, lime coagulation, reduction, activated carbon adsorption, electrolytic removal, ion exchange, reverse osmosis, membrane filtration and solvent extraction [39–46]. The major advantages of biosorption over conventional treatment methods include: low cost, high efficiency, minimisation of chemical and or biological sludge regeneration of biosorbent; and the possibility of metal recovery. Developing countries suffer from water pollution; the high costs operating treatment systems make the major problems in these countries. The cost of these biomaterials is negligible compared with ion exchange resins. Synthetic ion exchange resins are marketed for US$ 30–50/kg. With the same performance, natural new biosorbents could cost less than US$ 5/kg [13,47]. The search for a cheaper alternative reveals that utilizing natural processes and materials can significantly reduce the cost.

Cr(VI) is a common pollutant introduced into natural waters from a variety of industrial wastewaters including those from the textile dyeing, leather tanning, electroplating and metal finishing industries. Cr(III) and Cr(VI) are the chromium oxidation states usually encountered in the environment. The hexavalent form is of particular concern because of its greater toxicity [48]. The untreated effluent from electroplating industry contains approximately 100 mg/L Cr(VI), which is much higher than the permissible limit of 0.05–1 mg/L [49]. Cr(VI) is typically present as an anion and its direct precipitation is not a usual practice. Instead, the anionic species are usually reduced to trivalent state form and then precipitated as chromic hydroxide using lime. However, this method is only effective at high chromium concentrations and has several disadvantages such as a significant sludge production; an ever increasing cost of landfill disposal, and most importantly, long-term environmental consequences. In the literature, the removal of Cr(VI) was achieved by different biomasses and the optimum pH for removal was reported to be in the 2.0–3.0 range [50–52].

This study reports the use of shells of WNS, HNS and AS as a biosorbent to remove toxic Cr(VI) ion from aqueous solutions and compare their performance. This will permit the evaluation of shells for their utilization as an adsorbent in the elimination of Cr(VI) ion from aqueous solution. The effect of time, initial concentration of the metal, solution pH and adsorbent dosage on the biosorption at room temperature are also studied and compared.

2. Materials and methods

2.1. Materials

Shells of Turkish WNS, HNS and AS species were ground in a ball mill and the resulting crumbs were sieved to obtain particle size under 100 μm. Before their use, all the sorbents were washed thoroughly with deionized water and oven dried at 100 °C for 24 h. All solutions were prepared from analytical grade chemicals and Mili-Q filtered deionized water. One millimolar of Cr(VI) stock solution was prepared by dissolving 0.1471 g of $K_2Cr_2O_7$ (from Merck). The working solutions with a concentration of 0.1–1 mM Cr(VI) were prepared by appro-

priate dilutions of the stock solution immediately prior to their use. The electrolyte used to modify the ionic strength in the adsorption experiments was 0.1 M KNO_3.

2.2. Batch adsorption

Shells were ground using a with Retsch RM 100 model grinding machine. The pH measurements were performed with an Orion 900S2 Model pH meter. A thermo stated shaker (GFL 3033 model) and magnetic stirrer (IKAMAG-RO15 model) were used for the sorption experiments. The sorption of Cr(VI) on shells was studied by batch technique. The general method used for this study is described as follows: 0.5 g shell was equilibrated with 20 mL of the 1 mM Cr(VI) solution in a stoppered pyrex glass flask at a fixed temperature in a thermostatic shaker bath. The initial pH of the solution was adjusted with diluted 0.1 M HNO_3 or 0.1 M NaOH solution and the stirring speed was 200 rpm to maintain the sorbent particles in suspension. The WNS, HNS and AS sorbents and solution were separated by filtration through a membrane filter. The shells were washed with distilled water and filtrate was collected in a separate beaker. The Cr(VI) ion concentrations in the solutions were determined by the standard colorimetric method with 1,5-diphenylcarbazide [53]. Metal concentration in the solution was analyzed with UV–vis Spectrophotometer (Schmadzu UV-1700) (λ: 540 nm). The concentration of chromium metal ions was calculated from the change in metal concentration in the aqueous solution before and after equilibrium sorption. In all cases, mass balance was confirmed.

Contact time adsorption experiments were conducted at 25 ± 1 °C in a well-mixed Pyrex glass vessel with a cover. Shells were added into deionized water having different initial pH (2–9) values. The test tubes were agitated intermittently for 2 h at room temperature, and then left for settling of shells. The final pH of the solution was measured. After equilibrium was reached, the pH of the solution was measured and recorded. Sorption isotherms were carried out with different initial metal concentrations varying from 0.1 to 1 mM while holding the sorbent amount at constant value at room temperature (25 ± 1 °C). The sorbent amount in the batch vessel was varied from 0.1 to 1 g for adsorption studies. The same measurements were repeated three times and average values have been taken as the remaining metal amount in the solution phase. The maximum deviation was 2.1%.

Total unadsorbed chromium (VI) was calculated by taking the difference of initial concentration and total hexavalent chromium concentration in the filtrate.

Cr(VI) sorbed = (initial chromium concentration) − (chromium concentration in the filtrate)

The kinetic data of adsorbed amount of metal at time t, q_t (in mg g^{-1} of adsorbent), were obtained by the mass balance [54]:

$$q_t = \frac{[(C_o - C_t)\,V]}{m} \tag{1}$$

where q is adsorbed metal (mmol/g adsorbent) on the sorbents, m is the weight of sorbents (g), V is volume of metal solution (L), C_o is initial metal concentration (mmol/L), and C_t is metal
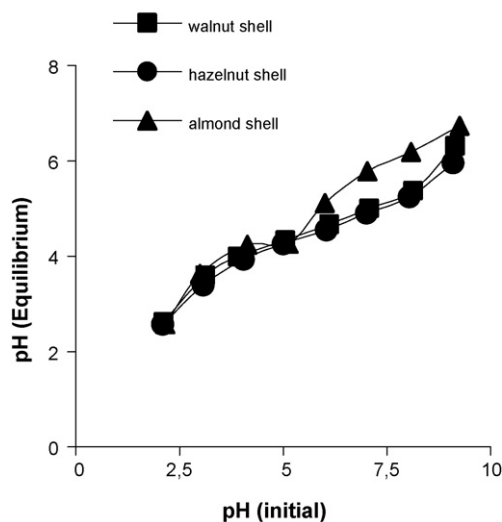
Fig. 1. The variation in equilibrium pH. Adsorption conditions: initial concentration of Cr(VI), 10^{-3} mol/L; 0.5 g sorbent; 20 mL of adsorption medium; temperature, $25 \pm 1\,^\circ$C.

concentration (mmol/L) at any time. When t is equal to the equilibrium contact time, then the amount of metal ion sorbed at equilibrium, q_e, is calculated using Eq. (1).

3. Results and discussion

3.1. Effect of pH on Cr(VI) ion removal

The pH_{PZC} was the equilibrium pH of the mixture that did not change after the contact with the Cr(VI) solution. Based on this study, the pH_{ZPC} of these three sorbents tested was approximately pH 4.0 (Fig. 1). The effect of pH on adsorption of Cr(VI) was studied at room temperature by varying the pH of metal solution–shell suspension from 2.0 to 9.0. The variation in equilibrium pH for WNS, HNS and AS sorbents is shown in Fig. 2. The equilibrium pH decreased non-linearly in the pH range of 5.0–9.0. The pH was stable in the range of 2.0–4.5 for WNS and
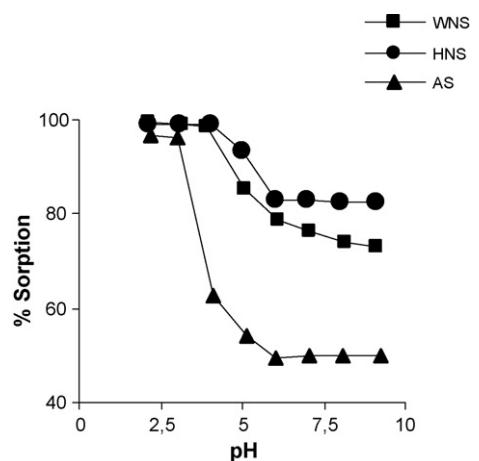

Fig. 2. Effect of pH on the adsorption of Cr(VI) using the WNS, HNS and AS. Adsorption conditions: initial concentration of Cr(VI), 10^{-3} mol/L; 0.5 g sorbent; 20 mL of adsorption medium; temperature, $25 \pm 1\,^\circ$C.

HNS. pH is stable in the range of 2.0–3.3 for AS. At higher initial pH there is no increase in the solution pH. The percent adsorption increased in the pH range of 2.0–4.5, showing an optimal adsorption at pH 3.5 for WNS and HNS. Optimum adsorption for AS was about 3.0. Agarwal et al. [55] and Marathe et al. [56] reported similar results in the biosorption of Cr(VI) by tamarind shells, which are a rich source of protein and amino acids. At lower pH, the biosorbent is positively charged due to protonation and dichromate ion exists as anion leading to an electrostatic attraction between them [57]. As pH is increases, deprotonation starts and thereby results in decrease of adsorption capacity. Cr(VI) forms stable complexes such as $Cr_2O_7^{2-}$, $HCrO_4^-$, CrO_4^{2-}, and $HCr_2O_7^-$ depending on the pH of the solution. The fraction of any particular species depends upon the chromium concentration and pH of the solution [58,59]. The shells used in the experiments are composed of cellulose, hemicellulose and lignin. Cellulose is a common material in plant cell walls and lignin is relatively hydrophobic and aromatic in nature. WNS, HNS and AS sorbents carry the some polar functionsal groups such as alcoholic, carbonylic, carboxylic and phenolic groups. Lignocelluloses and the cell walls of sorbents mainly consist of polyphenolic compounds and hydroxyl groups such as lignin, which are believed to be the active sites for attachment of metal ion [30].

Different mechanisms, such as electrostatic forces, ion exchange, chemical complexation, must be taken into account when examining the effect of pH on Cr(VI) sorption. One of the common proposed mechanisms is electrostatic attraction/repulsion between sorbent and sorbate. Thus, the increase of Cr(VI) sorption at acidic pH should be due to the electrostatic attraction between positively charged groups of biomaterial surface and the $HCrO_4^-$ anion, which is the dominant species at low pH. Moreover, the decrease of the sorption with increasing pH could be due to the decrease of electrostatic attraction and to the competitiveness between the chromium anionic species ($HCrO_4^-$ and CrO_4^{2-}) and OH^- ions in the bulk for the adsorption on active sites of the sorbent. From these assumptions it can be suggested that Cr(VI) removal takes place by physical adsorption.

Speciation studies of Cr(VI) in aqueous solution, on the basis of spectrophotometry, electrochemistry, indicates the existence of the following equilibria;

$$H_2CrO_4 = H^+ + HCrO_4^- \tag{2}$$

$$HCrO_4^- = H^+ + CrO_4^{2-} \tag{3}$$

$$2HCrO_4^- = Cr_2O_7^{2-} + H_2O \tag{4}$$

Equilibria are dependent on pH, with $HCrO_4^-$ and $Cr_2O_7^{2-}$ existing primarily in acidic media and CrO_4^{2-} being the lone species of Cr(VI) above pH 7.0. At higher pH range, the fraction of $Cr_2O_7^{2-}$ species rapidly decreases with increasing pH above 5. In the removal of Cr(VI) process, the anion is not a simple monovalent anion but rather a series of chromate anions depending upon the pH and concentration of the solution. The total chromate species will be represented as Cr(VI). In the neutral solution at low concentrations, Cr(VI) will be present in the
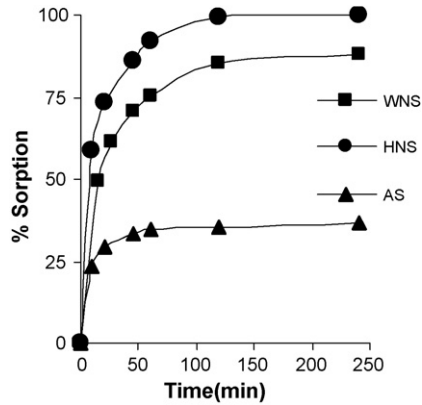
Fig. 3. Effect of contact time on the sorption of Cr(VI) by WNS, HNS and AS. Adsorption conditions: initial concentration of Cr(VI), 10^{-3} mol/L; 0.5 g sorbent; 20 mL of adsorption medium; temperature, $25 \pm 1\,°C$.

form of $HCrO_4^-$ and CrO_4^{2-}. At acidic pH, $HCrO_4^-$ is the predominant Cr(VI) species in the aqueous phase. The decrease in adsorption at high pH values may be due to the competitiveness of the oxyanion of chromium and OH^- ions in the bulk. Processes of oxo group protonation and Cr(VI) reduction were lowering because both these reactions require protons [41,60]. The decrease in the adsorption with increase of pH may be due to the decrease in electrostatic force of attraction between the sorbent and sorbate ions. At lower pH ranges, due to the high electrostatic force of attraction, the percentage of Cr(VI) removal is high. At very low pH value, the surface of sorbent would also be surrounded by the hydronium ions which enhance the Cr(VI) interaction with binding sites of the biosorbents by greater attractive forces. A decrease in adsorption above pH 4.5 may be due to occupation of the adsorption sites by anionic species like $HCrO4^-$, $Cr_2O_2^{7-}$, CrO_2^{4-}, etc., which retards the approach of such ions further toward the sorbent surface [61].

3.2. Effect of time on the removal of metal ions

Fig. 3 illustrates the effect of adsorption time on adsorption efficiency. The experimental results indicate that the percentage removal of metal becomes asymptotic to the time axis, nearly representing an equilibrium pattern. The removal rate of Cr(VI) increases with the increase of the adsorption time. However, it remains constant after an equilibrium time of 100 min, which indicates that the adsorption tends toward saturation at 150 min. Therefore, the adsorption time was set to 180 min in each experiment. The majority of metal ion in adsorption equilibrium were achieved in between 50 and 100 min for Cr(VI) ion. This phenomenon could be attributed to the instantaneous utilization of the most readily available adsorbing sites on the adsorbent surface.

3.3. Effect of initial Cr(VI) ion concentration

The effect of Cr(VI) concentration on the sorption by the WNS, HNS and AS sorbents was investigated by varying the concentration (0.1–1 mM) at a pH of 3.5 for 120 min equilibrium time (Fig. 4). Cr(VI) removal by WNS, HNS and AS was 85.32,
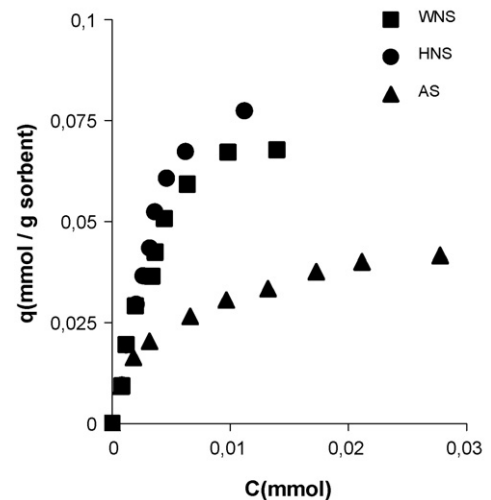

Fig. 4. Sorption isotherm of Cr(VI) ion on WNS, HNS and AS as a function of initial Cr(VI) concentration (10^{-4} to 10^{-3} mM) and 50 mL of Cr(VI) solution; 0.5 g sorbent; temperature, $25 \pm 1\,°C$.

88.46 and 55.00%, respectively at a concentration of 0.5 mM. The percent Cr(VI) ion removal efficiency of WNS, HNS and AS increased with increasing metal concentration. At higher concentrations, more Cr(VI) ions are left unabsorbed in solution due to the saturation of binding sites.

Langmuir and Freundlich isotherms have both been used to describe observed sorption phenomena of various metal ions on sorbents [2,3]. The sorption data of Cr(VI) ion have been correlated with Langmuir and Freundlich models [Eqs. (5) and (6)]. These isotherms relate metal uptake per unit weight of resin q_e to the equilibrium metal ion concentration in the bulk fluid phase C_e.

Langmuir equation:

$$\frac{C_e}{q_e} = \frac{1}{K_b A_S} + \frac{C_e}{A_S} \tag{5}$$

where A_S and K_b are coefficients, q_e is the weight adsorbed per unit weight of adsorbent and C_e is the metal concentration in bulk solution at equilibrium. Fig. 4 conforms to the Langmuir and Freundlich models.

Freundlich equation:

$$q = K_f C_e^n \tag{6}$$

where n is the Freundlich constant, and K_f is the adsorption coefficient, q is the weight adsorbed per unit weight of adsorbent and C_e is the equilibrium metal concentration in fluid. Taking logs and rearranging Eqs. (6) and (7) was obtained.

$$\log q = \log K_f + n \log C_e \tag{7}$$

The linear plots of C_{eq}/q vs. C_{eq} show that adsorption follows the Langmuir adsorption model. The correlation coefficients are 0.964, 0.976, and 0.972 for WNS, HNS and AS respectively. Since the correlation coefficients were high for each metal-sorbent equilibrium condition as seen from Table 1, the Langmuir-type sorption isotherm was suitable for equilibrium studies suggesting the formation of monolayer coverage of the

Table 1
Parameters of Langmuir and Freundlich isotherms for sorption of Cr(VI) on walnut, hazelnut and almond shells

Sorbent	Freundlich isotherm			Langmuir isotherm		
	K_f	n	R^2	K_b	A_S	R^2
WNS	0.244	3.36	0.989	2.980	0.076	0.964
HNS	0.386	2.83	0.992	4.423	0.086	0.976
AS	0.153	2.86	0.984	0.580	0.046	0.972

adsorbate on the surface of adsorbent in the concentration studied. The data for the uptake of metal ions by the resin has been processed in accordance with a linear form of the Langmuir isotherm equation. The amount of Cr(VI) ions adsorbed per unit mass of the shells increased with the initial metal concentration as expected and Cr(VI) sorption capacities were 8.01, 8.28, and 3.40 mg/g for WNS, HNS and AS, respectively (Table 1). HNS proved to be the most efficient sorbent followed by WNS and AS.

3.4. Effect of ionic strength

Ionic strength is one of the important factors influencing aqueous phase equilibrium. Generally, adsorption decreases with increasing ionic strength of the aqueous solution. The effect of the interfering ion KNO_3 was evaluated. The electrostatic attraction at low ionic strength appears to play a negligible role in the removal of Cr(VI) for sorbents. The results indicate that there was no significant decrease in the removal of Cr(VI) ion for the interval of (0.01–0.1 M) KNO_3 ionic concentration.

3.5. Amount of sorbent

The effect of variation of sorbent amount on the removal of Cr(VI) ion by WNS, HNS and AS is shown in Fig. 5. Amount of sorbent was varied from 0.1 to 1 g and equilibrated for 120 min at an initial Cr(VI) ion concentration of 0.5 mM. It is apparent that the equilibrium concentration in solution phase decreases with increasing sorbent amount for a given initial chromium concen-
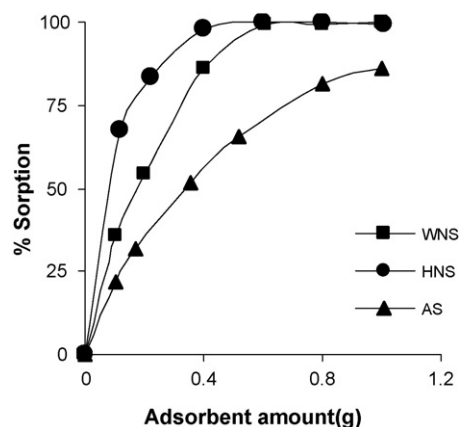

Fig. 5. Effect of sorbent dosage on the sorption of Cr(VI) on WNS, HNS and AS. Adsorption conditions: initial concentration of Cr(VI), 10^{-3} mol/L; 0.1–1 g sorbent; 20 mL of adsorption medium; temperature, $25 \pm 1\,°C$.

tration. This result was anticipated because for a fixed initial solute concentration, increasing amount of adsorbent provides greater surface area.

3.6. Desorption studies

Little information about biosorption mechanisms can be obtained from these desorption experiments since, in general, biomaterials are decomposed under either basic and/or high acidic conditions. The reversibility of the adsorption process was also investigated. Desorption studied are helpful to explore the possibility of recycling the adsorbents and recovery of the metal resource. Thus, 0.1, 0.5 and 1.0 mol L^{-1} NaOH or HCl solutions were tested to remove metal from the solids. Desorption experiments brought evidence that after two contacts neither HCl nor NaOH solutions were able to desorb all Cr(VI) ion completely. When NaOH solutions were tested, the material seemed not to be damaged and in spite of this, desorption from shells reached only about 42% when 1.0 mol L^{-1} NaOH solution was used. They were not damaged by the contact with 0.1 mol L^{-1} HCl solution, and after two contacts about 17.0% of Cr(VI) ion was recovered.

4. Conclusion

WNS, HNS and AS are effective sorbents in removing of Cr(VI) ion from aqueous solution. Adsorption of Cr(VI) is dependent on its initial concentration and pH of the metal solution. The results indicate that the optimum pH for the removal of Cr(VI) ion by WNS and HNS is around 3.5. Cr(VI) ion removal is built up, equilibrium conditions being reached attained after 100 min. The percent adsorption increased in the pH range of 2.0–3.3, showing an optimal adsorption at pH 3.0 for AS. Sorption data of Cr(VI) sorption system followed the Langmuir adsorption model with high coefficient of determination than Freundlich adsorption model for the shells concluded the surface sorption is dominant for the sorption process. The sorption capacities were 8.01, 8.28, and 3.40 mg of Cr(VI) per gram of WNS, HNS and AS respectively. The results indicate that there was no significant decrease in the removal of Cr(VI) ion for the interval of (0.01–0.1 M) KNO_3 ionic concentration.

WNS, HNS and AS are easily available, and can, therefore, be used in batched reactors by small scale industries having low concentrations of Cr(VI) in wastewater. At these adsorption levels, a process using WNS, HNS and AS for the removal of Cr(VI) is potentially more economical and all those add more credits to shell materials for removing pollutants from waste waters. From the results obtained in this work hexavalent chromium removal could be attributed to physical adsorption mechanism especially at low pH.

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