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UTILIZING WASTE MATERIALS PROCUREMENT FOR ADSORPTION OF CHROMIUM ONTO BIO-MATRIX FROM RICE HUSK TO MINIMIZE WATER CONTAMINATION

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Abstract

Agricultural waste has been explored as a productive adsorbent for efficient metal removal due to their lower cost. The presence of various chemical functional groups in agricultural wastes especially phenolic, amino, carbonyl, alcoholic and sulfhydryl group etc. facilitates the removal of heavy metals as they tend to form metal complexes or chelates by reacting with them. Biosorption is a process of removing metal ions using biological agents and it includes processes like chemisorption, complexation, adsorption on the surface, diffusion through pores and ion exchange etc. To enhance the adsorption ability of these adsorbents, chemical modification is required. Specific chemicals such as mineral and organic acids, bases, oxidising agents or polymeric acids are used for modification of adsorbents. The purpose of this article is to show the removal efficiency of rice husk based hydrogel as a bio-adsorbent to remove Cr ions. Characterisation of the bio-adsorbent is done using FTIR and SEM before and after adsorption in order to explore number and position of the functional groups present on the adsorbent surface for Cr(VI) binding and changes in adsorbent surface morphology.

Keywords**:** Heavy Metals, Agricultural wastes, Rice Husk, Bio-adsorbents Hydrogel, Adsorption, SEM, FTIR

Introduction

Major sectors contaminating water bodies with heavy metals includes tanneries, metal plating industry, mining operations, fertilizer industries, batteries, paper industry, petroleum refining, electroplating, manufacturing of dye and pesticide, metallurgy, textiles etc. (Renu *et al.*, 2017). These industries discharge heavy metals directly or indirectly into the environment specifically in developing countries. Heavy metals like chromium (Cr), cadmium (Cd), iron (Fe), nickel (Ni), selenium (Se), vanadium (V), copper (Cu), cobalt (Co), mercury (Hg), lead (Pb), zinc (Zn) and arsenic (As) are majorly discharged by industries. The industries mainly discharge. For the removal of heavy metals various conventional treatment technologies like chemical precipitation, ion exchange, oxidation, reduction, reverse osmosis, electrodialysis and ultrafiltration are used. (Azimi *et al.*, 2017). Chromium easily enters the ecosystem as an environmental contaminant from chromate preparation, cooling towers of heavy industry leather tanning, electroplating, metal finishing atomic power plants, mining, metallurgy operations etc. It exists in nature in two oxidation states, namely, Cr (VI) and Cr (III). Cr (VI) is considered to be more toxic than Cr(III). Cr(III) shows a complicated behavior during hydrolysis and produces $Cr(OH)^{2+}$, $Cr(OH)^{4-}$, neutral species $Cr(OH)_3$, and polynuclear species $Cr_2(OH)_2$ and $Cr_3(OH)_4{}^{5+}$. (Bansal *et al.*, 2009). Chromium sulphate is utilized as a tanning agent causing ground water pollution nearby tanneries, that further gets converted into chromium(VI). (Yang *et al.*, 2015). Strong and consistent exposure to Cr(VI) leads to cause lung cancer and cancer of digestive tract and can also result in vomiting, nausea, epigastria, hemorrhage and diarrhea. (Sinha *et al.*, 2016).

0.05 to 0.1 mg l−1 is the permissible limit of Cr(VI) for the effluents discharged from industries into the surface waters and this range varies in different countries. (Tiwari *et al.*, 2018). It is therefore necessary to remove Cr (VI) from wastewater before discharging it in water bodies.

Various conventional methods available are for Cr removal are ion exchange, chemical precipitation, chemical reduction, membrane separations, electrochemical precipitation, photo-catalytic reduction, biosorption and adsorption (Zhong *et al.*, 2016). These methods have been known for removing chromium contaminated waste water in yesteryears. But apart from being satisfactory in terms of removing Chromium, these methods produce sludge with higher concentrations of toxic compounds such as cadmium, chromium, nickel etc. creating a difficult problem to dispose off the sludge (Suganya *et al.*, 2016). It is also observed that proper landfill sites are not designated for hazardous and toxic wastes in various states of India. As a result of which, the industries have no option but to store such hazardous sludge in their own premises or dispose it without treatment in the open which may further lead to soil, surface water and groundwater contamination. Although activated carbon in powdered or granular form is really effective in removing metal ions from aqueous solutions but due to its higher cost, their use is limited in a developing economy like India. Ours is an agrarian country and hence a huge amount of agricultural waste is available in nature. This agricultural waste can be utilised for heavy metal removal as they have certain characteristics that makes them a good bio-adsorbent (De *et al*., 2018).

Recently a lot of research has been done to explore agricultural wastes for their efficiency to remove heavy metals from wastewater. Few studied agricultural wastes with potential adsorption efficiency in the recent years are sugarcane bagasse, Indian rosewood sawdust, jatropha oil cake, maize corn cob. A number of authors have reported the efficacy of rice husk as a bio-adsorbent for removing Zn(II), Ni(II) and Cd(II) ions from aqueous solutions (Bansal *et al*., 2016). The present research is based on the removal of Cr(VI) from synthetic aqueous wastewaters by using rice husk based polymer named rice husk hydrogel and the modified form with acrylic acid. Rice husk is available in large quantities in India. it is used either as a fuel in brick kilns or as a material for packing at cheaper prices. In this study the effects of pH, adsorbent dose, concentration of metal ions and contact time have been investigated.

Hydrogels consists of polymeric networks able to absorb water in good amount. The polymeric networks contain hydrophilic groups that become hydrated when in aqueous solution and therefore forms a hydrogel structure (Hennink *et al*., 2012). Cross-linkers are an integral part of hydrogels as they prevent the polymeric chains from dissolution before they are used. Since hydrogels have ability to absorb water, they find a great scope in research to find the fundamentals of its swelling properties and its application in various technical areas. Hydrogel have a unique ability to absorb water which makes them promising for research of swollen polymer networks and its application in areas like contact lenses, dyes, devices for controlled release of proteins, encapsulating cells and materials for protein separation and drugs and wastewater treatments. (Gong *et al*., 2016). To make the hydrogels biodegradable in nature, labile bonds are induced either in the network backbone or in the cross-links. Hydrolysis, either chemically or enzymatically is done under physiological conditions to remove any unstable linkages in the hydrogel.

Hydrogels are prepared by either Physical Cross-linking or chemical Cross-linking. Depending upon their methods of preparation, hydrogels have distinctive properties and applications. In a chemically cross-linked hydrogel covalent bonds are present between the polymeric chains whereas in a physically cross-linked hydrogel, physical interactions occur between polymeric chains to prevent the hydrogel from dissolution before use (Akhtar *et al*., 2016).

Synthesis of Biodegradable bio-adsorbent

Carboxymethylation: One of the most important methods of chemical modification of rice husk is carboxymethylation. Derivatives of Carboxymethylated rice husk were found to be anionic, water soluble and nontoxic in nature. Due to such excellent properties, carboxymethylation is used in environmental and medical fields as well. Various efforts have been made for the removal of heavy metals from aqueous solutions by using a number of hydrogels consisting of functional groups like amine, carboxylic acid, sulfonic acid groups, hydroxyl, or the ones capable to form complexes with toxic metal ions. To introduce functional groups in the hydrogel matrix we use grafting, copolymerization, semi-interpenetrating polymer network and IPN technologies. Till date, only a few studies have been reported for selective removal of metal ions using hydrogels. In order to fill this gap, this study specifically focuses on the synthesis of hydrogel from rice husk and modifying it for removing Chromium ions from aqueous solutions (Choi *et al*., 2009).

Plain Rice husk Hydrogel and modified Rice husk Hydrogel

Carboxymethylation of rice husk: It is found to be one of the most potential method for the chemical modification of chitosan. Carboxymethyl derivatives of chitosan (CMC) are basically anionic, water soluble and nontoxic in nature. All these propertied makes CMC efficient enough for its applications in environmental fields (Shi *et al*., 2006).

Hydrogels and Crosslinking

Water insoluble polymeric network capable of absorbing large amounts water are referred to as “Hydrogel. It is a macromolecular polymeric gel made of a network of cross-linked polymeric chains. A hydrogel is synthesized by using hydrophilic monomers either by step growth or by chain growth simultaneously using cross-linker which helps promoting formation of networks. that has capacity to absorb large amount of water (Ahmed *et al*., 2015). Homopolymers or copolymer and natural polymers or Synthetic polymers, are generally used to synthesize three dimensional networks by chemical cross-linking or molecular entanglements (Calo *et al*., 2015) N, N Methylene bis acrylamide is used as a cross-linker. Cross-linking provides a three-dimensional structure to the hydrogels.

In the presence of cross-linkers hydrogels possess good elasticity and swelling properties. The level of cross-linking in a hydrogel is important as change in the cross-linking levels may lead to changes in the physical state of the hydrogels (Bukhari *et al*., 2015). Grafting Initiated by Free Radicals: Recently a number of initiators are being used such as potassium persulfate (PPS. or $K_2S_2O_8$), ceric ammonium nitrate (CAN), ammonium persulfate (APS), thiocarbonate–potassium bromate (TCPB), 2, 20-azobisisobutyronitrile (AIBN), potassium diperiodatocuprate (III) (PDC) and ferrous ammonium sulfate (FAS)for grafting copolymerisation (Elkholy *et al*., 2006). In our present research, Ammonium persulfate is used as an initiator (Jayakumar *et al*., 2010).

Materials and Methods

The rice husk was obtained from a local nearby rice mill, it was thoroughly washed with distilled water and dried in an oven at 35-40ºC for 24 hrs. After that it was grounded and sieved to obtain a fine powder. Final material is stored in an airtight plastic container for use in the experiment further. The batch removal of Cr^{+6} from aqueous solution was carried out using rice husk based bio-adsorbent. Plain rice husk based hydrogel and chemically modified rice husk based hydrogel were used to remove chromium from the aqueous solutions.

The stock solution of 1000 mg/l of Cr (VI) was obtained by using 2.835 g of $K_2Cr_2O_7$ in 1000 ml of double distilled water and rice husk hydrogel is used as a bio-adsorbent to remove chromium from the aqueous solution and its efficiency for the removal of chromium is analyzed. Atomic Absorption Spectrophotometer was used to obtain the absorbance.

Preparation of Adsorbents

Synthesis of hydrogel: First step to synthesize rich husk hydrogel is Alkalization. Afterwards, chloroacetic acid was dissolved in 2-propanol and added dropwise in the flask for a period of 20-30 minutes. The synthesized carboxymethylated samples were then neutralized using acetic acid and subsequently precipitating them with methanol.

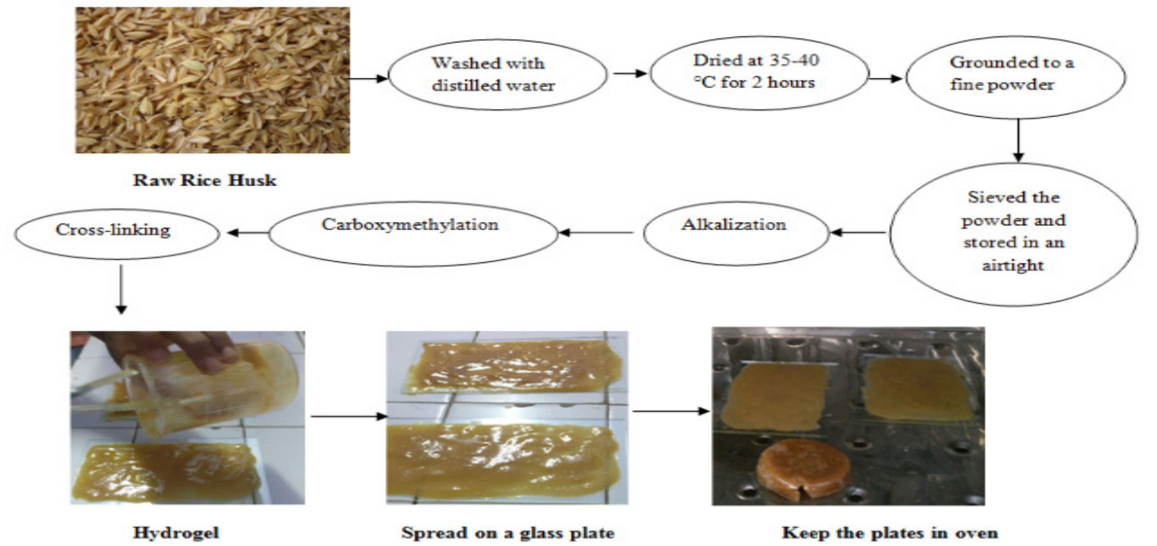

Fig. 1 : Process of synthesising hydrogel from Rice Husk

Results and Discussion

Characterisation of Adsorbents

FTIR and SEM were recorded, before and after adsorption, to explore number and position of the functional groups available for Cr(VI) binding on to studied adsorbents and changes in adsorbent surface morphology.

Fourier transformed infrared spectroscopy (FTIR) analysis of adsorbents : Shimadzu FTIR-8300 was used to obtain the FTIR spectra. The spectra obtained by FTIR of PRH and MRH (before and after adsorption of chromium) helps in determining the vibrational frequency changes in the functional groups in the adsorbent. Plotting of spectra was done by using the same scale on the transmittance axis for the adsorbent before and after adsorption. The FTIR spectra of the adsorbent display a number of absorption peaks, indicating the complex nature of the studied adsorbent. The obtained spectra denotes for a number of absorption peaks which gives a clear picture of the nature of the adsorbent examined. **In Plain Rice Husk hydrogel** the absorption peaks around 3280.254 cm^{-1} and 3364.64 cm^{-1} indicates the presence of free and intermolecular bonded hydroxyl groups. The peaks around 2923.56cm^{-1} and 2845.5414 cm^{-1} corresponds to the C-H stretching. The peak obtained at 1421.97cm^{-1} and 1358.280cm^{-1} is due to carboxylate groups (COO) in the hydrogel. Peaks at 695.859 cm^{-1}, 624.203cm^{-1} and 915.605cm^{-1} corresponds to C-H bond in plane bend. Peaks at 1114.64 cm^{-1} and 1050.955cm^{-1} corresponds to the presence of silica groups Si-O-Si and Si-O-C respectively.

In the **Chromium loaded plain rice husk hydrogel**, Hydroxyl groups were found at 3269.34. Bands at 1595.13, 1413.82 and 1332.81 are due to carboxylate groups. Peaks at 844.82 and 777.31 cm$^{−1}$ can be assigned to bending modes of aromatic compounds. The Hydroxyl group was found at 3269.34 cm^{-1}. It can be concluded that hydroxyl, carboxyl, and SiO_2 groups were the main components of plain rice husk hydrogel. It also shows that after adsorbing Cr ions, the peaks at 3280.6□cm$^{−1}$ reduced to 3269.34; peaks at 1358.280 reduced to 1332.81 and 1114.64 reduced to 1018.41 respectively due Cr ion adsorption.

In the **chemically modified rice husk hydrogel**, peaks at 3364.64 corresponds to OH stretch and after the adsorption of Cr in this peak gets reduced to 3327.21. Peaks at 2859.87, 2923.56 corresponds to C-H stretch. Peaks at 1707.006 is attributed to the presence of carboxylic group. It can be concluded that this group participates in metal binding as the peak shifts from 1706.006 to 1606.70 due to Cr loading. Peaks at 1151.27, 1022.29 corresponds to Si-O-C and Si-O-Si groups in the chemically modified hydrogel. After adsorbing chromium ions, Si-O-C peak is obtained at 1163.08.Chromium binding majorly occurred at OH and COO- groups. Physical adsorption, ionic exchange, surface precipitations and complexation with functional groups and chemical reaction with surface sites are possibly responsible for the adsorption of Cr ions on the adsorbent.

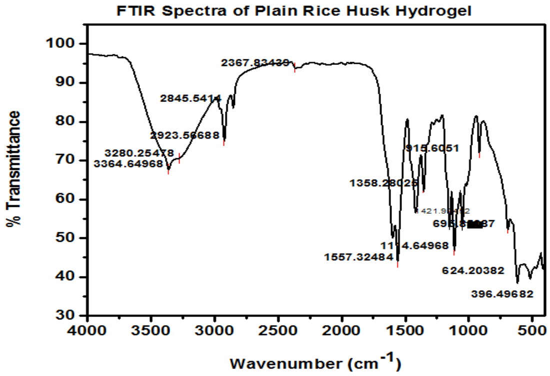

Fig. 2 : FTIR spectra (Plain Rice Husk Hydrogel)

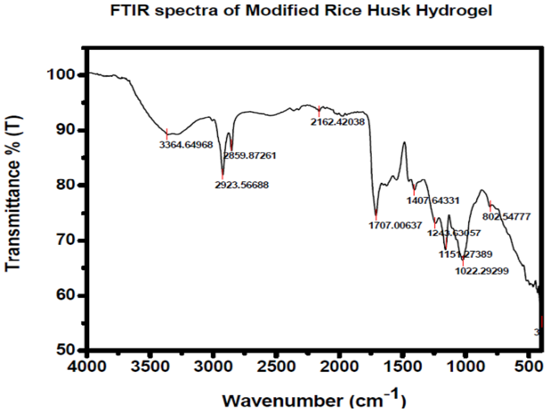

Fig. 3 : FTIR Spectra
(Modified Rice Husk Hydrogel)

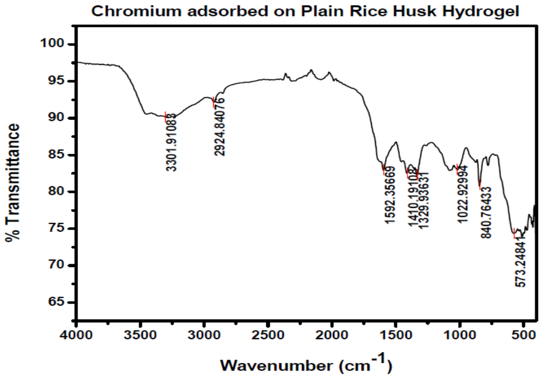

Fig. 4 : FTIR Spectra of Chromium
(Plain Rice Husk Hydrogel)

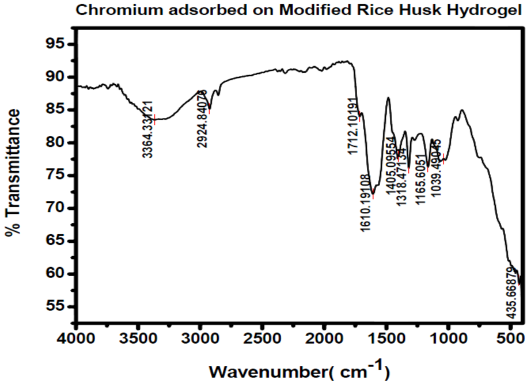

Fig. 5 : FTIR Spectra of Chromium
(Modified Rice Husk Hydrogel)

Scanning electron microscopy

For the direct observation of microstructures of different adsorbents on the surface SEM is used. Scanning electron microscopy shows morphology of different adsorbent. It is the most widely used technique for investigating the density of cross-linking, porosity of the developed hydrogel its morphology, size and shape. In case of plain rice husk numerous crack like structure were found, which facilitates good space for water penetration and further leads to the swelling of the hydrogel.

In the modified rice husk hydrogel with acrylic acid, the porosity is increased in the network structure thereby increasing the surface area, which allows enhanced diffusion of aqueous fluids across the hydrogel in the polymeric network leading to increased water adsorption (Singh *et al*., 2012).

The micrographs of SEM obtained before and after adsorption of Cr(VI) onto PRH (Figure 6a & b) and MRH (Figure 7a & b) are given. These respective SEM images clearly show the presence of Chromium adsorbed on its surface in the form of shiny highlighted area in PRH and shiny crystals in the MRH.

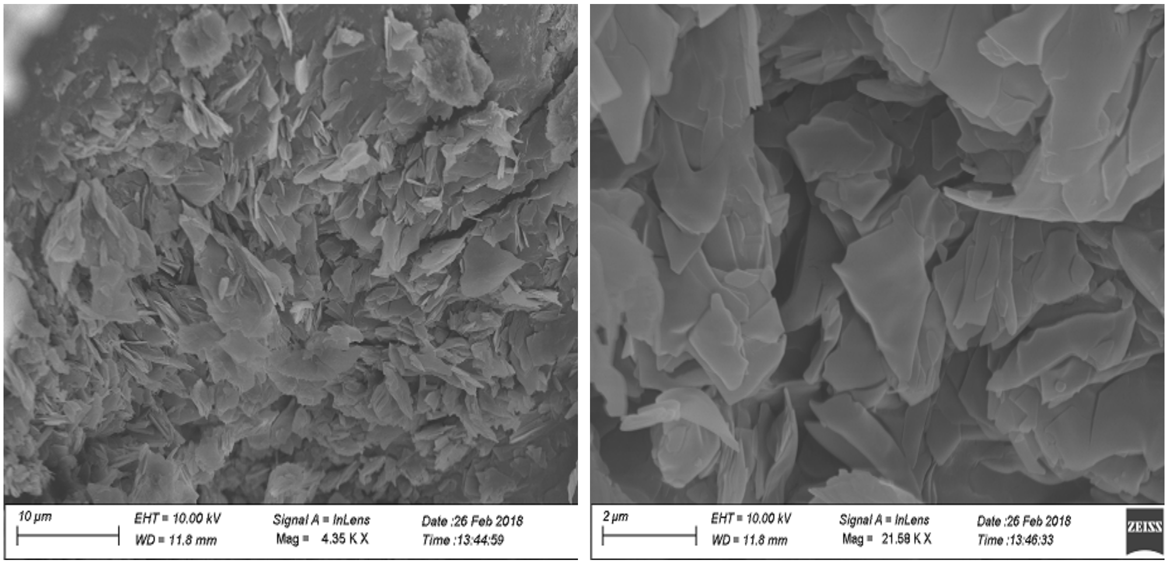

Fig. 6(a) : Scanning electron micrograph for Plain Rice Husk Hydrogel

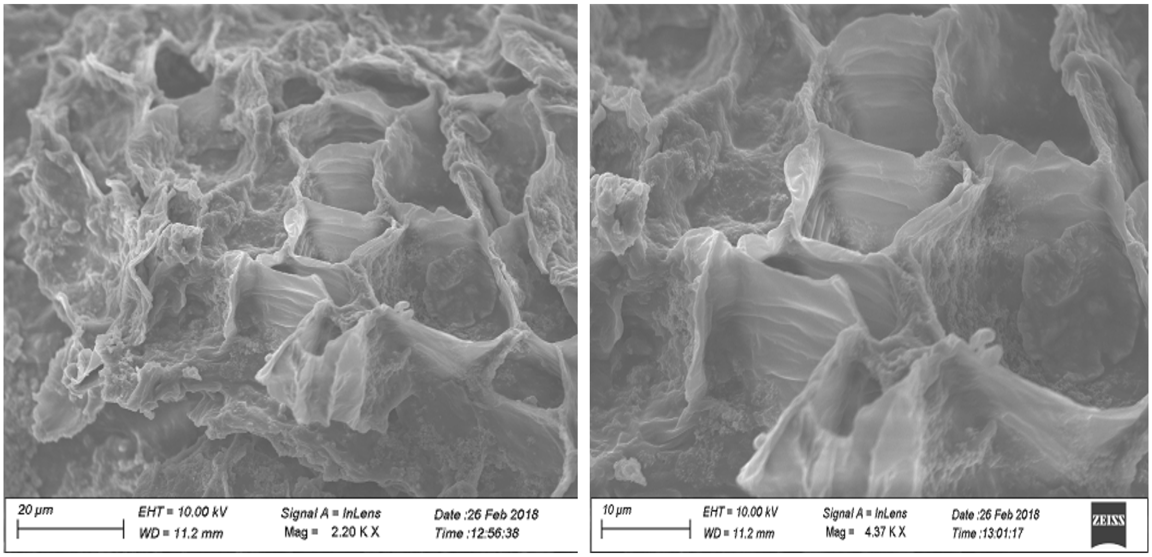

Fig. 6(b) : SEM for chromium adsorbed Plain rice husk hydrogel

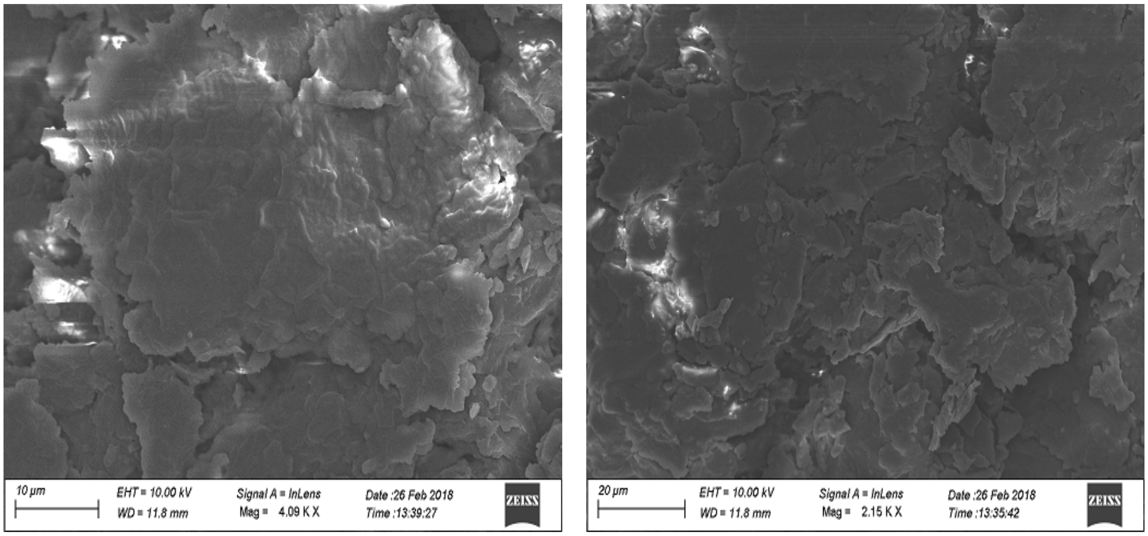

Fig. 7 (a) : Scanning electron micrograph for Modified Rice Husk Hydrogel.

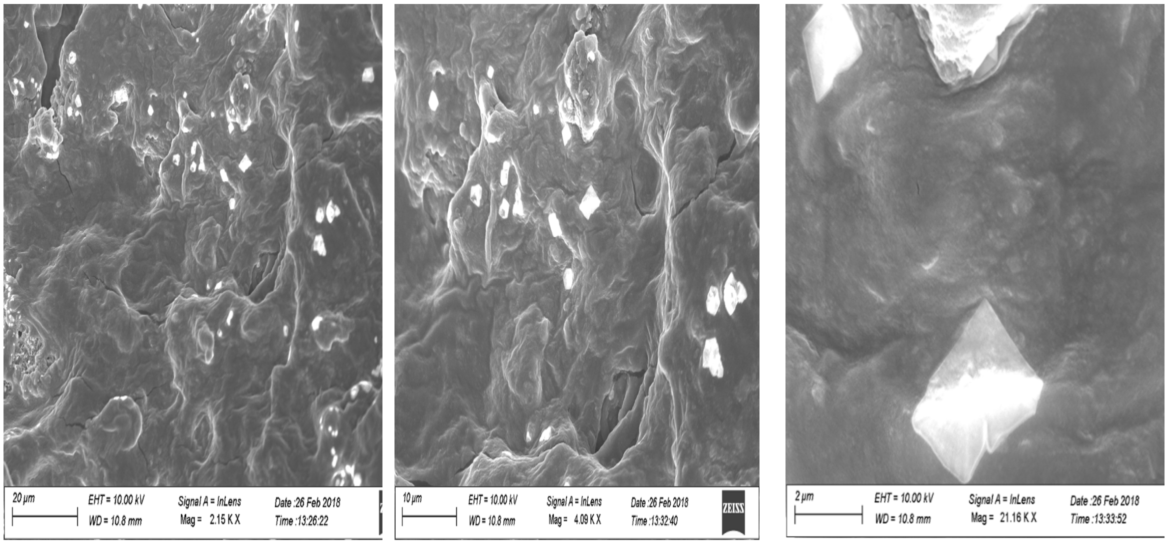

Fig. 7 (b) : SEM of chromium adsorbed on Modified rice husk hydrogel

Conclusions

Agricultural by-products have unique attributes like easy regeneration and desorption in the presence of basic and acidic solutions. This is because the surface possess functional groups like such as hydroxyl and carboxylic with a higher affinity towards metal cations. Methods like chemical pretreatment or surface modification helps in increasing the adsorption capacity of a specific adsorbent. The enhanced adsorption capacity generally compensates for the additional operational cost due to chemical pretreatment.

Even though various bio-adsorbents have been used for heavy metal removal from wastewater but agricultural wastes are found to be more economical for the removal of heavy metal because of their easy availability, and high affinity for heavy metals, biodegradability and renewability It was observed that the percent removal capacity for Cr removal is higher by using chemically modified rice husk than plain rice husk hydrogel.

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