# Synthesis and Characterization of Novel Rice Husk Hydrogel and Cross Linked Acrylic Acid-Rice Husk Hydrogel for the Adsorption of Chromium(VI) from Wastewater

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The main purpose of this research is to develop a low-cost and novel bioadsorbent hydrogel from rice husk (PRH) and modified rice husk (MRH) by carboxymethylation and grafting for the effective removal of chromium(VI) from aqueous solutions. The characterization and physico-chemical parameters of the bioadsorbents (PRH and MRH) was also performed. It was found that -CHO, >C=O, C-OH, Si-OH and -Si-H groups widely contributed towards the adsorption of chromium(VI) into the surface of bioadsorbents. The adsorption studies had been conducted using batch experiments. The adsorption equilibrium were analyzed and described by Freundlich, Langmuir and Dubinin-Radushkevish (D-R) isotherm models. It was observed that maximum adsorption of chromium(VI) was attained at pH 2. The optimized conditions regarding the removal of Cr(VI) using PRH (65%) and MRH (78%) as bioadsorbents were at 0.5 g/L of adsorbent dose, 120 min of contact time and pH 2. The results showed that rice husk residue based hydrogel has the potential to be used as a low-cost biosorbent for the removal of Cr(VI) from wastewater.

**Keywords: Bioadsorbents, Rice husk, Heavy metals, Adsorption.**

## INTRODUCTION

Heavy metals are released in waterbodies through industrial untreated wastewaters, which pose hazardous effects on human health and environment. Various diseases can occur if exposed to these heavy metals even at lower concentrations [1]. Chromium is one of the highly toxic metal and generally released in the environment from several sources like metal finishing, leather tanning, electroplating, metallurgy operations, *etc.* [2]. The cancer in digestive tract and lungs, epigastria, vomiting, diarrhea, *etc.* is caused due to consistent exposure to chromium(VI) [3]. The limit of Cr(VI) discharge from industrial effluents ranges from 0.05 to 0.1 mg/L in different countries [4]. Various methods of treatment like ion-exchange, chemical reduction, chemical precipitation, membrane separation, electrochemical precipitation, photo-catalytic reduction, adsorption and biosorption are in practice for the removal of chromium from wastewater remediation [5,6].

Disadvantage related to the above mentioned techniques includes being low in efficiency, usage of non-green solvents, laborious operations and sometimes lack of selectivity [7]. Commercial use of adsorbents like activated carbon becomes highly expensive so research in this direction to find an inexpensive adsorbent is the need of the hour. Hence, in this regard, development of new bioadsorbents for the decontamination of metal ions from water is needed [8].

India is an agrarian country and produces agricultural wastes in abundance. The biomass is capable of removing heavy metals from aqueous solution due to their specific characteristic [9]. Agricultural wastes like Indian rosewood saw dust, jatropha oil cake, maize corn cobs, sugarcane bagasse, *etc.* have been studied for the adsorption efficiencies for heavy metal removal [10]. Rice husk is an agronomical byproduct produced in huge quantities in India and hence available at a cheaper price [11].

Utilizing rice husk as potential bioadsorbent hydrogel for toxic metals remediation has gained increased attention these days as it is easily available, low-cost, re-usable, highly efficient, easy in processing and has any negative impact on the environment [12]. Rice husk based hydrogel (PRH) and modified rice husk-acrylic acid based hydrogel (MRH) has higher adsorption

ability even with low metal concentrations and selectively absorbs metal ions due to the presence of various binding functional groups on its surface. This study is based on exploring the usage of rice husk as a bioadsorbent for the removal of Cr(VI). The batch experiment is conducted in order to study the effects of pH, adsorbent dose, Cr(VI ) ion concentration and contact time for the efficient removal using natural and modified rice husk hyrogels. The adsorbent capacity was determined using Langmuir, Freundlich and Dubinin-Radushkevich adsorption isotherm models.

## EXPERIMENTAL

The majority of analytical grade chemicals *viz.* acrylic acid, propan-2-ol, chloroacetic acid, methanol, potassium dichromate and acetone were purchased from Rankem whereas ammonium per sulphate and *N,N*-bisacrylamide were procured from Merck, USA. About 100 g rice husk was collected from a nearby rice mill, it was washed with distilled water and dried in an oven at 35-40 ℃ for 24 h. The dried rich husk was grounded and sieved to obtain a fine powder. The material was stored in an airtight plastic container for further use.

**Preparation of adsorbents**

**Synthesis of rice husk based hydrogel (PRH):** In the first step, powdered rich husk (10 g) was mixed with 18% of NaOH solution and mixture was magnetically stirred at 120 rpm for 1 h. Afterwards, 14 g of chloroacetic acid was dissolved in 2-propanol and added dropwise in the flask for a period of 20-30 min and refluxed at 70 ℃ for 2.5 h. The resultant reaction mixture was allowed to cool and neutralized with 5 mL acetic acid followed by 3 mL of methanol. The carboxymethylated mixture was checked by putting a small fraction in 10 mL of distilled water, which remains insoluble. In the second step, the carboxymethylated mixture was now grafted with 1% initiator ammonium persulphate and 5% cross linker *N,N*-bisacrylamide in 10 mL of deionized water at 50 ℃ for 3 h. The grafted mixture was finally washed with double distilled water and immersed in 5 mL acetone for 1 h to remove excess water. Filtered and dried  the gel in an electric oven at 50 ℃.

**Preparation of modified rice husk acrylic acid based hydrogel (MRH):** The first step was carried out in a similar manner as mentioned above. The carboxymethylated mixture was grafted 10 g of acrylic acid along with 1% initiator ammonium persulphate and 5% crosslinker *N,N*-bisacrylamide in 10 mL of deionized water at 50 ℃ for 3 h.

**Batch adsorption experiments:** The bioadsorbents PRH and MRH were used to adsorb chromium(VI) from the aqueous solution. Potassium dichromate (25 mL) solution was mixed with 0.5 g bioadsorbent in a 250 mL conical flask. Adjustments of pH were done by using 0.1 N HCl or 0.1 N NaOH solutions. The flasks were then kept on a shaker for the desired contact time with 120-125 rpm at room temperature. The sample was taken in a falcon tube and centrifuged for 15 min and then the contents were filtered using Whatmann no.1 filter paper. The supernatant was collected and analyzed the Cr(VI) concentration in the sample using AAS [13]. All the experimental work was carried out in triplicate. To conduct batch experiments, each

25 mL of Cr(VI) solution (100 mg/L) was taken at different pHs (2, 4, 7 and 9), adsorbent dose (0.12-0.5 mg/L) at a stirring speed of 5000 rpm for a contact time of 120 min. The removal % of chromium(IV) was calculated using the following eqn. 1:

$$R\ (\%) = \frac{C_i - C_e}{C_i} \times 100 \qquad (1)$$

where $C_i$ and $C_e$ denote the initial and final concentration of chromium in the aqueous solution, respectively.

The adsorption capacity of hydrogel for Cr(VI) removal is calculated using eqn. 2:

$$q_e\ (mg/g) = \frac{C_i - C_e}{M} \times V \qquad (2)$$

where $C_i$ and $C_e$ signify the initial and final chromium concentration in the solution, respectively; V denotes the volume of solution and M denotes mass of the adsorbent (hydrogel).

## RESULTS AND DISCUSSION

**FTIR studies of adsorbents:** The FTIR spectral analysis of PRH and MRH (before and after adsorption of chromium) helps in determining the vibrational frequency changes in the functional groups in the adsorbents. The FTIR spectra of the adsorbent display a number of absorption peaks, indicating the complex nature of the studied adsorbents. In PRH , the absorption peaks around 3280.25 and 3364.64 cm$^{-1}$ indicates the presence of free and intermolecular bonded hydroxyl groups. The peaks around 2923.56 and 2845.54 cm$^{-1}$ corresponds to the C-H stretching and the peaks at 1421.97 and 1358.28 cm$^{-1}$ is due to carboxylate groups (COO$^-$) in the hydrogel. Peaks at 695.86, 624.20 and 915.60 cm$^{-1}$ correspond to C-H bond in plane bend. Peaks at 1114.64 and 1050.955 cm$^{-1}$ correspond to the presence of silica groups Si-O-Si and Si-O-C, respectively (Fig. 1a-b).

In chromium(VI) loaded PRH bioadsorbent, the hydroxyl groups peak was shifted to 3269.34 cm$^{-1}$. Similarly, carboxylate groups peaks were also shifted to a lower region of 1413.82 and 1332.81 cm$^{-1}$. Moreover,  the peak corresponds to silica group Si-O-Si was observed at 1018.41 cm$^{-1}$. At last, the peaks at 844.82 and 777.31 cm$^{-1}$ are due to the bending modes of aromatic compounds (Fig. 1c).

In MRH, a peak corresponds to OH stretching was observed at 3327.21 cm$^{-1}$, while the bands at 2859.87 & 2923.56  cm$^{-1}$ correspond to C-H stretching. The bands at 1707.01 cm$^{-1}$ are attributed due to the presence of carboxylic group and this also concluded that this group participates in Cr(VI)binding as the peak shifted to 1606.70 cm$^{-1}$ due to Cr(VI) loading. Finally, the peaks at 1151.27 & 1022.29 cm$^{-1}$ correspond to Si-O-C and Si-O-Si groups, respectively (Fig. 1d).

**SEM studies:** In PRH, numerous cracks like structure were found, which facilitates good space for water penetration and further leads to the swelling of the hydrogel. While in the crosslinked rice husk with acrylic acid (MRH) hydrogel, 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 [8]. The surface morphology of
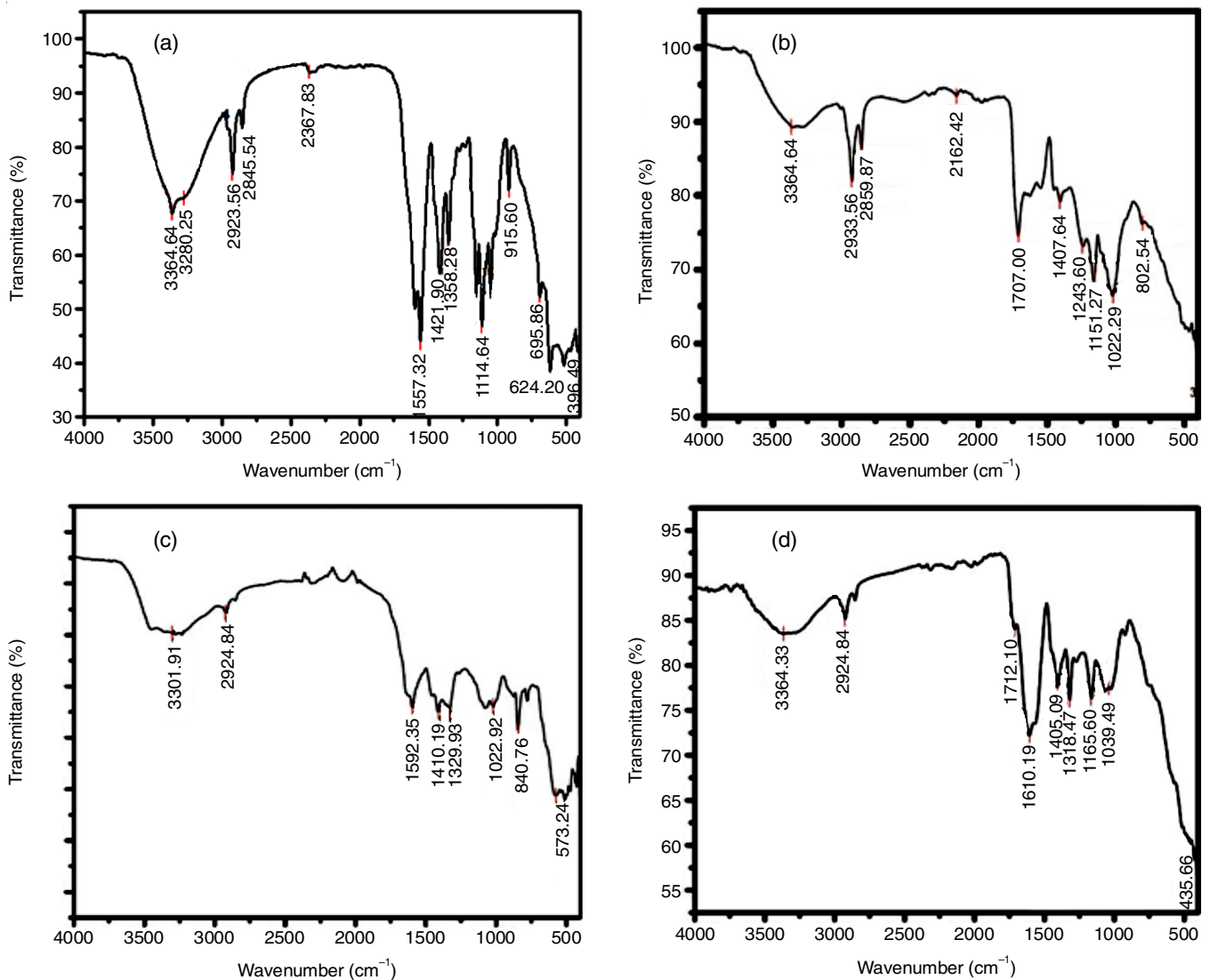
Fig. 1.  FTIR spectra of (a) plain rice husk hydrogel; (b) modified rice husk-acrylic acid hydrogel; (c) chromium loaded (PRH); (d) chromium (MRH)

obtained before and after adsorption of Cr(VI) onto PRH (Fig. 2a-b) and MRH (Fig. 2c-d) are shown, which clearly shows the presence of Cr(VI) adsorption in the form of shiny highlighted area in PRH and shiny crystals in MRH.

**Effect of pH:** Fig. 3 illustrates that by varying pHs, the adsorption of Cr(VI) ions on the surface of PRH and MRH bioadsorbents affects significantly. At pH 2, maximum rate of adsorption was observed at 19% and 31%, for PRH and MRH bioadsorbents, respectively, therefore it was chosen as the optimal pH value for further batch studies. At higher pH (< 2), the surface of the hydrogel gets negatively charged which leads to decrease the level of protonation on the surface (PRH & MRH) and hence the rate of Cr(VI) adsorption decreases [14].

**Effect of adsorbent dose:** The efficiency of PRH and crosslinked MRH was evaluated at different doses in 100 ppm of Cr(VI) solution, at pH 2 for contact time (120 min). It was found that as the dosage of bioadsorbent increases, the percentage removal of Cr(VI) also increased (Fig. 4). This could be due to more surface area of hydrogel and the presence of large number of adsorption sites on the surface of the hydrogel which

successfully adsorbed chromium ions onto the hydrogel surface. However, using 0.25 g of adsorbent gave the maximum results.

**Effect of initial metal ion concentration and contact time:** The optimal removal of Cr(VI) using PRH and MRH bio-adsorbents was further evaluated by varying intial Cr(VI) concentration (100 ppm, 125 ppm and 150 ppm) while keeping the adsorbent dose constant at 0.5 g/L, pH 2.0 and stirring speed of 120 rpm at room temperature. The removal of Cr(VI) by PRH and crossliked MRH was found to increase with time until 120 min and after that the rate of adsorption almost remains constant (Fig. 5). It was found that the percentage removal of Cr(VI) decreased with the increase in the concentration of metal ions.

**Adsorption isotherms:** Adsorption isotherms are used to establish the relationship between the amount of metal ion adsorbed and its equilibrium concentration in solution. Thus, in the present work, adsorption experiments were carried out at the equilibrium time of 120 min at pH 2 and using 0.5 g of PRH & MRH. Chromium(VI) ions that adsorbed and remained in the solution phase were measured and their compatibility
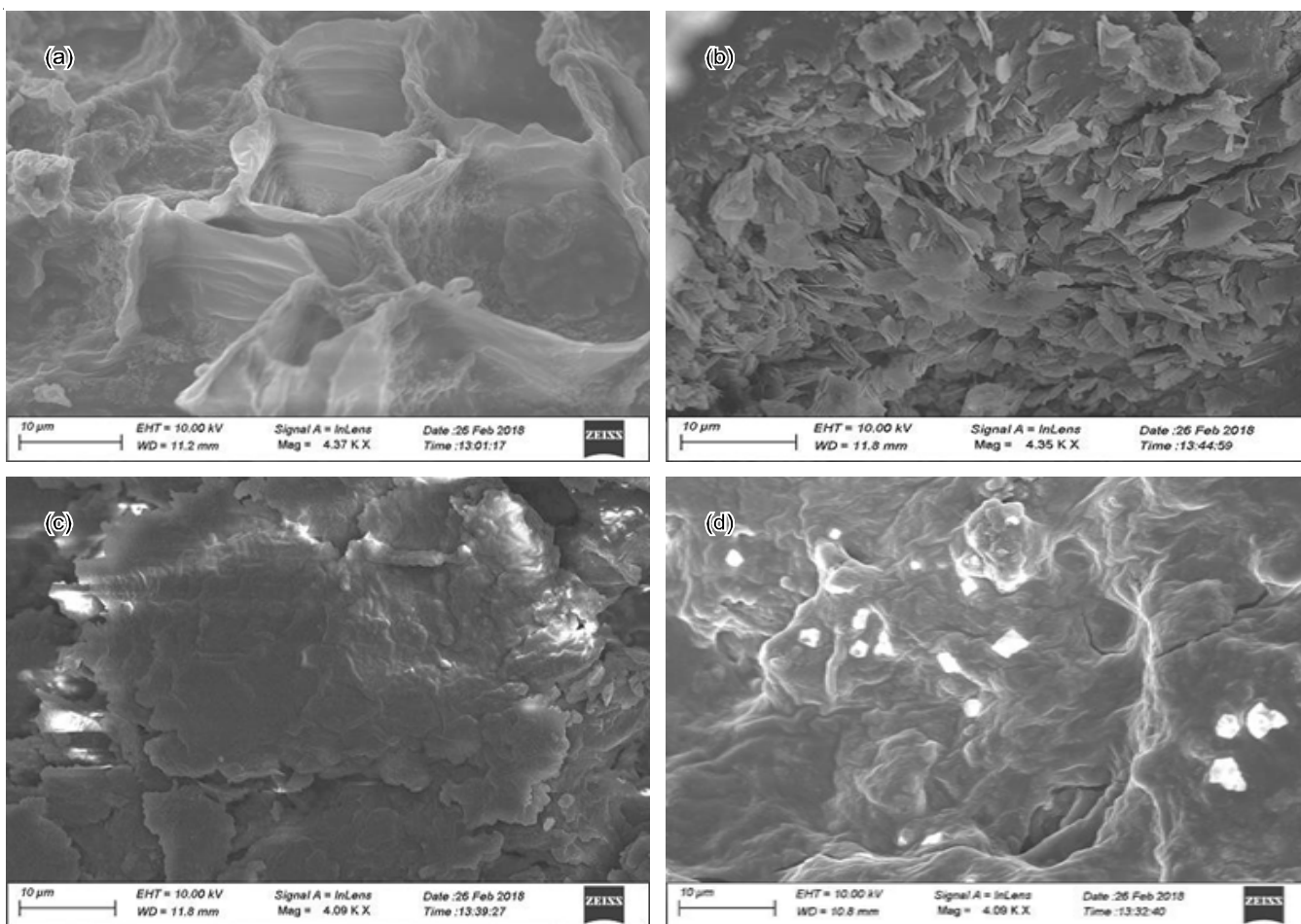
Fig. 2. Scanning electron micrograph for (a) plain rice husk hydrogel; (b) chromium adsorbed plain rice husk hydrogel; (c) modified rice husk hydrogel; (d) chromium adsorbed on modified rice husk hydrogel
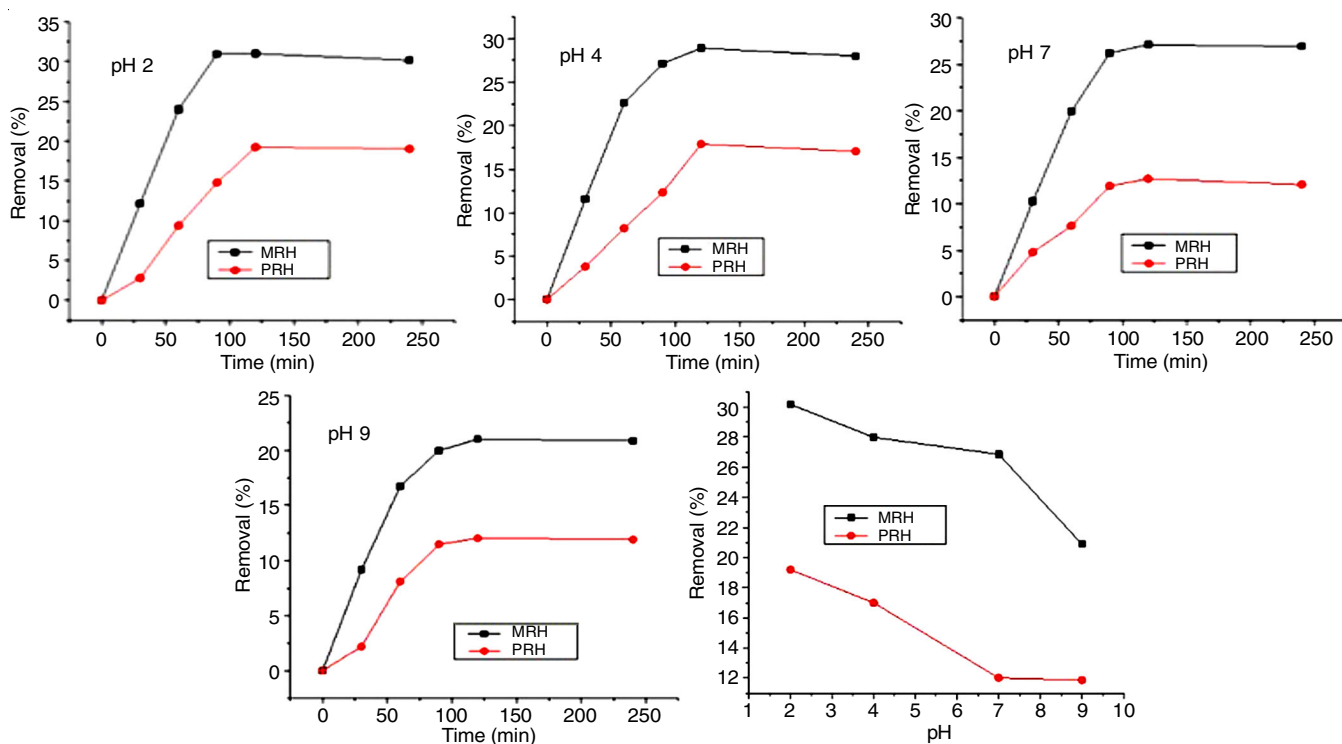


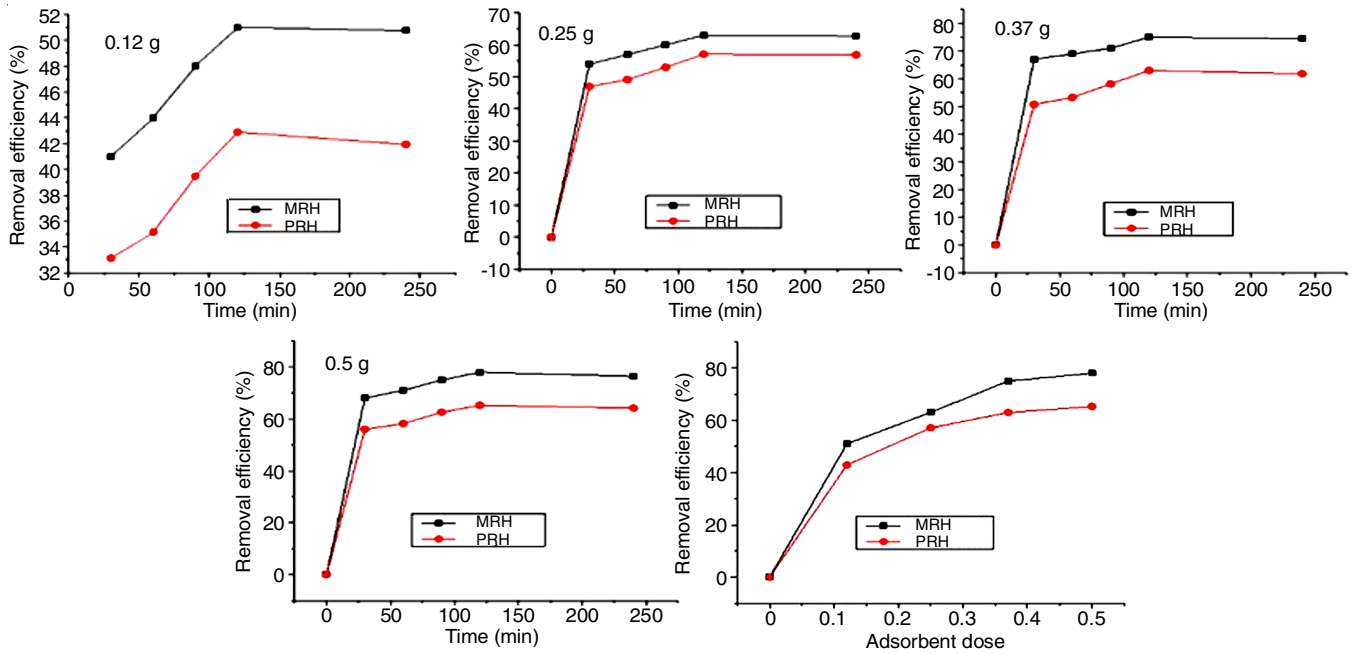Fig. 3. Adsorption of Cr(VI) on PRH and MRH at various pHs

Fig. 4. Effect of adsorbent dose 0.12 g, 0.25 g, 0.37 g and 0.50 g (PRH MRH) on Cr(VI) removal
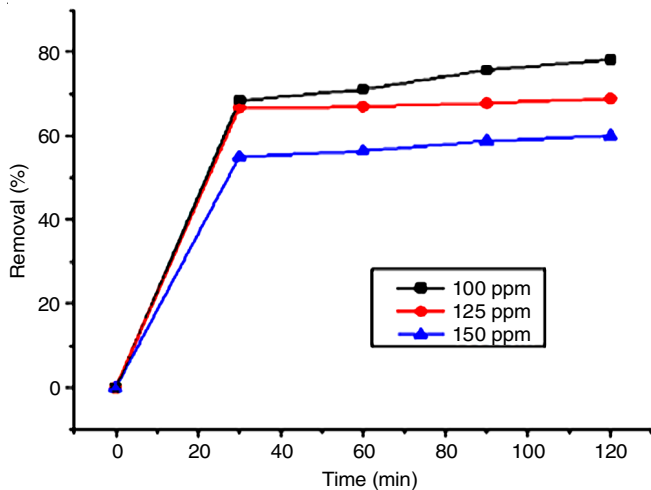


Fig. 5.   Effect of initial Cr(VI) concentration and contact time on chromium removal by PRH & MRH

with Freundlich, Langmuir and D-R adsorption isotherms was investigated.

The Freundlich equation is expressed linearly as:

$$\log_{10} q_e = \log_{10}(K_f) + \left(\frac{1}{n}\right)\log_{10}(C_e)$$

where $q_e$ is the amount of adsorbed chromium(VI) concentration in solution at equilibrium(mg/g)and $C_e$ gives the residual concentration of Cr(VI) in solution (mg/L). The intercept plot of log $q_e$ vs. log $C_e$ are used to calculate the values of $K_f$ and n which affects the adsorption isotherm.

Langmuir isotherm is express as follows:

$$\frac{C_e}{q_e} = \left(\frac{1}{Q_0 b} + \frac{C_e}{Q_0}\right)$$

where, $C_e$ denotes equilibrium concentration of adsorbate (mg/L) and $q_e$ is the adsorbed amount of Cr(VI) at equilibrium. $Q_0$

and b are two Langmuir constants, which signify the adsorption capacity and adsorption rate. Langmuir isotherm is expressed in a dimensionless constant also called separation factor ($R_L$), which is expressed as:

$$R_L = \frac{1}{(1+bC_o)}$$

where b denotes Langmuir constant and $C_o$ denotes initial concentration of Cr(VI). $R_L$ basically signifies the value of magnitude of the feasibility of adsorption process.

Dubinin-Radushkevich (D–R) isotherm model is defined as:

$$\log_{10} q_e = \log_{10} q_D - 2B_D R^2 T^2 \log_{10}\left(1+\frac{1}{C_e}\right)$$

where $q_D$ denotes the theoretical saturation capacity (mg/g) and $B_D$ is a constant which signify the adsorption energy, R is gas constant (kJ mol$^{-1}$ K$^{-1}$) and T is the temperature (K). The utility of this isotherm is that the D-R isotherm form can be applied on both homogenous and heterogonous surfaces.

The slope of the plot log $q_e$ versus log (1+1/$C_e$) provides the values of $q_D$ and $B_D$ [6]. Based on the correlation coefficient ($R^2$) value of isotherm model parameters for Cr(VI) as 0.9393, 0.8828 and 0.9393 for Freundlich, Langmuir and Dubinin-Radushkevich (D-R), respectively (Fig. 6), indicating that within the experimental range, the adsorption equilibrium was mainly dominated by monolayer chemical adsorption [5].

The experimental results of present analysis showed that MRH has the highest sorption capacity. The adsorption capacity of different bioadsorbents reported in the literature were compared with the PRH and MRH. The results (Table-1) revealed that the maximum adsorption capacity obtained in this research was higher compared to other low cost modified bioadsorbents.
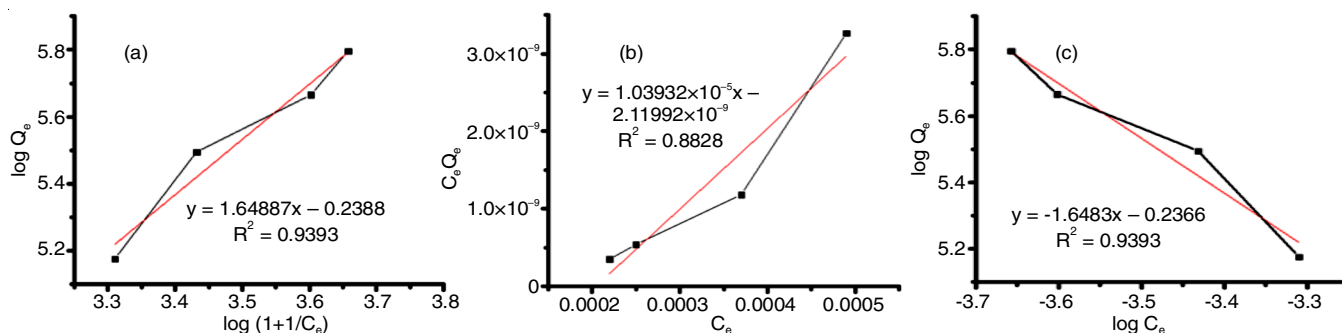
Fig. 6. Plot of D-R isotherm (a); Langmuir isotherm (b); and Freundlich isotherm (c)

TABLE-1
COMPARATIVE DATA OF CHROMIUM REMOVAL USING DIFFERENT BIOADSORBENTS

| Type of adsorbents | Metal conc. (mg/L) | pH | Best isotherm model | Contact time (min) | Adsorbent dose (g/L) | Removal (%) | Ref. |
|---|---|---|---|---|---|---|---|
| Iron oxide incorporated into silica derived from rice husk | 50-300 | 2 | Langmuir | 120 | 2 | 71 | [15] |
| CNT supported by activated carbon | 0.5 | 2 | Langmuir | 60 | 0.04 | 72 | [16] |
| Pre-treated orange peel | 10 | 3 | Langmuir | 260 | 10 | 79 | [17] |
| Composite of iron nanoparticles into orange peel pith | 10-50 | 1 | Langmuir | 60 | 5 | 71 | [18] |
| Plain rice husk hydrogel (PRH) | 100-150 | 2 | Freundlich & Dubinin-Radushkevich | 120 | 0.5 | 65 | Present work |
| Modified rice husk hydrogel (MRH) | 100-150 | 2 | Freundlich & Dubinin-Radushkevich | 120 | 0.5 | 78 | Present work |

## Conclusion

The batch adsorption studies indicated that the newly synthesized bioadsorbent hydrogel from rice husk (PRH) and modified rice husk (MRH) can be effectively used for the removal of Cr(VI) from wastewater. The adsorption process was found to follow Freundlich and D-R adsorption isotherms. The characterization studies of the PRH and MRH were done using FTIR and SEM techniques, which revealed that due the presence of functional groups like -OH, -COOH, C=O, Si-O-Si groups on the surface facilitates the adsorption of Cr(VI) ions from the aqueous solutions. A subtle comparison of the two samples of hydrogels revealed that MRH (78%) was more effective in Cr(VI) removal than the PRH *i.e.* 65%. As the cost of this biomatrix hydrogel obtained from rice husk is very low, it might be a novel, biodegradable and economic material for the treatment of chromium(VI) from contaminated water and can also be utilized as an additional feature in designing of waste or effluent treatment plant.

## CONFLICT OF INTEREST

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

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