

Removal of Chromium (VI) from Aqueous Solutions Using Poly(4-vinyl pyridine) Beads

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ABSTRACT: Sorption of hexavalent chromium ions from aqueous solution by poly 4-vinyl pyridine [Poly(4-VP)] was studied. The batch method was applied for adsorption processes. The effects of initial ion concentration, time, pH and temperature on adsorption were investigated. A treatment time of 60 min was found to be sufficient to reach equilibrium. pH 3.0 was found as the optimum pH value for the process. The maximum adsorption performance was

achieved at 86.7 mg g^{-1} using 500 mg L^{-1} Cr (VI) solutions. The process of adsorption of Cr (VI) was explained by Langmuir isotherm. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2865–2870, 2006

Key words: adsorption; chromium removal; desorption; poly(4-VP) beads

INTRODUCTION

The hazardous effect of heavy elements in the environment on human beings has limited their use considerably in various industries. With ever-increasing population and rapid industrial growth, the contamination of environment is inevitable because of the discharge of these metals from various industries. Chromium is used for making steel and other alloys, bricks in furnaces, dyes pigments, for chrome plating, leather tanning, and wood preserving. It is a necessary human nutrient. Chromium has three main forms, chromium (chromium 0), trivalent chromium (chromium III), and hexavalent chromium (chromium VI). Chromium III is a necessary dietary supplement at trace concentrations, is a stable compound and occurs naturally in the environment. Chromium (0) does not occur naturally. Cr(VI) has a significant impact on human health and other living organisms in the environment. Toxicity to humans includes lung cancer, liver, kidney and gastric damage, and epidermal irritation.¹ Therefore, the concentration of chromium ions has to be decreased to permissible levels, which are less than 0.05 mg L^{-1} .²

Adsorption has been one of the methods used to remove chromium species and toxic metals from aqueous solutions with relatively low ions concentra-

tion. In our previous work, the adsorption behavior of pure PET fibers toward heavy metal ions in aqueous solutions was studied by a batch equilibration technique.³ We have also used methacrylic acid grafted PET fibers⁴ and 4-VP-grafted PET fibers⁵ as an adsorbent for the removal of copper (II) ions from an aqueous solution.

There are many types of adsorbents, including activated carbon,^{6–8} biomaterials,^{9,10} chitosan,¹¹ sawdust,¹² polyacrylamide-grafted sawdust,¹³ polyacrylonitrile fibers,¹⁴ modified poly(4-VP)-coated gel,¹⁵ that have been studied for the adsorption of chromium from aqueous solutions. However, some of these adsorbents do not have high adsorption capacities or need long adsorption equilibrium times, while others may have difficulty for regeneration and reuse.

One of the recent developments in the removal of heavy metal ions from water or wastewater is the use of polymer beads as an adsorbent. This is mainly attributed to the relatively large external specific high surface areas, high adsorption kinetics, and low cost of this polymer beads.^{16,17}

It is therefore of practical and research interest to develop effective adsorbents from these cheap polymer beads, for the removal of chromium in water and wastewater treatment.

EXPERIMENTAL

Materials

4-VP was purified by vacuum distillation at 2 mmHg and 65°C. Benzoyl peroxide $[(\text{C}_6\text{H}_5\text{CO})_2\text{O}_2]$ was twice precipitated from chloroform in methanol and dried in a vacuum oven for 2 days. Other reagents were used as supplied. All reagents were Merck products.

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Polymerization procedure

Polymerization was carried out in a thermostated 250 mL flask under reflux. The mixture containing 34 mL monomer and $(C_6H_5CO)_2O_2$ at required concentration dissolved in 40 mL acetone was made up to 200 mL with deionized water. The mixture was immediately placed into the water bath adjusted to the polymerization temperature (55°C). At the end of the predetermined polymerization time (2 h), homopoly (4-VP) were vacuum-dried at 50°C for 48 h.

Preparation of beads

Poly(4-VP) beads were prepared from 10% (w/v) Poly(4-VP) in methanol by a using crosslinked to 0.3M $NiCl_2 \cdot 6H_2O$.

Sorption of chromium ions on the beads

Cr(VI) ion solution (10 mg L⁻¹, pH 3.5) of volume 25 cm³ was added onto 0.05 g of poly(4-VP) beads in 50 mL Erlenmeyer. The contents were shaken at 150 rpm for a predetermined period of time at 25°C using orbital shaker (Edmund Mühler TH 15). After filtration (used a Cole-Parmer micro filtration apparatus with membrane filter) of the solution, the chromium ion concentration of the filtrates was measured by a GBC 933A model flame atomic absorption spectrometer equipped with deuterium lamp background correction and hollow cathode lamps (HCL) and an air-acetylene burner was used for the determination of the metals. The instrumental parameters were those recommended by the manufacturer. The adsorption capacity of the poly(4-VP) beads were evaluated by using the following expression:

$$q = (C_0 - C)V/m \quad (1)$$

where q is the amount of ion adsorbed onto unit mass of the poly(4-VP) beads (mg g⁻¹), C_0 and C are the concentration of the ion in the initial solution and in the aqueous phase after adsorption treatment for a certain period of time (mg L⁻¹); V is the volume of the Cr(VI) solution used (L); and m is the amount of poly(4-VP) beads used (g), respectively.

Effect of pH on chromium sorption

To study the effect of pH on sorption, the beads were incubated for 60 min with aqueous Cr(VI) solution (10 mg L⁻¹) adjusted to required pH values in a range of 2–5.5 using buffer solutions (glycine/HCl, acetic acid/sodium acetate).

Effect of contact time

The time required for the solid–liquid system to achieve the equilibrium conditions was determined by placing 25 cm³ of 10 mg L⁻¹ aqueous solution of Cr (VI) with 0.05 g of the beads. At each time (range of 5–120 min) the supernatant was separated and the Cr (VI) ion concentration was determined as above.

Effect of ion concentration

To obtain the maximum adsorption capacity for Cr (VI), 25 cm³ of aqueous solutions at varying the initial concentrations from 10 to 1000 mg L⁻¹ were shaken (150 rpm) with 0.05 g of the beads for 1 h at 25°C. After filtration of the solution, the Cr (VI) ion concentration of the filtrates was determined as above.

Desorption of Cr (VI)

Desorption assay were carried out with the Cr (VI)-loaded beads at maximum capacity. The ion was eluted by shaking 0.05 g of the beads with 25 cm³ of 1M KCl, Na₂CO₃, NaOH, and KOH for 30 min. The beads were separated by filtration and the Cr (VI) ion was analyzed in the supernatants by the method mentioned above. The desorption percentage was calculated using the following equation:

$$\% \text{ Desorption} = \frac{\text{Amount of Cr(VI) (mg) desorbed}}{\text{Adsorbed amount of Cr(VI) (mg) by adsorbant}} \times 100 \quad (2)$$

Scanning electron microscopy

SEM studies of the whole image of the Cr (VI) adsorbed onto poly(4-VP) beads, coated with gold, were performed using a JEOL Model JSM 5600 microscope.

FTIR spectrum

Fourier transform infrared (FTIR) spectra of the Cr (VI) adsorbed onto poly(4-VP) beads at pH 3.5 was recorded using a Jasco FTIR-480 Plus model FTIR spectrophotometer with KBr discs.

RESULTS AND DISCUSSION

Effect of pH

The uptake of Cr (VI) ions as a function of pH was examined over a pH range of 3–5.5. It is evident from Figure 1 that the adsorption is higher at lower pH, it is maximum at pH 3.5, and beyond that point decreases sharply. A similar type of behavior is also reported for

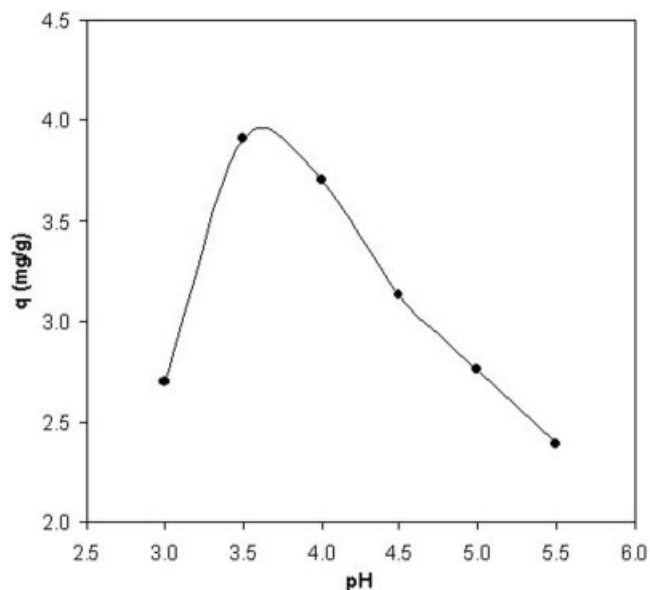


Figure 1 The pH-dependence of Cr(VI) ions adsorbed by poly(4-VP) beads. (Ion concentration = 10 ppm; temperature = 298 K; contact time = 60 min.).

the adsorption of hexavalent chromium by different adsorbents.^{18–20}

To explain the observed behavior of Cr (VI) adsorption with varying pH, it is necessary to examine various mechanisms such as electrostatic interaction and ion exchange, which are responsible for adsorption on sorbent surface. From the stability diagram,^{21,22} it is evident that the most prevalent forms of Cr(VI) in aqueous systems are acid chromates (HCrO_4^-), chromates (CrO_4^{2-}), dichromate ($\text{Cr}_2\text{O}_7^{2-}$), and other oxyanions. From the stability diagram for the Cr(VI)– H_2O system, it is evident that at low pH, acid chromates ions (HCrO_4^-) are the dominant species, while chromates (CrO_4^{2-}) became the main species in solution at pH 7.0 and above. For the adsorption of Cr(VI) species on the poly(4-VP) beads at pH 3.5, most of the amine groups surface of the sorbent were protonated and possessed positive electric charges. The protonated pyridine nitrogens can therefore attract the Cr (VI) species, which carried negative electric charges in the solution through the electrostatic interaction. On the other hand, at pH around 5.5, the protonation of the pyridine nitrogens on the poly (4-VP) beads were probably insignificant and the electrostatic interaction would not play an important role in the adsorption of Cr (VI) on the sorbent. The similar adsorption mechanisms of hexavalent chromium species on aminated polyacrylonitrile fibers was proposed by Deng and Bai.²⁰

Effect of contact time

The effect of contact time on the adsorption amount of Cr (VI) on poly(4-VP) beads were investigated at 25°C.

The results are shown in Figure 2. It is seen that the adsorption takes place rapidly at first, then slows down and levels off. The similar type of curve was observed in the previous work.^{3–5,23} The adsorption equilibrium was attained within 60 min of examination. The similar results were observed in the previous works.^{4,5} The relation between the nature of the polymer and sorption rate is generally complicated by many possible interactions on the surface. Commonly, the electrostatic interaction, surface complexation, and ion exchange mechanisms may be identified as the major adsorption mechanisms. In particular, the carboxyl and amino groups on the surface of an adsorbent have been reported to be effective in the adsorption of chromium ions.^{24,25} Thus those groups of poly(4-VP) beads are responsible for the interaction of chromium ions with the beads.

The kinetics of adsorption may be described^{5,26} by first-order rate expression and is shown in Figure 3. Adsorption rate constant (k) is calculated as $4.61 \times 10^{-4} \text{ s}^{-1}$ from Figure 3. Similar results were observed in the previous works.^{4,5,27,28}

Effect of ion concentration

The effect of initial Cr (VI) concentration on the adsorption efficiency by poly(4-VP) beads were systematically investigated by varying the initial concentration between 10 mg L^{-1} and 1000 mg L^{-1} . Figure 4 shows the adsorbed amount of Cr (VI) ions as a function of initial concentration at pH 3.5. The adsorption increased with increasing initial Cr (VI) concentration. The maximum adsorption performance was achieved at 86.7 mg g^{-1} using 500 mg L^{-1} Cr (VI) solution.

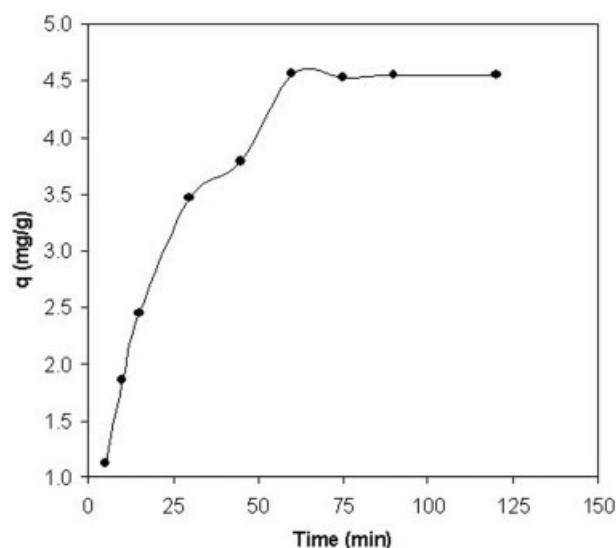


Figure 2 Relationship between adsorption time and adsorbed amount of Cr(VI) with poly(4-VP) beads. (Ion concentration = 10 ppm; pH = 3.5; temperature = 298 K).

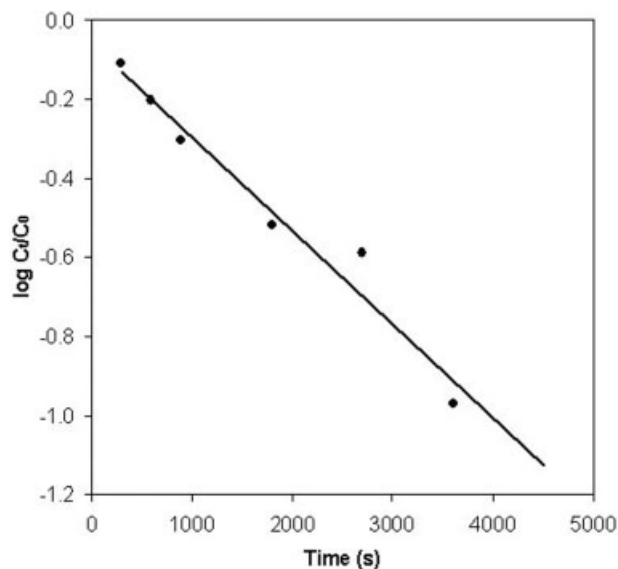


Figure 3 Plots of time versus $\log(C_t/C_o^{-1})$.

The values reported varied in the range of 1.4–91 mg g^{-1} for adsorption capacities of Cr(VI).^{13,20,21,29} It has been recognized that the adsorption capacity of poly(4-VP) beads is in that range. Thus, it would be an interesting alternative and an economical industrial adsorbent.

Adsorption isotherm

The simplest adsorption isotherm is based on the assumptions that every adsorption site is equivalent and

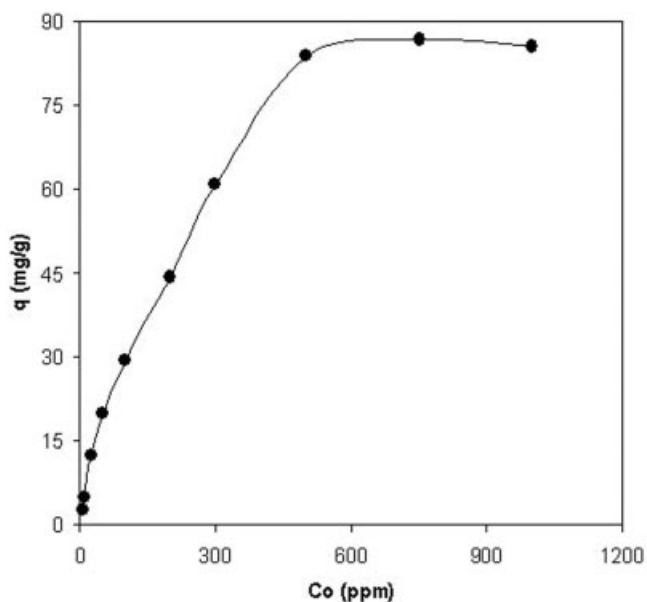


Figure 4 Effect of initial concentration of Cr(VI) on adsorption. (pH = 3.5; temperature = 298 K; contact time = 60 min).

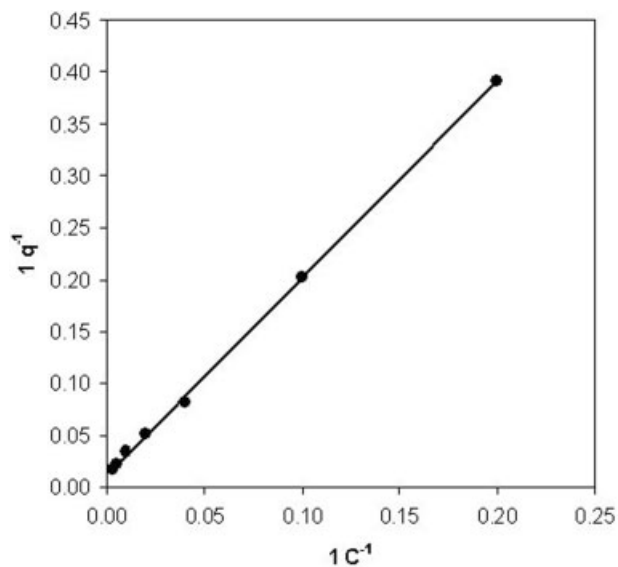


Figure 5 Langmuir plot of the removal of Cr(VI) ions on poly(4-VP) beads.

that the ability of a particle to bind there is independent of whether or not adjacent sites are occupied. The adsorption ability of an adsorbent can be described by two parameters. That is, saturation constant or monolayer capacity K_s (mg g^{-1}) and equilibrium binding constant K_b (L mg^{-1}).^{3–5} These constants can be calculated from the adsorption isotherm data according to Langmuir equation:

$$\frac{1}{q} = \frac{1}{CK_bK_s} + \frac{1}{K_s} \quad (3)$$

Where C and q are the quantities of ions remained in the solution and adsorbed on the beads at equilibrium, respectively. Thus a plot of q^{-1} versus C^{-1} should yield a straight line having a slope of $(K_bK_s)^{-1}$ and intercept of K_s^{-1} . Therefore, the relevant experimental data were treated and it was observed that the relationship between q^{-1} and C^{-1} is linear, indicating that the adsorption behavior follow the Langmuir adsorption isotherm (Fig. 5).

The K_b and K_s values are 0.06 L mg^{-1} and 86.21 mg g^{-1} respectively. The correlation coefficient was found to be 0.999.¹⁸

TABLE I
Effect of Solution Types on Desorption

Solution type	Concentration (mol L^{-1})	% Desorption
KCl	1	81
Na_2CO_3	1	47
NaOH	1	34
KOH	1	29

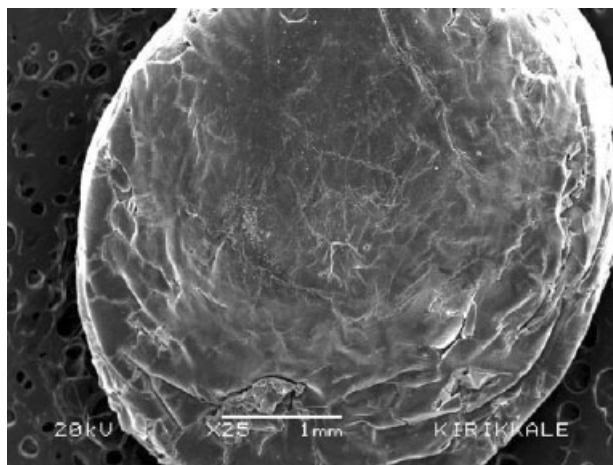


Figure 6 SEM micrographs of whole image (25 \times) the Cr (VI) adsorbed onto poly(4-VP) beads at pH 3.5.

Desorption studies

The study of desorption of Cr (VI) ions was carried out and the results are represented in Table I. The Cr (VI) ions adsorbed were easily desorbed by treating the adsorbent with the different solutions mentioned in Table I. It was observed that acidic solutions (pH until 2.0) are not relevant for desorption process of the beads that were used in acidic solutions. At room temperature ($T = 25^{\circ}\text{C}$), within 30 min, a desorption of 81% was obtained with 1M KCl. The reason why KCl is the best reagent to remove the absorbed ions may be explained with the hard and soft acids and bases

theory.³⁰ According to that borderline acids prefer to bind to borderline bases. $\text{C}_5\text{H}_5\text{NH}^+$ should be borderline acid and Cl^- is a lower hard base than CO_3^{2-} and OH^- . It should be a borderline base.

It has been recognized that poly(4-VP) beads should be effectively used for the removal of Cr (VI) ions from industrial effluents.

Microstructure of poly(4-VP) beads

The scanning electron micrographs of whole image of Cr (VI) adsorbed onto the poly(4-VP) beads at pH 3.5 are shown in Figure 6. It is clear from the SEM result that the prepared beads were approximately spherical and that the beads had a high surface area.

FTIR spectrum

The FTIR spectrum of Cr (VI) adsorbed onto poly(4-VP) beads at pH 3.5 is shown in Figure 7. The absorptions at 1599, 1556, and 3449 cm^{-1} are typical to those aromatic C=C, C=N, and N—H stretching. The peak at 934 cm^{-1} in the spectrum is due to the resonance peak of the Cr—O and Cr=O bonds from the Cr(VI) species, and suggests that Cr(VI) was adsorbed on the surface and the nitrogen atoms on the poly(4-VP) beads was involved in the adsorption.^{20,31}

CONCLUSIONS

The following conclusions are obtained:

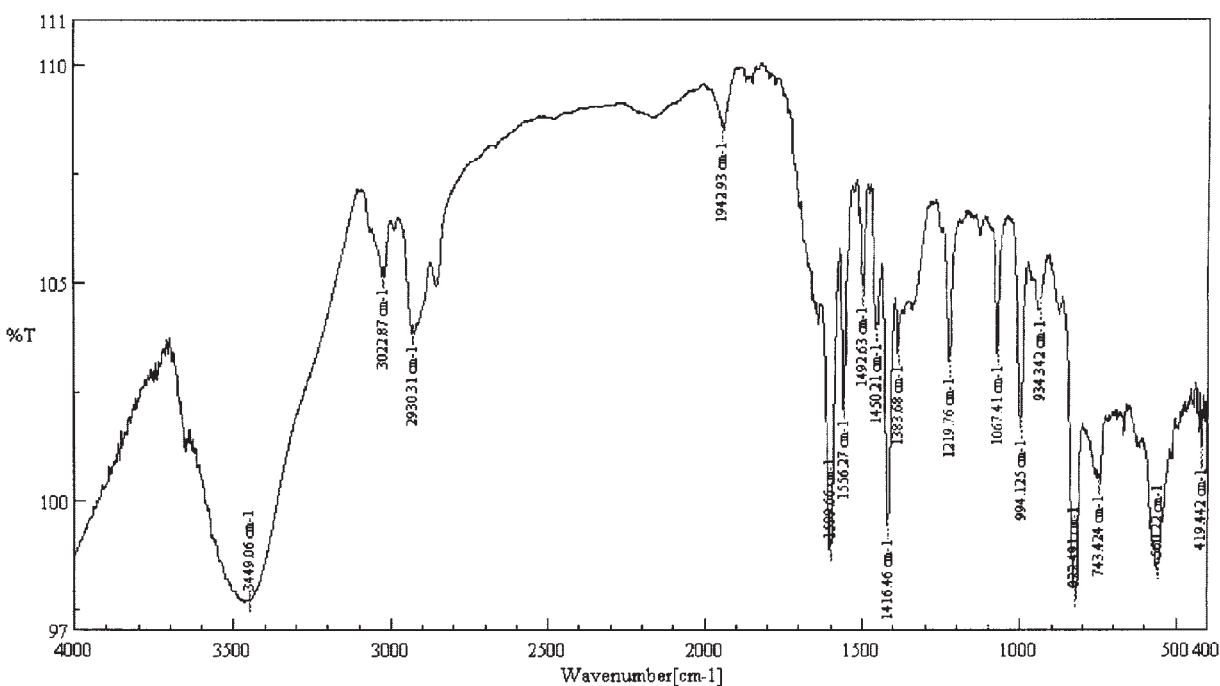


Figure 7 The FTIR spectrum of the Cr (VI) adsorbed onto poly(4-VP) beads at pH 3.5

1. It was observed that pH is the most important parameter and pH 3.5 was found as the optimum pH value in the process.
2. One hour of treatment time was found to be sufficient to reach the adsorption equilibrium value.
3. A Langmuir type of adsorption was observed.
4. It was recognized that poly(4-VP) beads should be used as an adsorbent for removal of hexavalent chromium from aqueous medium. Thus, the material should be addressed for other heavy metals.

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