Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.21575

95 (2017) 355–364
November

Studies on chitosan-based superhydrophilic adsorbent for phasing out Rhodamine 6G dye and Cd^{2+} ions from aqueous solutions

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Received 29 June 2017; Accepted 18 October 2017

ABSTRACT

Chemically modified chitosan-based superhydrophilic adsorbent (CSA) was prepared to prevent its dissolution in acidic medium. Microwave radiations induced free radical polymerization was employed successfully to synthesize CSA with high percentage grafting (2,086%). The process involves the in situ polymerization of biopolymer chitosan as backbone, with monomer acrylic acid in the presence of initiator ($K_2S_2O_8$). Analytical techniques such as Fourier transform infrared spectroscopy, X-ray diffraction, thermogravimetric analysis and scanning electron microscopy (SEM) were employed to characterize the synthesized adsorbent. Hydrophilic nature of CSA was reflected from high swelling capacity (1,224%). Batch experiments were performed for removal of organic (synthetic dye Rhodamine 6G [Rh6G]) and inorganic (cadmium [Cd^{2+}] ions). Adsorption parameters such as adsorbent dose, initial concentration of pollutants, contact time and pH of the solutions were optimized for removal of 10 mg/L of 50 mL of Rh6G and 25 mg/L of 50 mL of Cd^{2+} ions from aqueous solutions. The removal efficiency of CSA for Rh6G was found to be 80.34% at pH 10 and 92.04% for Cd^{2+} ions at pH 6 for constant CSA dose 1 g/L and the data were subjected to adsorption isotherm analysis.

Keywords: Chitosan; Adsorption; Cd^{2+} ions; Rhodamine 6G dye; Microwave radiations

1. Introduction

Stringent environment legislations and need for development of eco-friendly materials and methodologies for abatement of pollution have diverted the attention toward the development of biomaterial-based technologies to find the solution of environmental problems. Pollutants both of organic as well as inorganic nature are often released into the environment from different industries such as tanneries, electroplating, galvanizing, pigments and dyes, paper and pulp, metallurgical and other chemical industries [1]. The majorities of the toxic pollutants released in environment are persistent in nature and have bioaccumulation tendency. The different processes such as advanced oxidation process, chemical and electrochemical techniques, biological processes and adsorption technologies are widely used for the removal of organic and inorganic pollutants from aqueous environment [2–4]. However, these processes have their own limitations such as high cost; insufficient to meet stringent environmental regulations and their transformed or by-products formed are toxic in nature and cannot be treated easily [5–7]. Adsorption technology is one of the efficient and economic processes for the treatment of persistent organic and inorganic substances [8–10]. For the last three decades, the research is diverted toward the utilization of natural materials having high sorption potential for the removal of heavy metals and synthetic dyes. Eventually the focus was shifted toward the utilization of agricultural waste cellulosics as potential candidate for removal of pollutants [11,12].

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Heavy metals such as cadmium, chromium, arsenic, nickel and zinc are toxic even at very minute concentrations. Presence of toxic metal ions is of special concern, because of their potential to get accumulated in different components of the environment [13]. The presence of cadmium in environment is from electroplating industries, batteries, phosphate fertilizers, mining, pigments, stabilizers and alloys [14]. The permissible limit for cadmium in the wastewater discharge is 0.1 ppm in India. Cadmium interferes with the normal functions in human beings and some of its adverse effects are high blood pressure, damage of kidneys, destruction of testicular tissues and red blood cells [15]. The cationic dyes generated by textile, printing and dye industries are source of non-aesthetic pollution. The release of considerable amounts of colored water which is considered as hazardous and toxic because it generates by-products due to the chemical reactions taking place in wastewater phase [16]. Efficient and environment-friendly adsorbents are needed to reduce chemical load of wastewaters to acceptable level at affordable cost.

Polysaccharide biopolymers are employed as an adsorbent because of their diverse structure, chemical stability, high reactivity and selectivity due to the presence of various reactive functional moieties (hydroxyl, amine or acetamide) on the polymeric chains. Their abundance, renewable tendency, low cost and biodegradability are added advantages. Chitosan, a heteropolymer is obtained by partial alkaline deacetylation of chitin, a second most abundant biomaterial, found in the exoskeleton of crabs and others such as *arthropod* prawns, lobsters and shrimps. Chitosan is used as adsorbent because of its interesting chemical properties such as hydrophilicity, biodegradability, antibacterial activity and adsorption potential [17]. However, its low porosity, weak mechanical strength, less stability and crumbling tendency impairs its applications for wastewater treatment [18]. Chemical modification of chitosan helps to improve solubility characteristics and adsorption properties of chitosan. The various researchers attempted to improve the metal adsorption capacity through grafting technique [19–22]. Polymeric hydrogels are 3D networks of hydrophilic polymeric chains containing a large amount of water permeability to variety of molecules along with good biocompatibility and their ability as adsorbent was studied by different researchers [23–26].

The detailed literature study reflects that the different synthetic techniques resulted in variation in product yield and swelling behavior of polymeric gels. Further, no studies have been reported on microwave assisted synthesis of chitosan-based superadsorbent gel and its applications for removal of model pollutants selected for present investigations. The present work aims to prepare the polymeric hydrogel with high yield, improved swelling and adsorption characteristics. In continuation of our earlier work on sequestering of heavy metal ions using natural polymeric materials [27,28], the focus of the present work is to synthesize superadsorbent from vinyl monomer acrylic acid grafting to natural biopolymer chitosan backbone using the microwave radiations with improved percentage grafting. Synthesized adsorbent was characterized and its adsorption potential for facile removal of organic and inorganic pollutants namely synthetic dye, Rhodamine 6G (Rh6G) and heavy metal, Cd^{2+} as model compound was investigated.

2. Experimental

2.1. Materials

Analytical grade chitosan obtained from Hi-Media (Mumbai, India), acetic acid and acrylic acid from SD Fine Chemicals (Mumbai, India) were used without further purification. Rh6G and cadmium stock solutions were prepared by dissolving synthetic Rh6G dye (Merck, Germany) and cadmium nitrate (Merck, Germany) in millipore water. pH of the solution was adjusted by adding 0.1 M NaOH and 0.1 M HCl (Fluka, USA) solutions. Millipore water was used for the preparation of solutions, buffers and during polymerization process.

2.2. Synthesis and characterization of synthesized CSA

The aqueous solution of chitosan was prepared by dissolving 0.5 g chitosan flakes in 10 mL of 3% acetic acid solution and kept overnight at room temperature under continuous stirring. The requisite amount of acrylic acid of 5 mol/L concentration was added dropwise in homogenized viscous chitosan solution under continuous stirring. The mixture was further stirred for 10–20 min for proper distribution of monomer, followed by the addition of requisite amount of potassium per sulfate (KPS) initiator. The mixture was poured into the reaction flask which was immersed in water bowl to ensure the uniform distribution of microwave radiations operating at 100 W for 45 min. The synthesized gel obtained was washed properly with warm millipore water to remove the unreacted monomer and dried in the oven at 60°C till a constant weight was obtained. Product yield and water uptake capacity were recorded in terms of the percentage grafting (P_g) and percentage swelling (P_s) in aqueous medium.

The percentage grafting (P_g) and percentage swelling (P_s) of synthesized chitosan-based superhydrophilic adsorbent (CSA) were obtained by using following equations [29,30]:

$$P_g = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

where W_1 and W_2 are the weight of pure chitosan and chitosan-based adsorbent (CSA), respectively.

$$P_s = \frac{W_s - W_d}{W_d} \times 100 \quad (2)$$

where W_s and W_d are the swelled weight and dry weight, respectively.

Fourier transform infrared spectroscopy (FTIR spectra) of synthesized CSA was recorded on FTIR Bruker tensor 27 running on Opus software. Thermogravimetric analysis (TGA), derivative thermogravimetric analysis (DTA) and differential thermal analysis (DTG) of the chitosan and CSA were carried out using TG/DTA 6300, SII EXSTAR 6000 under 50°C–700°C range with heating rate of 10°C/min^{-1}. X-ray diffraction (XRD) was recorded using Philips Xpert diffractometer (Almelo, Netherlands) with monochromatic Cu K_α radiation operating at 40 kV and 20 mA. Scanning electron microscopy (SEM) images were obtained with Model JSM6100 (Jeol, UK).

2.3. Batch adsorption experiments for removal of organic and inorganic pollutants

Batch experiments were carried out for investigating the adsorption potential of chitosan-based hydrogel for removal of pollutants from aqueous solution. All experiments were carried out in 150 mL conical flask with 50 mL of aqueous solution containing Rh6G or cadmium nitrate and equilibrated at 100 rpm at temperature of 25°C. Solution pH was adjusted using 0.1 M of HCl and NaOH solutions. Variations in concentration of adsorbate solution, contact time, pH of solution and adsorbent dose have been investigated to get optimized parameters for maximum pollutant removal. For Cd^{2+} ions, removal efficiency (%*R*), was recorded for studies carried out by varying pH (2–7 pH), adsorbent dose (25–500 mg) keeping Cd^{2+} ions concentration 25 mg/L, stirring speed 100 rpm and contact time 120 min. The Cd^{2+} solution was agitated on mechanical shaker for 120 min followed by separation of adsorbent and the residual concentration of cadmium was determined potentiometrically using Thermo Orion 920A ion selective meter.

For Rh6G, adsorption efficiency was studied by varying pH from 2 to 10, adsorbent dose 25–100 mg keeping Rh6G concentration 10 mg/L, stirring speed 100 rpm and contact time 240 min. The UV–Vis spectra of Rh6G showed the presence of absorbance peaks at 246 and 525 nm. The removal percentage (%*R*) of Rh6G was measured by monitoring the change in absorbance at 525 nm using UV–Vis Spectrophotometer. All the experiments were replicated three times and results were averaged. The removal percentage of pollutants (%*R*) was calculated for each run using the following equation:

$$\%R = \frac{(C_i - C_e)}{C_i} \times 100 \tag{3}$$

where C_i and C_e are the initial and final concentration in mg/L of Rh6G or cadmium ions (Cd^{2+}).

The adsorption capacity of synthesized chitosan-based gel was obtained from the mass balance on the sorbate in the system with solution volume *V*, which is often used to acquire the experimental adsorption isotherms. The adsorption capacities of grafted biopolymer for each concentration of Cd^{2+} ions at equilibrium were calculated as follows:

$$q_e\,(\text{mg/g}) = \frac{(C_i - C_e)V}{M} \tag{4}$$

where C_i and C_e are initial and final concentrations of Cd^{2+}/Rh6G in mg/L in the solution, respectively, *V* and *M* are volume (L) and mass of adsorbent (g), respectively.

3. Results and discussion

Chitosan-based superadsorbent gel was synthesized by in situ polymerization of chitosan and acrylic acid using $K_2S_2O_8$ as free radical initiator system under the influence of microwave radiations as shown in Fig. 1. Persulfate molecules on irradiation with microwave radiation generates the free radicals ($SO_4^{2-\bullet}$ and $OH^\bullet$) species and their interaction with chitosan backbone and acrylic acid moieties, led to generation of more and more active sites on vinyl monomer molecule and chitosan. Active sites of the chitosan (–OH and –NH_2 functional groups) play an important role in the grafting of poly(acrylic acid) chains to form CSA. The percentage grafting (P_g) and percentage swelling (P_s) of synthesized CSA were found to be 2,086% and 1,224%, respectively. High water holding capacity of synthesized CSA reflecting, its superhydrophilic nature as compared with the earlier results [31].

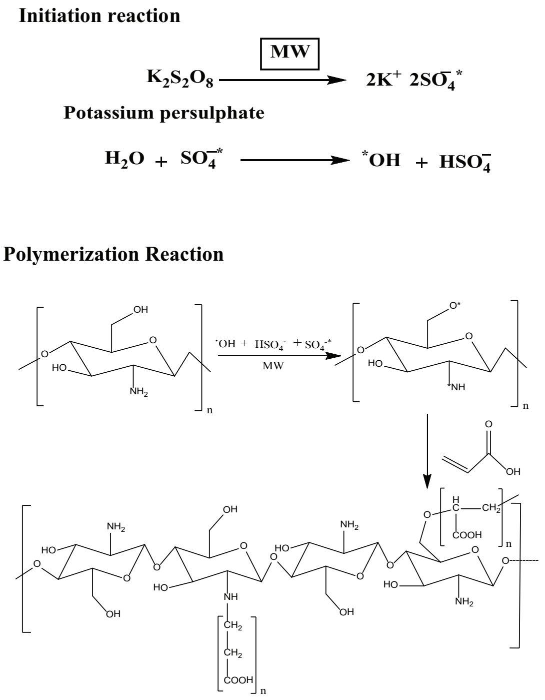

Fig. 1. Acrylic acid grafted chitosan (CSA).

3.1. Characterization of chitosan-based superadsorbent

3.1.1. Spectroscopic investigations (FTIR)

The IR spectra of chitosan showed a strong adsorption band at 3,365 cm^{-1} due to –OH and amine N–H symmetrical stretching vibrations. A peak at 2,883 and 1,153 cm^{-1} was due to symmetric –CH_2 stretching vibration attributed to pyranose ring and the structure of saccharide [32]. The characteristic absorption peaks of the chitosan were observed at 1,662 and 1,598 cm^{-1} due to the stretching vibration of amino group. Peaks at 1,081 and 1,030 cm^{-1} were assigned to the skeletal vibrations involving the C–O and O–H stretching vibrations and was in configuration with the earlier studies [33]. The small peak at ~890 cm^{-1} corresponded to wagging of the saccharide structure of chitosan. In the FTIR spectra of synthesized CSA, a broad peak above 3,000 cm^{-1} corresponded to hydrogen bonded COOH groups of acrylic acid polymer. The grafting of acrylic acid on to the chitosan backbone was confirmed from the sharp peak corresponding to C=O at 1,706.14 and O–H peak at 1,163 cm^{-1} in CSA (Fig. 2).

3.1.2. Thermal analysis

Thermal analysis curves depicting TGA, DTG and DTA data for chitosan and grafted hydrogel are shown in Figs. 3(a) and (b). Chitosan showed initial decomposition temperature (IDT) at 225.3°C and final decomposition temperature (FDT) at 631.6°C. The first stage decomposition showed 6.7% weight loss of chitosan, corresponding to evaporation of free and bound water molecules along with other volatile compounds. The second stage lies within the range of 225°C to 325.5°C and showed 38% weight loss probably due to breakage of linkages present in chitosan. The final decomposition stage demonstrated gradual loss of weight till 631.6°C due to thermal decomposition of polysaccharide structure. DTG graph of chitosan showed 1.651 and 0.367 mg/min rate of weight loss at 295°C and 604°C, respectively. TGA and DTG curves of CSA adsorbent exhibit well differentiated weight loss steps. The first step at 150.9°C corresponds to loss of water molecule (4.7%). The IDT of CSA adsorbent corresponds to 291.7°C with (41.2%) weight loss and FDT at 580.7°C with 4.8% polymeric mass were observed. Decomposition at higher temperature corresponds to breakdown of grafted chains and backbone along with other side chains. DTA analysis curve showed peaks for exothermic reactions which took place during thermal degradation at 300.5°C and 603.4°C with release of 113.6 and 82.5 μV energy, respectively. CSA DTA graphs showed prominent exothermic reaction peak at 533.6°C corresponding to release of 147.5 μV energy.

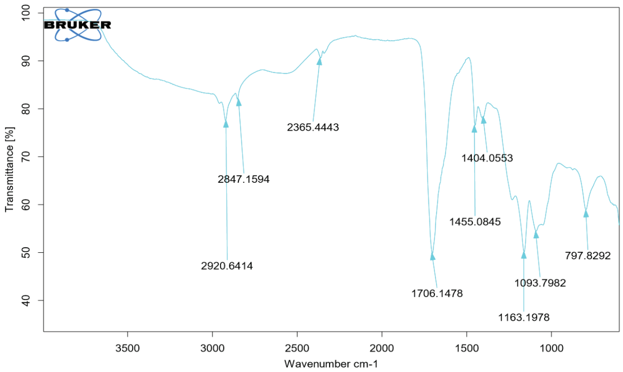

Fig. 2. FTIR spectra of synthesized CSA.

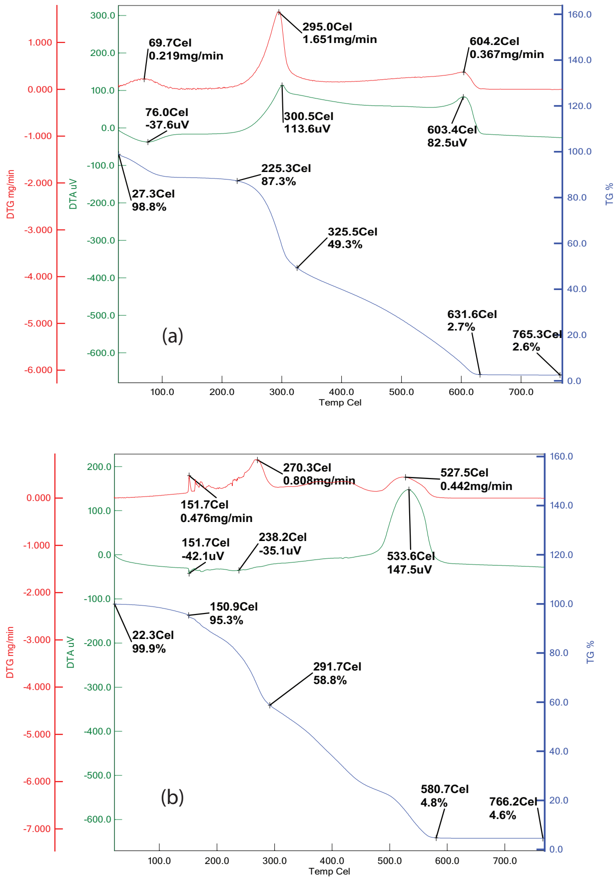

Fig. 3. DTG/DTA/TG of (a) chitosan and (b) synthesized CSA.

3.1.3. X-ray diffraction studies

Figs. 4(a) and (b) show the XRD pattern for pure chitosan and chitosan-based grafted hydrogel, respectively. In chitosan X-ray diffractogram, a strong peak was found at 21.9° (2θ) which reflected the high crystallinity of the chitosan while the amorphous nature for superhydrophilic adsorbent was observed. This confirmed the grafting of poly(acrylic acid) chains onto backbone.

3.1.4. Scanning electron microscopy

SEM images for chitosan and CSA were recorded and are shown in Figs. 5(a) and (b), respectively. A clear demarcation in surface morphology of chitosan was observed and layered highlands appeared on the surface of CSA indicating the polymerization has been occurred.

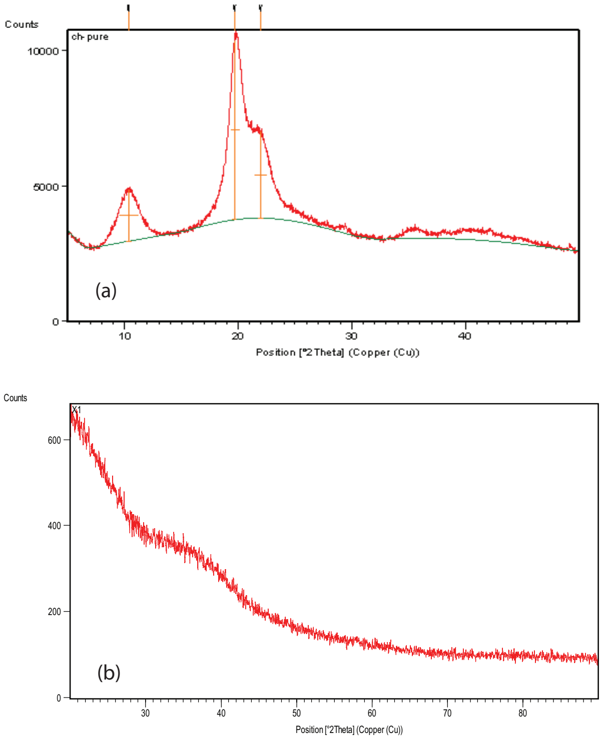

Fig. 4. XRD of (a) chitosan and (b) synthesized CSA.

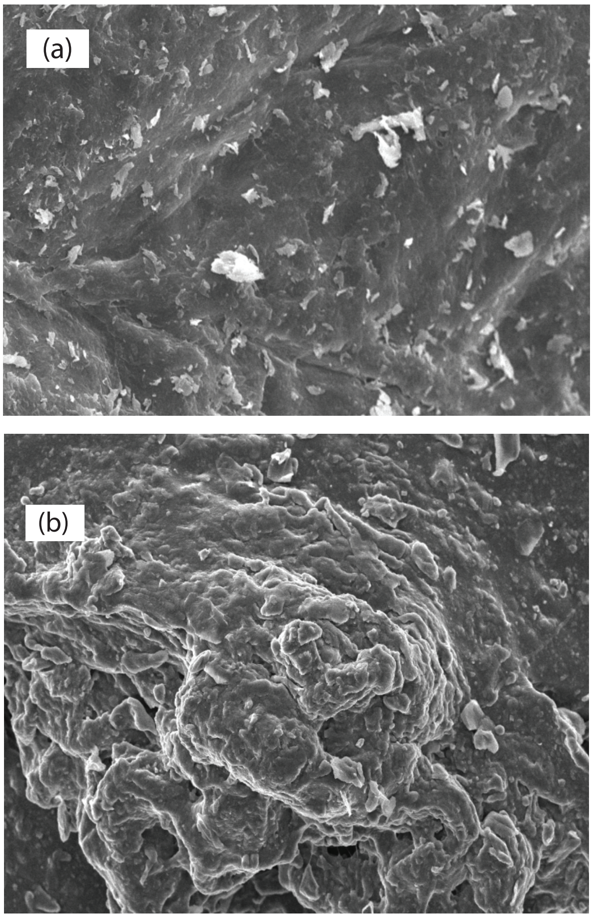

Fig. 5. SEM of (a) chitosan and (b) synthesized CSA.

3.2. Removal of Cd^{2+} and Rh6G with superadsorbent (CSA) hydrogel

Synthesized superhydrophilic adsorbent hydrogel ability to remove pollutants from aqueous solutions was assessed by taking Cd^{2+} and Rh6G as model compounds.

3.2.1. Parameters affecting the removal of Cd^{2+} ions

Batch experiments were performed for removal of cadmium ions from the aqueous solution. The effect of pH of solution, adsorbent dose, concentration of Cd^{2+} ions and contact time were investigated in relation to removal potential of CSA.

3.2.2. Effect of pH

Fig. 6(a) shows the effect of pH on percentage removal of cadmium ion (Cd^{2+}). Experiments were carried out at pH ranging from 2 to 7 for constant cadmium ion solution (25 mg/L) and adsorbent dose (1 g/L) with constant stirring at 100 rpm and 120 min contact time. Beyond pH 7, hydrolysis of cadmium ions occurs. It can be noted from the figure that the percentage removal of metal ions increased with the increase in pH of the Cd^{2+} solution and maximum 92.04% occurred at pH 6. The pH of the medium has a significant effect on the sorption of adsorbate on different adsorbents. The less adsorption at low pH may be explained on the basis of competitions of H^+ with Cd^{2+} for adsorption sites of the adsorbent. At higher pH, the dissociation of COOH groups into COO^- ion increases and led to chelation of Cd^{2+} with CSA as shown in Fig. 6(b). pH also influences the chemical speciation of the metal ions and nature of the adsorbent surface.

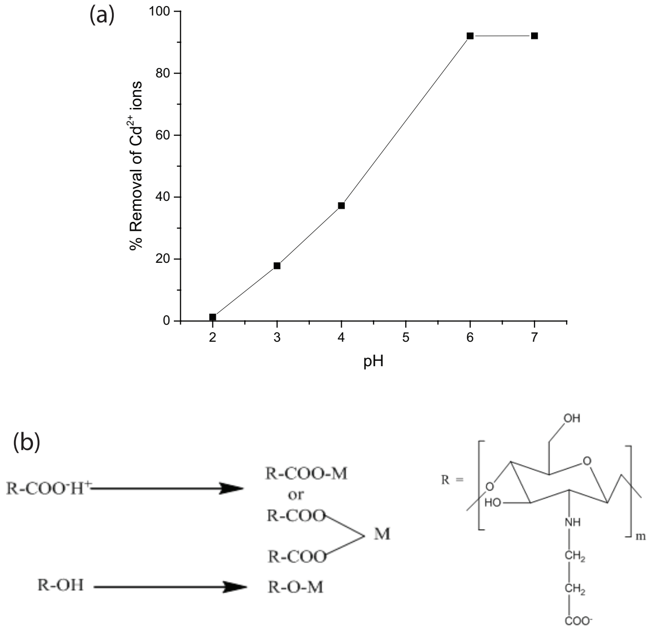

Fig. 6. (a) Effect of initial pH on percentage removal of Cd^{2+} ions onto CSA (concentration = 25 mg/L, stirring speed = 100 rpm, contact time = 180 min and adsorbent dose = 1 g/L). (b) Effect of adsorption time.

3.2.3. Effect of adsorption time

The effect of agitation time is inevitable in the adsorption study because it ascribes the time required before the adsorption process becomes constant and equilibrium is reached. Fig. 7 shows the enhancement in percentage removal of Cd^{2+} ions by increasing the adsorption time during the Cd^{2+} ion adsorption by CSA. The adsorption experiment was carried out using 25 mg/L metal ion concentrations with 1 g/L of CSA amount and pH 6. The percentage removal was fast till 180 min of adsorption duration and then gets slowed down and the adsorption equilibrium state was achieved in 240 min. The slow metal removal during the last stage of adsorption may be due to the formation of aggregates around the active sites of the adsorbent.

3.2.4. Effect of adsorbent dose

Fig. 8 shows the effect of adsorbent amount on the adsorption capacity and removal efficiency of Cd^{2+} ions. The removal of Cd^{2+} ion at different dosages (25–500 mg of CAS for 25 mL of Cd^{2+} solution) was studied by keeping stirring speed 100 rpm, pH 6 and contact time 180 min. The result indicates that increase in adsorbent dose resulted in higher removal of metal ion, which may be due to the increase in

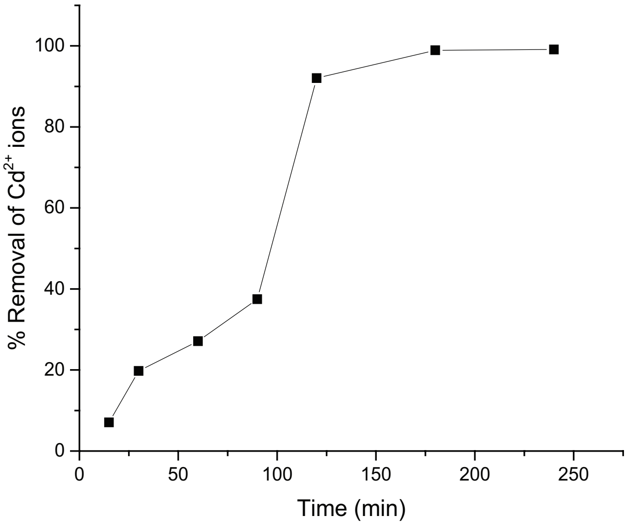

Fig. 7. Effect of contact time on percentage removal of Cd^{2+} onto CSA (solution concentration = 25 mg/L, stirring speed = 100 rpm, pH = 6, adsorbent dose = 1 g/L and temperature = 25°C).

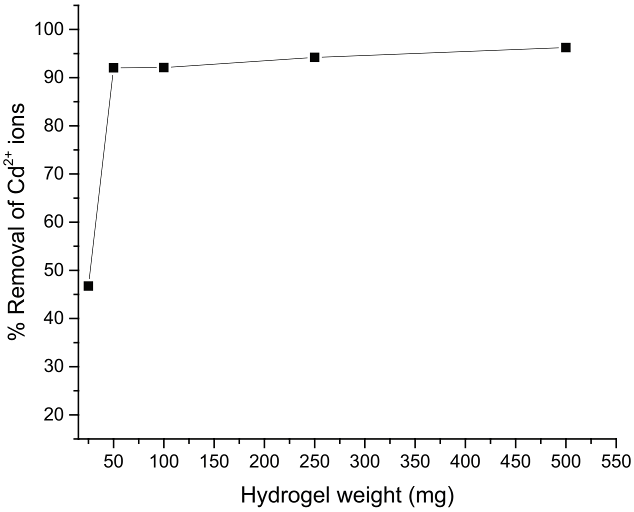

Fig. 8. Effect of CSA dose on percentage removal of Cd^{2+} ion onto CSA hydrogel (concentration = 25 mg/L, stirring speed = 100 rpm, pH = 6, temperature = 25°C and contact time = 180 min).

the number of adsorbent sites [34]. On the other hand, the adsorption capacity decreases with increase in adsorbent dose due to unsaturation of adsorption sites during adsorption process.

3.2.5. Effect of metal ion concentration

To study the percentage removal of Cd^{2+} ions from original concentration ranging from 10 to 100 mg/L of Cd^{2+} solution, experiments were conducted keeping adsorbent dose 1.0 g/L, stirring speed 100 rpm, pH 6, temperature 25°C and contact time 180 min. Fig. 9 shows the percentage cadmium removal decreased with increase in the initial concentration, as the Cd^{2+} ions concentration in experiment solution was increased from 10 to 100 mg/L, the adsorption capacity of CSA found to be 89.92 mg/g for 100 mg/L of Cd^{2+} solution.

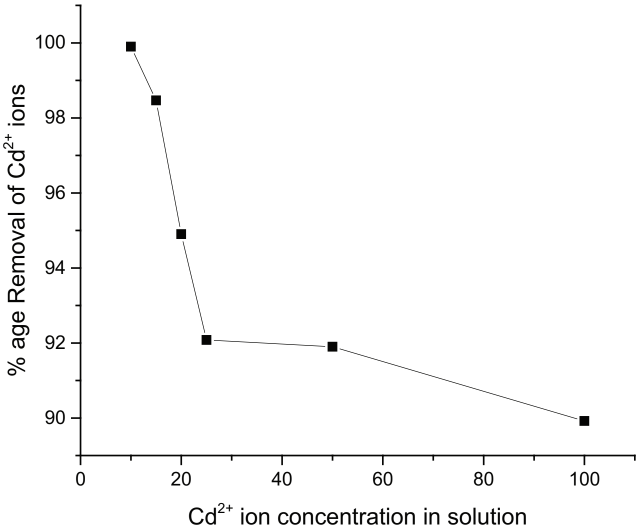

Fig. 9. Effect of initial concentration of Cd^{2+} on percentage removal under optimized conditions (adsorbent dose 1 g/L, pH 6 and time = 180 min).

3.3. Parameters affecting the removal of Rhodamine 6G

To investigate the color removal potential of CSA for synthetic dye Rh6G, batch experiments were performed and the effect of operational parameters such as pH of solution, adsorbent dose, concentration of Rh6G dye and contact time were investigated. The removal efficiency was recorded in terms of change in intensity of characteristic peak observed in visible region at 525 nm.

3.3.1. Effect of pH

The influence of pH on adsorption of Rh6G onto the CSA at different pH values are illustrated in Fig. 10(a). The result showed that the decolorization efficiency increased with increase in pH and maximum efficiency of 80.34% was observed at pH 10. pH of the medium influences the dye adsorption either due to (i) surface charge of CSA, (ii) ionization of Rh6G or CSA. At the lower pH values (2–4) the CSA exists in protonated from (COOH) and at higher pH, increase in OH^- concentration lead to the more ionization of COOH groups to COO^- ion. Rh6G, being cationic dye gets adsorbed on to the surface and the interaction of Rh6G with COO^- groups of CSA is shown in Fig. 10(b).

3.3.2. Effect of adsorption time and adsorption dose

The percentage color removal of Rh6G dye on CSA was followed as a function of time. Fig. 11 shows percentage removal of Rh6G increased rapidly within 240 min, afterward much change is observed till 500 min.

In order to optimize the adsorbent dose, the experiments were performed by varying CSA feed dose from 0.25 to 1 g/L keeping other conditions constant (pH 7.5 at temperature 25°C, contact time 240 min). Fig. 12 reveals the percentage removal increase was observed with increased adsorbent dose. The higher dye removal (74.95%) was obtained for 100 mg CSA dose at stirring speed 100 rpm.

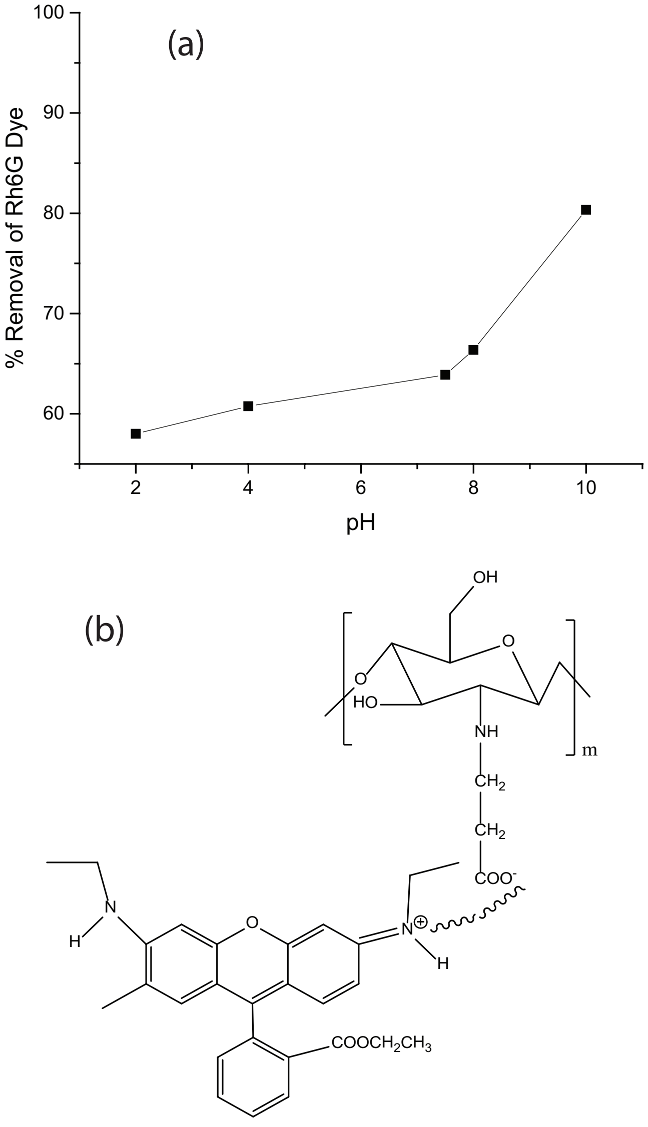

Fig. 10. (a) Effect of pH on percentage removal rate of Rh6G dye (initial concentration 10 mg/L and adsorbent dose 1 g/L). (b) Effect of adsorption time and adsorption dose.

3.3.3. *Effect of initial concentration*

The impact of the variation in the initial concentration of synthetic Rh6G dye was studied by performing experiments in concentration range of 5–20 mg/L. As the concentration of the dye increased, the percentage decolorization decreases indicating either to increase the adsorbent dose or more time span is required for the complete removal. Fig. 13 shows dye concentration of 5 mg/L removed almost 100% within 120 min and solutions of 10 and 20 mg/L removed up to 62.25% and 28.27%, respectively, within 240 min at 7.5 pH, 1 g/L of CSA dose, temperature 25°C and 100 rpm stirring speed.

4. Adsorption equilibrium isotherm

The adsorption isotherm study was performed to relate the adsorbate concentration in the bulk and the adsorbed amount at the interface [35]. The basic assumption of adsorption isotherm is that every adsorption site is equivalent and the ability of a particle to bind is not dependent on the occupancy of adjacent sites [36]. Langmuir and Freundlich isotherm are commonly used in batch adsorption studies. The Langmuir adsorption isotherm describes quantitatively the formation of a layer of molecules on an adsorbent surface as a function of the concentration of the adsorbed material in the liquid in which it is in contact. The shape of the isotherm is a gradual positive curve that flattens to a constant value. The assumptions for Langmuir isotherms are the formation of a monolayer of adsorption and no interaction between molecules adsorbed on adjacent binding sites [37].

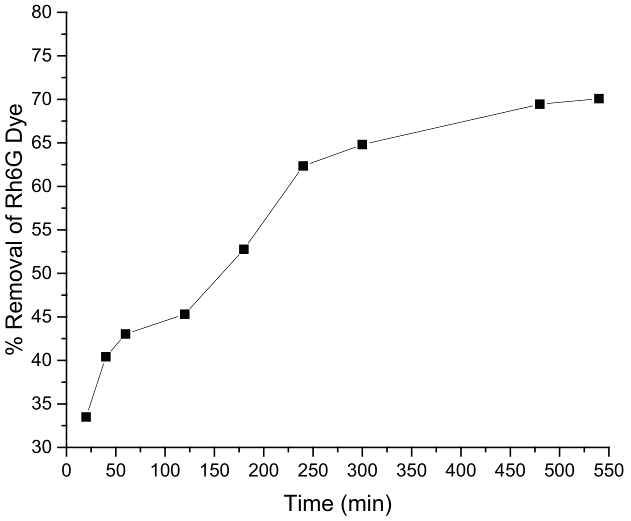

Fig. 11. Removal of Rh6G dye (pH 7.5, dye initial concentration 10 mg/L and adsorbent dose 1 g/L).

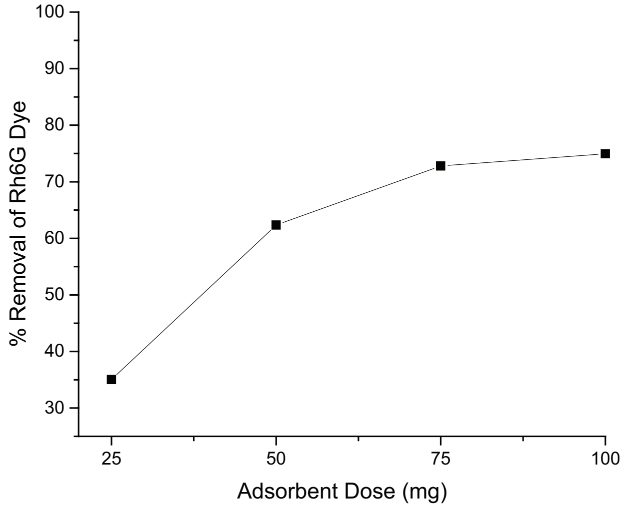

Fig. 12. Effect of adsorbent dose on percentage removal of Rh6G dye (initial concentration 10 mg/L and pH 7.5).

Langmuir isotherm equation is as follows:

$$\frac{C_e}{Q_e} = \left(\frac{1}{Q_o b}\right) + \left(\frac{C_e}{Q_o}\right) \tag{5}$$

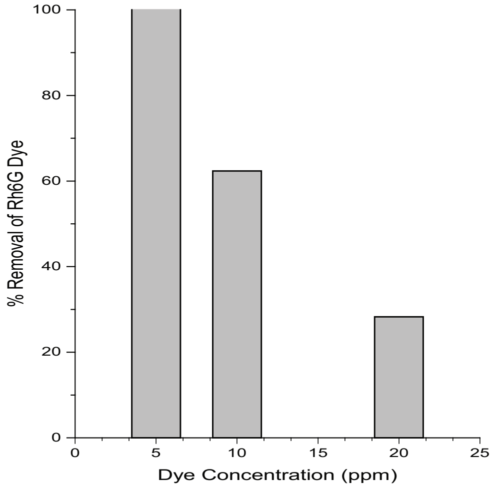

Fig. 13. Effect of initial concentration of Rh6G dye on percentage removal under optimized conditions (adsorbent dose 1 g/L and pH 7.5).

where Q_o and b are the Langmuir constants related to adsorption capacity and energy of adsorption.

The Freundlich expression is an empirical equation based on sorption on a heterogeneous surface and is represented as:

$$\ln q_e = \{\ln K_F\} + \left\{\frac{1}{n}(\ln C_e)\right\} \quad (6)$$

where q_e is the amount of metal ion sorbed at equilibrium per gram of adsorbent (mg/g), C_e is the equilibrium concentration of metal ion in the solution (mg/L), K_F and n are the Freundlich model constants. The Langmuir isotherm (Fig. 14(a)) shows best fit and results obtained for removal of Rh6G are Q_o (mg/g) 7.692; b (L/mg) 0.592; R^2 0.996 and K_F (L/g) 5.093; n 11.494; R^2 0.709, respectively. Adsorption isotherm studies for adsorption of Cd^{2+} reveal that the Freundlich isotherm (Fig. 15(b)) fits well for Cd^{2+} and values are K_F (L/g) 15.958; n 2.24 and R^2 0.956 and Langmuir values are Q_o (mg/g) 83.33; b (L/mg) 0.214; R^2 0.853, which indicate the heterogeneous nature and the involvement of diverse groups for removal of cadmium.

4.1. Adsorption kinetics

The kinetics of adsorption study was done by applying pseudo-first-order and pseudo-second-order kinetic models to the experimental data. The first-order rate expression of Lagergren based on solid capacity is generally expressed as follows [38]:

$$\log(q_e - q_t) = \log(q_e) - \left(\frac{k_1}{2.303}\right)t \quad (7)$$

where q_e and q_t are the amount of dye adsorbed (mg/g) at equilibrium and at time t (min), respectively, and k_1 is the adsorption rate constant of pseudo-first-order sorption (min^{-1}). The plotting of $\log(q_e - q_t)$ vs. time deviated considerably from the theoretical data after a short period. The pseudo-second-order equation is based on the sorption capacity of the solid phase and expressed as:

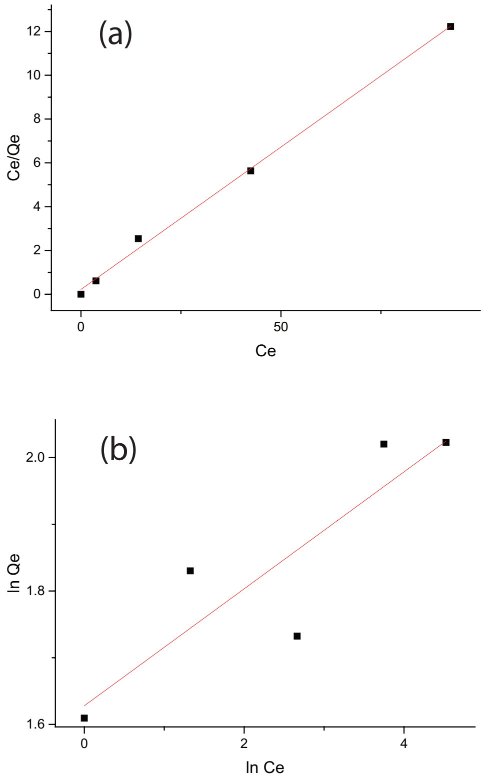

Fig. 14. (a) Langmuir isotherm for Rh6G dye. (b) Freundlich isotherm for Rh6G dye.

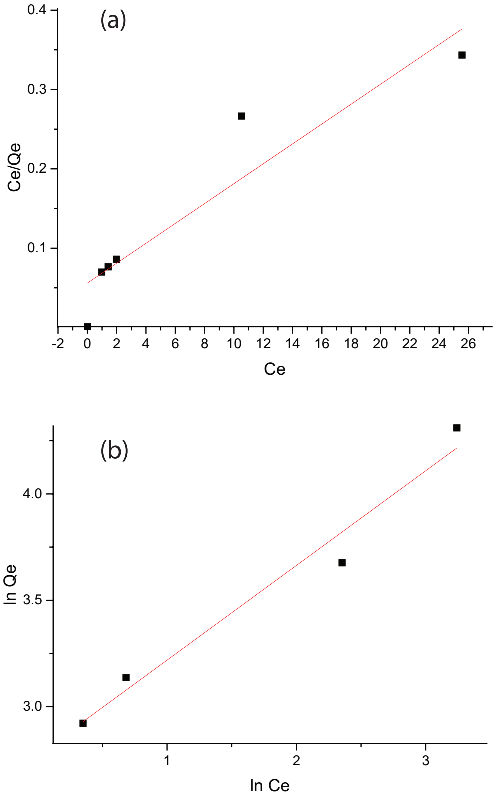

Fig. 15. (a) Langmuir isotherm for Cd^{2+} ions. (b) Freundlich isotherm for Cd^{2+} ions.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\ 2}} + \frac{t}{q_e} \tag{8}$$

where k_2 is the rate constant of second-order sorption (mg/g), q_e is the amount of dye ions adsorbed at equilibrium and q_t is the amount of solute sorbate on the surface of the sorbent at any time t (mg/g).

First-order and second-order kinetic models were applied and the perfect fit of experimental data of Rh6G removal was observed for pseudo-second-order equation (Fig. 16(b)). The correlation coefficient R^2 and rate constant k_2 were found to be 0.989 and 0.010, respectively. Similarly, Fig. 16(a) shows the best fit of experimental data of Cd^{2+} ions removal was obtained for pseudo-second-order equation with R^2 (0.957) and k_2 (0.00018).

4.2. Reusability of CSA

Reusability of gel is evaluated by its sorption performance in consecutive adsorption and desorption cycle. Two different approaches were employed to regenerate the adsorbent and the regeneration efficiency (%) was recorded. The first method involves the regeneration with 0.1 M HNO_3 and studies were carried up to 10 cycles. Regeneration efficiency decreases slowly up to six adsorption–desorption cycles, thereafter, it decreases significantly in the ninth and tenth cycle and 20% efficiency has been observed after tenth cycle. This may be due to repeated contact with desorption agent lead to loss of sorption performance. The second method involves the regeneration of CSA by exposure to UV radiations. The CSA adsorbent after adsorption cycle was cleaned and added to 50 mL of distilled water. The solution was placed under UV bulb of 30 W for 8 min. The complete regeneration of the CSA has been occurred, the procedure was repeated after every adsorption cycle till 10 cycles, regeneration efficiency was reported to be 60% after tenth cycle. It has been found that exposure to UV radiation offers better method of regeneration of adsorbent.

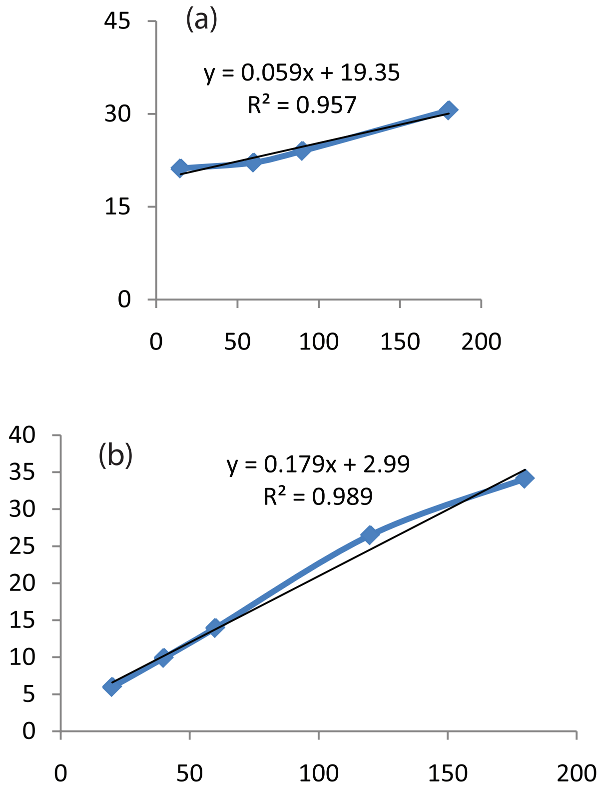

Fig. 16. (a) Second-order kinetic analysis of Cd^{2+} ion. (b) Second-order kinetic analysis of Rh6G dye.

5. Conclusions

- Superhydrophilic adsorbent (CSA) obtained by microwave assisted grafting of vinyl monomer acrylic acid on to chitosan was characterized by different physicochemical methods. FTIR analysis confirmed the successful grafting of polyacrylic acid on to chitosan backbone.
- High percentage grafting (P_g) and percentage swelling (P_s) of synthesized CSA reflect its chemical conversion and high water uptake potential as a hydrogel.
- CSA was found to be an excellent adsorbent for removal of organic and inorganic pollutants. Further investigations on the CSA for the removal of pollutants will provide an insight on the development of new adsorbent materials for wastewater treatment.
- The removal efficiency of CSA for Rh6G was found to be 80.34% at pH 10 and 92.04% for Cd^{2+} ions at pH 6 for constant CSA dose 1 g/L.
- Exposure to UV radiations for short duration led to the better regeneration of adsorbent as compared with chemical regeneration.

Acknowledgments

This research project could not have been accomplished without the support of Sant Longowal Institute of Engineering and Technology, Longowal. We are pleased to acknowledge the facilities provided by National Institute of Technology Jalandhar and Punjab University, Chandigarh. This project is not funded by any organization. The authors declare no conflict of interest.

References

[1] M.P. Waalkes, Cadmium carcinogenesis in review, J. Inorg. Biochem., 79 (2000) 241–244.
[2] T. Robinson, G. McMullan, R. Marchant, P. Nigam, Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative, Bioresour. Technol., 77 (2001) 247–255.
[3] G. Crini, Kinetic and equilibrium studies on the removal of cationic dyes from aqueous solution by adsorption onto a cyclodextrin polymer, Dyes Pigm., 77 (2008) 415–426.
[4] L. Yang, Y. Yang, Z. Chen, C. Guo, S. Li, Influence of super absorbent polymer on soil water retention, seed germination and plant survivals for rocky slopes, Ecol. Eng., 62 (2014) 27–32.
[5] Z. Reddad, C. Gerente, Y. Andres, P. Le Cloirec, Adsorption of several metal ions onto a low-cost biosorbent: kinetic and equilibrium studies, Environ. Sci. Technol., 36 (2002) 2067–2073.
[6] T.A. Kurniawan, G.Y.S. Chan, W.H. Lo, S. Babel, Physico-chemical treatment techniques for wastewater laden with heavy metals, Chem. Eng. J., 118 (2006) 83–98.
[7] E.R. Christensen, J. T. Delwiche, Removal of heavy metals from electroplating rinse waters by precipitation, flocculation and ultrafiltration, Water Res., 16 (1982) 729–737.

[8] C. Namasivayam, R. T. Yamuna, Removal of congo red from aqueous solutions by biogas waste slurry, J. Chem. Technol. Biotechnol., 53 (1992) 153–157.

[9] G. Crini, Non-conventional low-cost adsorbents for dye removal: a review, Bioresour. Technol., 97 (2006) 1061–1085.

[10] K.H. Chu, Removal of copper from aqueous solution by chitosan in prawn shell: adsorption equilibrium and kinetics, J. Hazard. Mater., 90 (2002) 77–95.

[11] E. Guibal, Interactions of metal ions with chitosan-based sorbents: a review, Sep. Purif. Technol., 38 (2004) 43–74.

[12] E.W. Wilde, J.R. Benemann, Bioremoval of heavy metals by the use of microalgae, Biotechnol. Adv., 11 (1993) 781–812.

[13] M. Gavrilescu, Removal of heavy metals from the environment by biosorption, Eng. Life Sci., 4 (2004) 219–232.

[14] K.A. Matis, A.I. Zouboulis, I.C. Hancock, Waste microbial biomass for cadmium ion removal: application of flotation for downstream separation, Bioresour. Technol., 49 (1994) 253–259.

[15] EPA (US Environmental Protection Agency) Office of solid Waste draft PBT Chemical List, EPA/530/D-98/001A, Office of Solid Waste and Emergency response, Technology Innovation Office, Washington, D.C., USA, 1998.

[16] S. Li, X. Liu, T. Zou, W. Xiao, Removal of cationic dye from aqueous solution by a macroporous hydrophobically modified poly(acrylic acid-acrylamide) hydrogel with enhanced swelling and adsorption properties, CLEAN–Soil Air Water, 38 (2010) 378–386.

[17] P. Shankar, T. Gomathi, K. Vijayalakshmi, P.N. Sudha, Comparative studies on the removal of heavy metals ions onto cross linked chitosan-*g*-acrylonitrile copolymer, Int. J. Biol. Macromol., 67 (2014) 180–188.

[18] R. Camarillo, J. Llanos, L. García-Fernández, Á. Pérez, P. Canizares, Treatment of copper (II)-loaded aqueous nitrate solutions by polymer enhanced ultrafiltration and electro deposition, Sep. Purif. Technol., 70 (2010) 320–328.

[19] G.A. Vikhoreva, E.A. Shablyukova, N.R. Kil'deeva, Modification of chitosan films with glutaraldehyde to regulate their solubility and swelling, Fibre Chem., 33 (2001) 206–210.

[20] J. Wu, M. Luan, J. Zhao, Trypsin immobilization by direct adsorption on metal ion chelated macroporous chitosan-silica gel beads, Int. J. Biol. Macromol., 39 (2006) 185–191.

[21] G.Z. Kyzas, P.I. Siafaka, D.A. Lambropoulou, N.K. Lazaridis, D.N. Bikiaris, Poly(itaconic acid)-grafted chitosan adsorbents with different cross-linking for Pb(II) and Cd(II) uptake, Langmuir, 30 (2014) 120–131.

[22] G.Z. Kyzas, D.N. Bikiaris, Recent modifications of chitosan for adsorption applications: a critical and systematic review, Mar. Drugs, 13 (2015) 312–337.

[23] A. Kishida, Y. Ikada, Hydrogels for Biomedical and Pharmaceutical Applications, Polymeric Biomaterials, 2001, pp. 133–145.

[24] J. Ostrowska-Czubenko, M. Pieróg, M. Gierszewska-Drużyńska, Equilibrium swelling behavior of crosslinked chitosan hydrogels, Pol. J. Appl. Chem., 55 (2011) 49–56.

[25] J. Maity, S.K. Ray, Enhanced adsorption of methyl violet and congo red by using semi and full IPN of polymethacrylic acid and chitosan, Carbohydr. Polym., 104 (2014) 8–16.

[26] H. Tang, H. Chen, B. Duan, A. Lu, L. Zhang, Swelling behaviors of superabsorbent chitin/carboxymethylcellulose hydrogels, J. Mater. Sci., 49 (2014) 2235–2242.

[27] G. Mahajan, U. Garg, D. Sud, V. Garg, Utilization properties of jatropha de-oiled cake for removal of nickel (II) from aqueous solutions, Bioresources, 8 (2013) 5596–5611.

[28] U.K. Garg, M.P. Kaur, V.K. Garg, D. Sud, Removal of nickel(II) from aqueous solution by adsorption on agricultural waste biomass using a response surface methodological approach, Bioresour. Technol., 99 (2008) 1325–1331.

[29] K. Kumar, B.S. Kaith, H. Mittal, A study on effect of different reaction conditions on grafting of psyllium and acrylic acid-based hydrogels, J. Appl. Polym. Sci., 123 (2012) 1874–1883.

[30] M. Maiti, R. Jindal, B.S. Kaith, A.K. Jana, Synthesis of graft copolymers of binary vinyl monomer mixtures onto acetylated *Saccharum spontaneum* L and characterization, J. Appl. Polym. Sci., 121 (2011) 2060–2071.

[31] M. Yazdani-Pedram, J. Retuert, R. Quijada, Hydrogels based on modified chitosan, 1. Synthesis and swelling behavior of poly(acrylic acid) grafted chitosan, Macromol. Chem. Phys., 201 (2000) 923–930.

[32] A. Pawlak, M. Mucha, Thermogravimetric and FTIR studies of chitosan blends, Thermochim. Acta, 396 (2003) 153–166.

[33] H. Kweon, I.C. Um, Y.H. Park, Structural and thermal characteristics of *Antheraea pernyi* silk fibroin/chitosan blend film, Polymer, 42 (2001) 6651–6656.

[34] U.K. Garg, M.P. Kaur, V.K. Garg, D. Sud, Removal of hexavalent chromium from aqueous solution by agricultural waste biomass, J. Hazard. Mater, 140 (2007) 60–68.

[35] O. Demirbaş, M. Alkan, M. Doğan, The removal of Victoria blue from aqueous solution by adsorption on a low-cost material, Adsorption, 8 (2002) 341–349.

[36] S.S. Shukla, L.J. Yu, K.L. Dorris, A. Shukla, Removal of nickel from aqueous solutions by sawdust, J. Hazard. Mater., 121 (2005) 243–246.

[37] H.L. Liu, B.Y. Chen, Y.W. Lan, Y.C. Cheng, Biosorption of Zn(II) and Cu(II) by the indigenous *Thiobacillus thiooxidans*, Chem. Eng. J., 97 (2004) 195–201.

[38] Y.S. Ho, G. McKay, Kinetic models for the sorption of dye from aqueous solution by wood, Process Saf. Environ. Prot., 76 (1998) 183–191.