



Activated Carbon and Manganese Coated Activated Carbon Precursor to Dead Biomass in the Remediation of Arsenic Contaminated Water

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Abstract

The two different dead biomasses were employed to obtain the activated carbon samples viz., rice hulls (AC-R) or *areca* nut waste (AC-N). Further, the surfaces of these activated carbons were modified with manganese to obtain the manganese coated activated carbons (MCAC-R and MCAC-N). These solids were assessed for their possible implication in the remediation of the aquatic environment contaminated with arsenic. The surface morphology of these solids was discussed with the scanning electron microscope/energy dispersive X-ray spectroscopy (SEM/EDX) analysis. Various parametric studies viz., the effect of sorptive pH, concentration, background electrolyte concentration and contact time were studied under the batch reactor operations. The increase in sorptive pH (i.e., 2.0 to 10.0) and concentration (i.e., 1.0 to 10.0 mg/L) caused a great decrease in the percent removal of As(III) and As(V). Equilibrium modeling studies suggested that the data is fitted well to the Freundlich and Langmuir adsorption isotherms. The simultaneous presence of background electrolytes concentration (i.e., maximum 1,000 times NaNO₃) could not significantly affect the uptake of these two ions which inferred that the sorption of As(III) and As(V) by these solids predominantly occurred through strong chemical forces and may ultimately form 'inner-sphere' complexes. The kinetic data was best fitted to the pseudo-first order kinetic model. Studies conferred that AC obtained from these agricultural by-products/wastes modified with manganese were found to be potential and promising solid materials in the attenuation of As(III) and As(V) from the aquatic environment.

Keywords: Activated carbon, Arsenic, Attenuation, Chemisorption, Manganese coated activated carbon

1. Introduction

The enhanced level of arsenic in drinking and ground water has created a serious environmental/health impact. The ground waters around Bangladesh and parts of India are contaminated greatly with arsenic, which poses a serious health hazard. Further, because of severe toxic effects; arsenic toxicity was termed as one of the greatest calamities known around the globe [1-3]. The sources of arsenic contamination of surface or ground waters were mainly due to the discharge of industrial wastes, mining, and agriculture activities, etc. [4]. Arsenic is introduced into the human bodies through drinking water and foodstuffs. Moreover, the long term drinking of arsenic contaminated water were causes for lung, liver, kidney, bladder, and skin cancer as well as pigmentation changes, skin thickening (hyperkeratosis), neurological disorders, muscular weakness, loss of appetite, nausea, etc. [5, 6]. A variety of methods were described for arsenic removal from drinking water, however there is a great need for the development of efficient and cost effective methods regarding

this purpose [7].

The most widely used methods for the removal of arsenic from wastewater includes flocculation or co-precipitation, electrochemical methods, ion-exchange process, membrane filtration and sorption process. Among these known techniques, the adsorption method is more versatile, simple to perform and if the sorbent is chosen in such a way it may likely be cost effective [8]. Agricultural by-products may have a potential as adsorbents for wastewater treatment due to their low cost and large abundance [9, 10]. A literature survey reveals that agricultural by-products such as olive cake, coconut shell, *areca* waste; grape stalk, sugarcane bagasse and peanut shell, rice husk, *Moringa oleifera* bark, etc. were used for wastewater treatment to remove several toxic heavy metal ions [11-19]. However, at instances, it was found that these materials showed a somewhat lesser sorption capacity and selectivity for several metal ions which restricted their ultimate use in such a strategy. Hence, the enhanced capacity one may attribute with obtaining the activated carbons using these dead biomasses. The present work dealt with utilizing two ag-

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gricultural waste materials viz., rice husk and areca nut waste for the removal of As(III) and As(V) from aqueous solutions. Rice husk is an abundant agricultural waste, 96% of which is generated in developing countries and approximately 100 million tons of rice husk are available annually in these countries. Due to its typical composition, rice husk was reported to have a potential as inexpensive adsorbents for heavy metal ions and studies also demonstrated that rice husks were suitable for the production of activated carbons [20-22]. The areca nut also called betel nut is a very popular chewing nut in different parts of the world and its wide use caused for huge amounts of waste to be introduced into the environment. It was reported that this waste could have possible use in the attenuation/removal of cadmium, copper and lead from aqueous solutions [23, 24].

Recent studies suggested that many nano-sized metal oxides exhibit very favorable sorption to heavy metals in terms of high capacity and selectivity, which would result in the improved removal of toxic metals ions from aqueous solution. Among the available adsorbents of nano-sized metal oxides, ferric oxide, manganese oxide, aluminium oxide, titanium oxide, magnesium oxide, cerium oxide etc. were classified as the promising adsorbents for the removal of heavy metals from aqueous systems [25]. There was enhanced attention towards the use of nano-sized manganese oxide for cleaner treatment technologies. Immobilizing nano-sized manganese oxides onto the surface of the adsorbents showed superior absorption to its bulk counterpart because of its polymorphic structures and higher specific surface area [26]. It was reported that either manganese oxide or immobilized nano-sized manganese oxide adsorbents showed promising behaviour in the effective sorption of cationic or anionic pollutants from aquatic environments [27-30]. Our previous studies demonstrated that the immobilized manganese dioxide particles onto the surface of various sand or substrates provide an excellent medium for the treatment of waters contaminated with several heavy metal toxic ions [31-35]. The present study presents a possible implication of rice husk and betel nut wastes obtaining the activated carbons followed by its impregnation with manganese in order to attain the manganese coated activated carbon for its possible application in the remediation of arsenic contaminated waters.

2. Materials and Methods

2.1. Materials

Rice husk and areca nut waste were collected from Aizawl, Mizoram, India. H_2SO_4 and NH_3 having analytical reagent (AR) grade were used and the de-ionized (18 M Ω -cm) water was further purified using the millipore water purification system (Milli-Q⁺). The chemicals viz., manganese nitrate as $Mn(NO_3)_2 \cdot 6H_2O$; 97% extra pure (Junsei Chemicals, Tokyo, Japan) and the arsenic salts, sodium metaarsenite and sodium arsenate were of AR Grade obtained from Wako Pure Chemical Industries Ltd., Japan.

2.2. Preparation of Activated Carbon (AC)

The raw materials, rice husk and areca nut waste were repeatedly washed with de-ionized distilled water to remove any impurities. Then, they were dried in a hot air oven at 60°C for 24 hr and the solid materials were digested with concentration H_2SO_4 and the content was kept at 120°C for 2 hr. The carbonized carbon

obtained was washed with distilled water till the filtrate reached pH ~4. Afterwards, it is dried again at 70°C and the samples were then titrated with concentration NH_3 solution to neutralize excess acids. The solid samples were washed thoroughly with distilled water several times (pH = ~7) and completely dried at 70°C. The sample was cooled at room temperature and grounded to obtain a fine powder. Further, this carbonized carbon was activated by using a muffle furnace at 800°C in a N_2 environment for 6 hr and the activated carbon obtained from rice husk (AC-R) and areca nut waste (AC-N) were used for a batch experiment as well as for the preparation of manganese coated activated carbons (MCAC-R and MCAC-N).

2.3. Manganese Coating of Activated Carbon

The MCAC was prepared by taking 60 g of AC in a round bottom flask with 100 mL of 0.025 M manganese nitrate solution (pH ~9) and was kept in a rotary evaporator at 60°C at the rotating speed of 30 rpm. Further, almost 90% of the water was removed by slowly applying the vacuum. The slurry was taken out in a beaker and kept in a drying oven at 90°C to dry it completely. Further, the sample was kept for 2 hr at 110°C for the stabilization of coated manganese. Samples were taken out from the oven and cooled at room temperature and washed with distilled water 5 times and dried again at 60°C. These samples were then used for further investigations.

2.4. Characterization of the Materials.

The surface morphology and composition of these solids AC and MCAC were obtained by using the scanning electron microscope (SEM) machine (FE-SEM-Model: SU-70; Hitachi, Tokyo, Japan) equipped with the energy dispersive X-ray spectroscopy (EDX) system.

2.5. Sorption Experiments

Batch experiments were performed to obtain adsorption data with the variation of sorptive pH, initial sorptive concentration, and background electrolyte concentrations and contact time. The adsorption of As(III) and As(V) was investigated by taking 0.25 g of AC and MCAC in 0.10 L of sorptive solution. The solution mixture was equilibrated by using an automatic shaker for 24 hr at room temperature. The solution was then filtered by using a 0.45 μ m syringe filter and the bulk metal concentration was measured using with fast sequential atomic absorption spectrometer (AA240FS; Varian, Palo Alto, CA, USA). While doing the experiments, adjustment of the pH was done by adding drops of dilute HNO_3 and dilute NaOH.

3. Results and Discussion

3.1. SEM-EDX Analysis of the Solid Samples

The SEM images of AC-R, AC-N, MCAC-R, and MCAC-N were obtained and presented in Fig. 1. The SEM images clearly indicated that the surface structure of manganese coated activated carbons was greatly changed from the activated carbon samples. Surface morphology of AC showed a porous surface structure, whereas MCAC possessed newly born manganese oxide particles on its surface. The presence of small sized manganese ox-

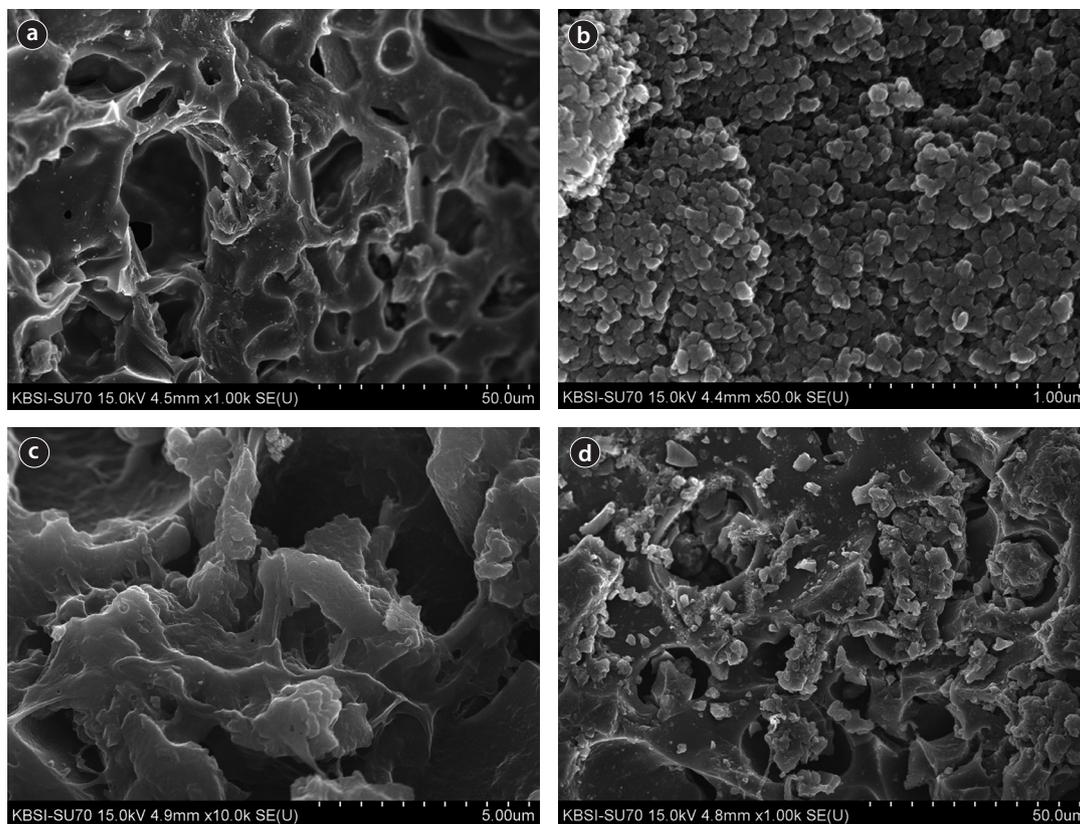


Fig. 1. Scanning electron microscope images of AC-R (a), MCAC-R (b), AC-N (c), and MCAC-N (d). AC: activated carbon, MCAC: Manganese coated activated carbon, R: rice husk, N: areca nut waste.

ide particles may ultimately enhance the specific surface area of the solid samples which may increase the adsorption capacity of the material. Further, the EDX data, shown in Fig. 2 indicated the composition of the sample MCAC-R and MCAC-N which contains a reasonable weight percent of manganese, i.e., 15.71% and 9.33%, respectively. These results indicated that the manganese oxide particles were significantly immobilized on the surface of AC-R and AC-N; moreover the manganese oxide particles were almost uniformly distributed onto the surface of the AC as also shown in the SEM images.

3.2. Speciation of As(III) and As(V)

The speciation of As(III) and As(V) in aqueous solution at different pH values were studied using the MINEQL+ ver. 4.5 (Environmental Research Software, Hallowell, ME, USA) computer simulation program. These studies could assist in better understanding the sorption mechanism of these ions onto the solid surface regarding studies using various levels of pH. The species of As(III) and As(V) were analyzed at an initial sorptive (As(III) or As(V)) concentration of 10.0 mg/L. The speciation data obtained were returned in Fig. 3. It was observed that As(III) existed as H_3AsO_3 uncharged species even up to pH ~8.0 beyond which it was dissociated and the anionic $H_2AsO_3^-$ species was dominant. On the other hand, As(V) existed predominantly as $H_2AsO_4^-$ and for the H_3AsO_4 species at lower pH, i.e., up to pH ~6.8 and above pH 6.8, the anionic species $HA_2O_4^{2-}$ species were fully dominant.

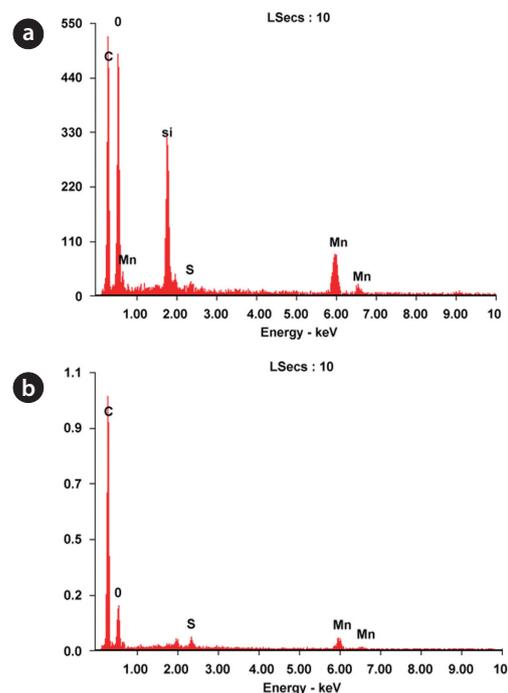


Fig. 2. Energy dispersive X-ray spectroscopy analytical results for MCAC-R (a) and MCAC-N (b). MCAC: Manganese coated activated carbon, R: rice husk, N: areca nut waste.

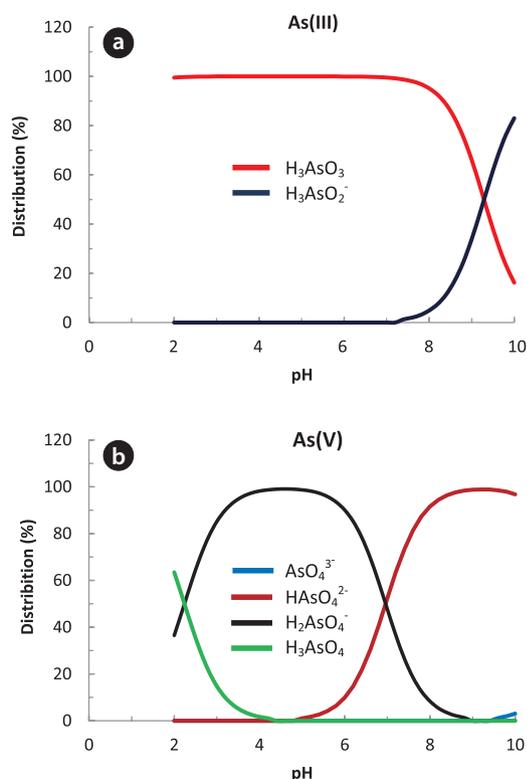


Fig. 3. Percentage distribution of various species of As(III) and As(V) as a function of pH at concentration 7.5 mg/L.

3.3. Batch Experiments

3.3.1. Effect of pH

The effect of pH was studied with the initial concentration of 10.0 mg/L and the data obtained for As(III) and As(V) were presented graphically in Fig. 4. The uptake of these ions was greatly affected by the change in solution pH. Increasing the solution pH from 2.0 to 10.0 caused a continuous decrease in the adsorption percent of As(III) and As(V). This may be explained from the speciation of As(III) and As(V) as discussed earlier, it was mentioned that As(III) existed as the H_3AsO_3 species up to pH ~8 and As(V) exists as the H_3AsO_4 and $H_2AsO_4^-$ species up to pH ~6.8. Moreover, the surface of AC and MCAC may likely to be positively charged at lower pH enhancing the higher uptake of these ions. However, increasing the pH may cause the acidic dissociation of the active sites of the adsorbents or Mn-OH in MCAC forming a negatively

charged surface on the solids which inhibited the adsorption of As(III) and As(V) [36].

3.3.2. Effect of sorptive concentrations

The effect of sorptive concentration was carried out by changing the initial concentration from 1.0 to 10.0 mg/L for both As(III) and As(V) at 25°C and at pH ~4.5. The equilibrium stage sorption data obtained for these two ions were plotted between the percent of As(III) and As(V) removed versus the initial bulk sorptive concentration (mg/L) and results were returned graphically in Fig. 5 for As(III) and As(V). An enhanced percentage of adsorption was observed at a low sorptive concentration for both As(III) and As(V) ions which was gradually decreased with increasing the initial sorptive concentration. These figures clearly indicated that increasing the initial sorptive concentration from 1.0 to 10.0 mg/L for As(III) and As(V) caused a decrease in the percent removal for these two ions obtained in regards to these solid materials or increasing the sorptive dilution caused to enhance the percent uptake of these sorbing ions. This is explicable on the basis of the fact that more and more active centers are available for relatively smaller number of sorbing ions at higher dilutions, which consequently enhances the relative increase in the percent sorption of arsenic at higher dilutions [37, 38].

The concentration dependence data obtained at equilibrium between solid and solution interfaces were further analyzed by Freundlich adsorption isotherm [21]. The Freundlich adsorption equation was taken as its usual form as Eq. (1):

$$\log a_e = \frac{1}{n} \log C_e + \log K_f \tag{1}$$

where a_e and C_e are the amount adsorbed (mg/g) and bulk sorptive concentration (mg/L) at equilibrium, respectively, and K_f and $1/n$ are the Freundlich constants referring to adsorption capacity and adsorption intensity or surface heterogeneity, respectively [21]. The concentration dependence data were fitted well to the linearized form of the Freundlich Eq. (1) and the results were estimated for the Freundlich constants. The results obtained along with the R^2 values were returned in Table 1. The higher values of R^2 obtained for these studied systems indicated a fairly good applicability of Freundlich adsorption isotherms. The fractional values of $1/n$ ($0 < 1/n < 1$) obtained for these systems pointed it towards the heterogeneous surface structure of these solid materials. The applicability of Freundlich adsorption isotherm presents it chemisorptive type of the sorption taking place at the solid/solution interface [32].

Similarly, the linearized Langmuir adsorption model [39] has been utilized for the estimation of maximum metal uptake (q_0) at various initial concentrations:

$$\frac{C_e}{q} = \frac{1}{q_0 b} + \frac{C_e}{q_0} \tag{2}$$

Table 1. Freundlich constants obtained for the adsorption of As(III) and As(V) using different samples of AC and MCAC

Sample	As (III)			As(V)		
	K_f (mg/g)	$1/n$	R^2	K_f (mg/g)	$1/n$	R^2
AC-R	0.342 ± 0.002	0.504 ± 0.004	0.990	0.376 ± 0.002	0.442 ± 0.002	0.880
AC-N	0.211 ± 0.001	0.501 ± 0.003	0.984	0.276 ± 0.001	0.541 ± 0.003	0.916
MCAC-R	0.603 ± 0.003	0.429 ± 0.003	0.962	0.837 ± 0.005	0.402 ± 0.002	0.792
MCAC-N	0.317 ± 0.002	0.462 ± 0.004	0.924	0.421 ± 0.004	0.481 ± 0.003	0.920

AC: activated carbon, MCAC: manganese coated activated carbon, R: rice husk, N: areca nut waste.

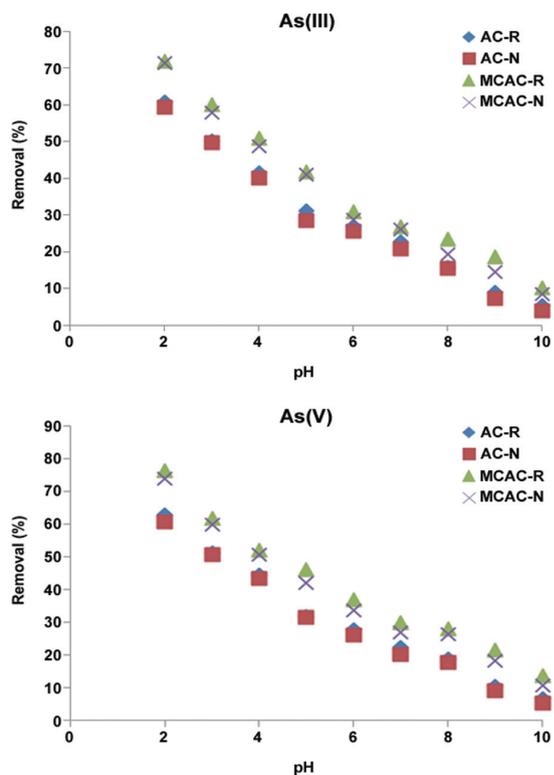


Fig. 4. Removal of As(III) and As(V) using AC-R, AC-N, MCAC-R, and MCAC-N as a function of pH (initial As(III) or As(V) concentration: 10 mg/L). AC: activated carbon, MCAC: manganese coated activated carbon, R: rice husk, N: areca nut waste.

where q is the amount of solute adsorbed per unit weight of adsorbent (mg/g) at equilibrium; C_e the equilibrium bulk concentration (mg/L); q_0 the Langmuir monolayer adsorption capacity, i.e., the amount of solute required to occupy all the available sites in the unit mass of the solid sample (mg/g) and ' b ' is the Langmuir constant (L/g) [39]. Graphs were plotted between the C_e/q versus C_e values. A fairly good applicability of Langmuir adsorption model was obtained for these systems studied since a reasonably high value of R^2 was obtained for these systems. The values of Langmuir monolayer adsorption capacity (q_0), Langmuir constant (b), and the R^2 values were obtained and returned in Table 2. Comparing the values of Langmuir monolayer adsorption capacity (q_0) between the AC and MCAC, it was evident that the MCAC demonstrated relatively higher sorption capacity than the corresponding AC samples. Moreover, from comparing

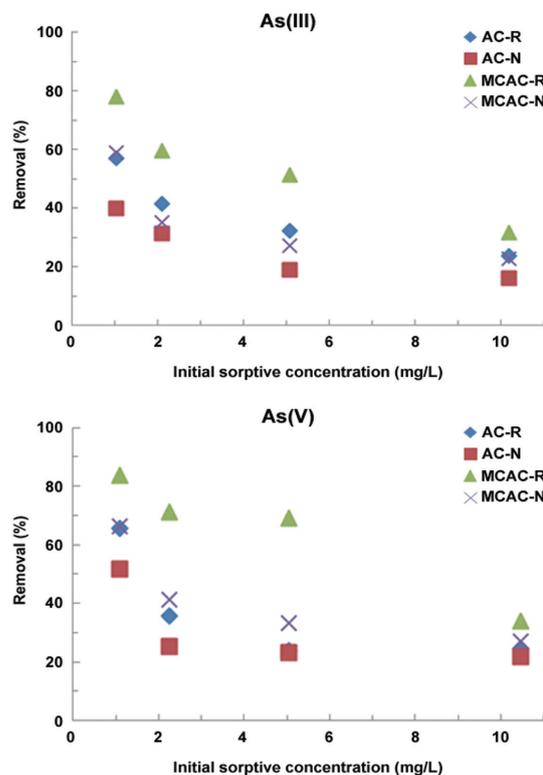


Fig. 5. Effect of initial concentration for the removal of As(III) and As(V) onto AC-R, AC-N, MCAC-R, and MCAC-N (sorptive pH ~4.5). AC: activated carbon, MCAC: manganese coated activated carbon, R: rice husk, N: areca nut waste.

these two different types of precursor materials for AC or MCAC, it was observed that AC-R or MCAC-R possessed higher sorption capacity than AC-N or MCAC-N. This could be explained by the fact that rice hulls contain a significant amount of silica which favoured greatly the uptake of these oxyanions.

3.3.3. Effect of background electrolyte concentrations

The specific and non-specific adsorption could be explained with the help of background electrolyte concentrations. It was reported that the specific sorption was unaffected with the change in ionic strength, whereas the non-specific adsorption was greatly influenced by the change of ionic strength because of the competitive adsorption with counter ions. Hence, the study was elaborated for background electrolyte concentrations. The background concentration was increased from 0.001 to 1.0

Table 2. Langmuir constants q_0 and b along with R^2 values estimated for the adsorption of As(III) and As(V) onto the different samples of AC and MCAC

Sample	As(III)			As(V)		
	q_0 (mg/g)	b (L/mg)	R^2	q_0 (mg/g)	b (L/mg)	R^2
AC-R	1.28 ± 0.03	0.362 ± 0.003	0.961	1.37 ± 0.03	0.328 ± 0.003	0.855
AC-N	0.87 ± 0.04	0.290 ± 0.002	0.904	1.39 ± 0.04	0.218 ± 0.002	0.811
MCAC-R	1.52 ± 0.05	0.819 ± 0.004	0.985	1.55 ± 0.05	1.946 ± 0.006	0.983
MCAC-N	1.24 ± 0.04	0.298 ± 0.002	0.848	1.50 ± 0.04	0.379 ± 0.003	0.906

AC: activated carbon, MCAC: manganese coated activated carbon, R: rice husk, N: areca nut waste.

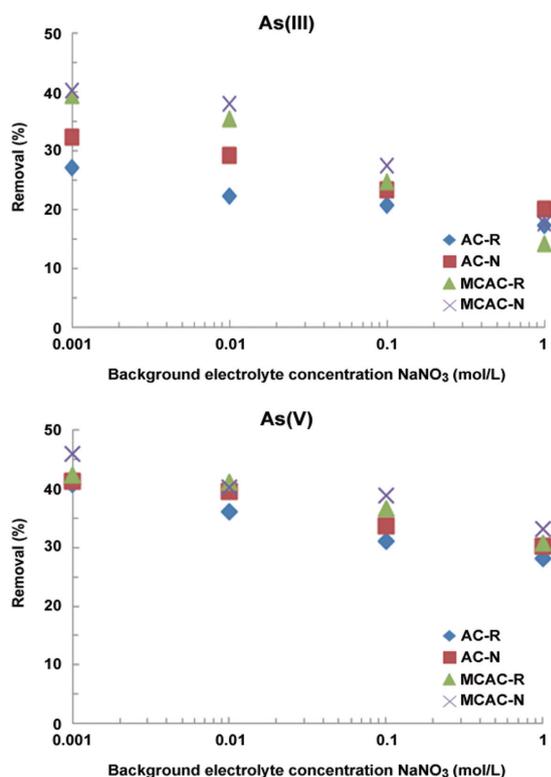


Fig. 6. Effect of background electrolyte concentration for the removal of As(III) and As(V) using different samples of activated carbon (AC) and manganese coated activated carbon (MCAC). Initial As(III) or As(V) concentration: 10 mg/L; sorptive pH ~4.5, R: rice husk, N: areca nut waste.

mol/L of NaNO₃ (1,000 times) at pH 4.5 keeping the concentration of As(III) and As(V) at ~10 mg/L as the constant. The results obtained were shown in Fig. 6. From the figure it was clearly observed that with increasing the background electrolyte concentration caused insignificantly the uptake of As(III) and As(V) by these solids. Further, quantitatively it was observed that a 1,000-fold increase in ionic strength caused a maximum percent decrease of these ions by only 15%. These results clearly inferred that As(III) and As(V) were specifically adsorbed and the sorbing ions were predominantly bound by strong forces and form inner sphere complexes onto the surface of the solid materials. Previous studies also showed that the As(V) was sorbed specifically onto the surface of inorgano-organo-modified-sericite [40] and the sorption of Cu(II) and Pb(II) onto the surface of sericite [39].

3.3.4. Effect of contact time

Studies were also carried out with the variation of contact time for the adsorption of As(III) and As(V) keeping the initial concentration at 9.95 mg/L and pH ~4.5. The obtained results were presented graphically in Fig. 7. The figure showed that, the uptake of these ions by these solids was very fast during the initial period of contact. It was explicable with the fact that the surface coverage was low at the initial stage of contact and sorptive ions occupy the active surface site rapidly in a random manner, as a result, the percent adsorption increased rapidly during the initial period. At latter stages, the surface coverage was increased

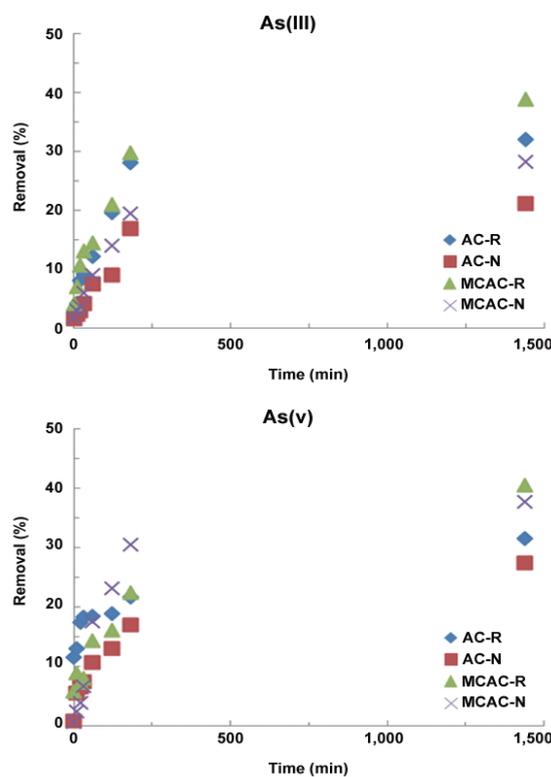


Fig. 7. Effect of contact time on the removal of As(III) and As(V) using different samples of activated carbon (AC) and manganese coated activated carbon (MCAC). Initial As(III) or As(V) concentration: 10 mg/L; sorptive pH ~4.5, R: rice husk, N: areca nut waste.

and the percent adsorption was slower and finally could attain an apparent saturation [32]. The simplified pseudo-first order kinetic model was used to analyze the data obtained in the kinetic studies between 0 and 180 minutes. The equation was employed as Eq. (3):

$$\ln(c_e - q_t) = \ln q_e - k_t t \quad (3)$$

where k_t is the adsorption rate constant (1/min), q_t is the amount adsorbed at time t (mg/g) and q_e is the amount adsorbed at equilibrium (mg/g) [41]. The values of q_e , k_t , and R^2 values obtained for four different samples with As(III) and As(V) are returned in Table 3. From the results it can be seen that the MCAC-R and MCAC-N followed the first order kinetic model better than AC-R and AC-N for both As(III) and As(V).

4. Conclusions

The results revealed that activated carbon and manganese coated activated carbons prepared from rice husk and areca nut wastes can be used as an alternative sorptive material for the removal of As(III) and As(V) from aqueous solutions. The experimental result conferred that the surface modifications of AC by aggregating manganese oxide with small-sized particles onto the surface of AC enhanced the uptake of both As(III) and As(V) from aqueous solutions. It is to be observed that all these ma-

Table 3. Values of q_e , k_t , and R^2 obtained for the sorption of As(III) and As(V) onto the solids using the pseudo-first order kinetic model

Sample	As(III)			As(V)		
	$k_t \times 10^{-3}$	q_e	R^2	$k_t \times 10^{-3}$	q_e	R^2
AC-R	4.4 ± 0.6	1.106 ± 0.008	0.942	1.3 ± 0.8	1.208 ± 0.007	0.733
AC-N	3.3 ± 0.5	1.075 ± 0.007	0.891	2.0 ± 0.7	1.052 ± 0.009	0.957
MCAC-R	2.9 ± 0.4	1.142 ± 0.009	0.954	1.5 ± 0.8	1.120 ± 0.008	0.952
MCAC-N	2.6 ± 0.5	1.033 ± 0.007	0.989	3.9 ± 0.9	1.178 ± 0.009	0.985

AC: activated carbon, MCAC: manganese coated activated carbon, R: rice husk, N: areca nut waste.

materials exhibited higher removal capacity for As (V) than As(III) in the present work. The percent uptake of As(III) or As(V) was decreased with increasing the solution pH and sorptive concentration. The increase in maximum background electrolyte concentration up to a 1,000-fold NaNO_3 caused an insignificant change in percent removal of As(III) or As(V) from aqueous solutions demonstrating that the sorbing species were bound with strong chemisorptive forces and formed an 'inner-sphere' complexation. Similarly, the time dependence data showed the applicability of the pseudo-first order rate uptake of these ions onto the surface of solids.

References

- Urik M, Littera P, Sevc J, Kolencik M, Cernansky S. Removal of arsenic (V) from aqueous solutions using chemically modified sawdust of spruce (*Picea abies*): kinetics and isotherm studies. *Int. J. Environ. Sci. Technol.* 2009;6:451-456.
- Amin MN, Kaneco S, Kitagawa T, et al. Removal of arsenic in aqueous solutions by adsorption onto waste rice husk. *Ind. Eng. Chem. Res.* 2006;45:8105-8110.
- Sinha S, Amy G, Yoo Y, Her N. Arsenic removal from water using various adsorbents: magnetic ion exchange resins, hydrous iron oxide particles, granular ferric hydroxide, activated alumina, sulfur modified iron, and iron oxide-coated microsand. *Environ. Eng. Res.* 2011;16:165-173.
- Chen W, Parette R, Zou J, Cannon FS, Dempsey BA. Arsenic removal by iron-modified activated carbon. *Water Res.* 2007;41:1851-1858.
- Bang S, Meng X. A review of arsenic interactions with anions and iron hydroxide. *Environ. Eng. Res.* 2004;9:184-192.
- Mohan D, Pittman CU Jr. Arsenic removal from water/wastewater using adsorbents: a critical review. *J. Hazard. Mater.* 2007;142:1-53.
- Muniz G, Fierro V, Celzard A, Furdin G, Gonzalez-Sanchez G, Ballinas ML. Synthesis, characterization and performance in arsenic removal of iron-doped activated carbons prepared by impregnation with Fe(III) and Fe(II). *J. Hazard. Mater.* 2009;165:893-902.
- Daus B, Wennrich R, Weiss H. Sorption materials for arsenic removal from water: a comparative study. *Water Res.* 2004;38:2948-2954.
- Reddy DH, Seshaiha K, Reddy AV, Lee SM. Optimization of C(II), Cu(II) and Ni(II) biosorption by chemically modified *Moringa Oleifera* leaves powder. *Carbohydr. Polym.* 2012;88:1077-1086.
- Kadirvelu K, Thamaraiselvi K, Namasivayam C. Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste. *Bioresour. Technol.* 2001;76:63-65.
- Doyurum S, Celik A. Pb(II) and Cd(II) removal from aqueous solutions by olive cake. *J. Hazard. Mater.* 2006;138:22-28.
- Amuda OS, Giwa AA, Bello IA. Removal of heavy metal from industrial wastewater using modified activated coconut shell carbon. *Biochem. Eng. J.* 2007;36:174-181.
- Chakravarty P, Sarma NS, Sarma HP. Biosorption of cadmium(II) from aqueous solution using heartwood powder of *Areca catechu*. *Chem. Eng. J.* 2010;162:949-955.
- Villaescusa I, Fiol N, Martinez M, Miralles N, Poch J, Serarols J. Removal of copper and nickel ions from aqueous solutions by grape stalks wastes. *Water Res.* 2004;38:992-1002.
- Mohan D, Singh KP. Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse: an agricultural waste. *Water Res.* 2002;36:2304-2318.
- El-Shafey EI. Removal of Se(IV) from aqueous solution using sulphuric acid-treated peanut shell. *J. Environ. Manag.* 2007;84:620-627.
- Soleimani M, Kaghazchi T. Adsorption of gold ions from industrial wastewater using activated carbon derived from hard shell of apricot stones: an agricultural waste. *Bioresour. Technol.* 2008;99:5374-5383.
- Farajzadeh MA, Monji AB. Adsorption characteristics of wheat bran towards heavy metal cations. *Sep. Purif. Technol.* 2004;38:197-207.
- Reddy DH, Seshaiha K, Reddy AV, Rao MM, Wang MC. Biosorption of Pb^{2+} from aqueous solutions by *Moringa oleifera* bark: equilibrium and kinetic studies. *J. Hazard. Mater.* 2010;174:831-838.
- Mahvi AH, Maleki A, Eslami A. Potential of rice husk and rice husk ash for phenol removal in aqueous systems. *Am. J. Appl. Sci.* 2004;1:321-326.
- Mishra SP, Prasad SK, Dubey RS, Mishra M, Tiwari D, Lee SM. Biosorptive behaviour of rice hulls for Cs-134 from aqueous solutions: a radiotracer study. *Appl. Radiat. Isot.* 2007;65:280-286.
- Nakbanpote W, Goodman BA, Thiravetyan P. Copper adsorption on rice husk derived materials studied by EPR and FTIR. *Colloids Surf. A Physicochem. Eng. Asp.* 2007;304:7-13.
- Zheng W, Li XM, Wang F, Yang Q, Deng P, Zeng GM. Adsorption removal of cadmium and copper from aqueous solution by areca: a food waste. *J. Hazard. Mater.* 2008;157:490-495.
- Li XM, Zheng W, Wang DB, et al. Removal of Pb (II) from aqueous solutions by adsorption onto modified areca waste: kinetic and thermodynamic studies. *Desalination* 2010;258:148-153.
- Hua M, Zhang S, Pan B, Zhang W, Lv L, Zhang Q. Heavy metal

- removal from water/wastewater by nanosized metal oxides: a review. *J. Hazard. Mater.* 2012;211-212:317-331.
26. Wang HQ, Yang GF, Li QY, et al. Porous nano-MnO₂: large scale synthesis via a facile quick-redox procedure and application in a supercapacitor. *New J. Chem.* 2011;35:469-475.
 27. Trivedi P, Axe L. A comparison of strontium sorption to hydrous aluminum, iron, and manganese oxides. *J. Colloid Interface Sci.* 1999;218:554-563.
 28. Mishra SP, Vijaya. Removal behavior of hydrous manganese oxide and hydrous stannic oxide for Cs(I) ions from aqueous solutions. *Sep. Purif. Technol.* 2007;54:10-17.
 29. Han R, Zou W, Zhang Z, Shi J, Yang J. Removal of copper(II) and lead(II) from aqueous solution by manganese oxide coated sand. I. Characterization and kinetic study. *J. Hazard. Mater.* 2006;137:384-395.
 30. Fan HJ, Anderson PR. Copper and cadmium removal by Mn oxide-coated granular activated carbon. *Sep. Purif. Technol.* 2005;45:61-67.
 31. Tiwari D, Laldawngliana C, Choi CH, Lee SM. Manganese-modified natural sand in the remediation of aquatic environment contaminated with heavy metal toxic ions. *Chem. Eng. J.* 2011;171:958-966.
 32. Lee SM, Kim WG, Laldawngliana C, Tiwari D. Removal behavior of surface modified sand for Cd(II) and Cr(VI) from aqueous solutions. *J. Chem. Eng. Data* 2010;55:3089-3094.
 33. Lee SM, Kim WG, Yang JK, Tiwari D. Sorption behaviour of manganese-coated calcined-starfish and manganese-coated sand for Mn(II). *Environ. Technol.* 2010;31:445-453.
 34. Kim WG, Kim SJ, Lee SM, Tiwari D. Removal characteristics of manganese-coated solid samples for Mn(II). *Desalin. Water Treat.* 2009;4:218-223.
 35. Lee SM, Tiwari D, Choi KM, Yang JK, Chang YY, Lee HD. Removal of Mn(II) from aqueous solutions using manganese-coated sand samples. *J. Chem. Eng. Data* 2009;54:1823-1828.
 36. Lee SM, Laldawngliana C, Tiwari D. Iron oxide nano-particles-immobilized-sand material in the treatment of Cu(II), Cd(II) and Pb(II) contaminated waste waters. *Chem. Eng. J.* 2012;195-196:103-111.
 37. Mishra SP, Dubey SS, Tiwari D. Inorganic particulates in removal of heavy metal toxic ions IX. Rapid and efficient removal of Hg(II) by hydrous manganese and tin oxides. *J. Colloid Interface Sci.* 2004;279:61-67.
 38. Tiwari D, Mishra SP, Mishra M, Dubey RS. Biosorptive behaviour of mango (*Mangifera indica*) and neem (*Azadirachta indica*) bark for Hg²⁺, Cr³⁺ and Cd²⁺ toxic ions from aqueous solutions: a radiotracer study. *Appl. Radiat. Isot.* 1999;50:631-642.
 39. Tiwari D, Kim HU, Lee SM. Removal behavior of sericite for Cu(II) and Pb(II) from aqueous solutions: batch and column studies. *Sep. Purif. Technol.* 2007;57:11-16.
 40. Tiwari D, Lee SM. Novel hybrid materials in the remediation of ground waters contaminated with As(III) and As(V). *Chem. Eng. J.* 2012;204-206:23-31.
 41. Akcay G, Kilinc E, Akcay M. The equilibrium and kinetics studies of flurbiprofen adsorption onto tetrabutylammonium montmorillonite (TBAM). *Colloids Surf. A Physicochem. Eng. Asp.* 2009;335:189-193.