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ORIGINAL ARTICLE

Utilization of chitosan-coated superparamagnetic iron oxide nanoparticles for chromium removal

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Abstract
Superparamagnetic iron oxide nanoparticles (SPIONs) have been widely used for their versatility, while it is coated with a biopolymer like chitosan that adds attraction and also increases its applications. In this study, SPION was synthesized by chemical co-precipitation method, characterized using various analytical techniques like UV–Vis, FTIR, SEM, EDX, TEM, AFM, XRD, zeta potential and Raman spectroscopy analysis. Chitosan was coated onto the SPIONs and used for water treatment to remove chromium (450 ppm concentration). Chitosan-coated SPIONs were found to remove about 80% of chromium. Freundlich model was found to be fitting better for the current study.

Keywords Chitosan · SPIONs · Metal removal · Characterization · Chromium

Introduction

In today's world, alarming water pollution has become a major threat to the environment and has led to the development of new technologies to minimize the potential contaminants from the water bodies. Effluents from the mining industries, power generating industries, electronic industries and tanneries contain large amounts of heavy metals that pose a great risk to the surviving population in and around the water bodies (Liu et al. 2012) and cause bioaccumulation in beings that ingest these waters directly or indirectly (Yousafzai et al. 2017). Heavy metals such as uranium, mercury, chromium, arsenic, lanthanum, lead, cadmium and zinc are few of the commonly found metals that contaminate the water bodies (Boddu et al. 2003; Tchounwou et al. 2012). Chromium (Cr, $Z=24$, $A=51.9961$ u ± 0.0006 u) is said to be relatively stable among the heavy metal ions of the periodic table and exists in several ionic forms. It is toxic and it is considered to be one of the major carcinogens as well as a mutagenic compound (Geng et al. 2009; Dayan and Paine 2001; Aitio et al. 1988). Thus, removal of this hazardous heavy metal has become a major goal and research interest among several researchers and led to the development of diverse methods. Although several methods have been devised, bio-sorption using bio-based particles/nanoparticles has been considered highly efficient (Lasheen et al. 2013; Sheet et al. 2014; Abdel-Raouf and Abdul-Raheim 2017; Mane et al. 2011; Ahluwalia and Goyal 2007) due to the large surface-to-volume ratio of nanoparticles compared to the bulk materials (Rajput et al. 2016). Using SPIONs is the better option, since superparamagnetic iron oxide nanoparticles (SPIONs) obey to external magnetic field; thus, it is easier to remove after the adsorption process (Gill et al. 2017) and also it is low toxic and non-reactive to human and majorly it has very strong adsorption capacity (Lasheen et al. 2013). Further, crystallinity, dispersion, size and shape also play an important role in the removal of heavy metals efficiently. One of the major challenges of aggregation faced by SPIONs can be overcome by surface modification or by following up certain parameters (coating a sorbent material) that result in the formation of monodispersed SPIONs (Justin et al. 2018; Mahmoudi et al. 2011).

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In order to increase the chemisorption efficiency of SPIONs, biopolymers such as chitosan can be used to coat the nanoparticles. Chitosan is an abundant biodegradable biopolymer available in the nature, which can be extracted from the exoskeletons of marine organisms such as crabs, lobsters, shrimps as well as fungi. Literature studies have suggested that chitosan is more efficient than its precursor chitin (Boddu et al. 2003). The free amine groups present on the surface of chitosan aid in the chemisorption of the metal ions and subsequently result in their removal from wastewater (Kaveeshwar et al. 2018). The coating of chitosan on SPIONs makes it less toxic to the environment resulting in an eco-friendly method of heavy metal removal. This use of nanoparticles in this method is highly cost-effective process (Gill et al. 2017) and hence can be executed in a large-scale clean-up processes. In this study, SPIONs were synthesized by chemical method, coated with chitosan and utilized for chromium removal from water.

Materials and methods

Materials

All chemicals used in this work were of analytical grade. Ferrous sulphate and ferric sulphate were procured from M/s Merck, India. Ammonia solution, tetramethyl ammonium hydroxide solution (TMAOH) and chitosan were obtained from SRL, India; acetic acid was purchased from Fisher Chemical, India. Potassium dichromate was obtained from Rankem, India.

Synthesis of superparamagnetic iron oxide nanoparticles (SPIONs)

SPIONs were synthesized by following chemical co-precipitation method. The synthesis procedure is as follows: 0.91 g ferrous sulphate ($FeSO_4$) and 3.2 g ferric sulphate ($Fe_2(SO_4)_3$) were taken in 8 ml and 2 ml nitrogenated Milli-Q water, respectively, and stirred well. The two solutions were mixed together while manually stirring it for 15 min. 15 ml of 25% ammonia solution was added dropwise to the precursor solution under constant vigorous stirring, and 15 ml of 25% TMAOH was also added dropwise to the solution. As soon as the colour of the solution turned black, the addition of ammonia and TMAOH was stopped. The nanoparticles were allowed to settle using a magnet, and excess reducing agent was pipetted out. Nanoparticles were washed several times with Milli-Q water until the pH dropped to neutral. Further, the nanoparticles were lyophilized in vacuum to obtain powder particles (Eom et al. 2010).

Preparation of chitosan-coated SPIONs

Chitosan-coated SPIONs were prepared according to the protocol followed by Sureshkumar et al. (2016) with some modifications. 100 mg of chitosan was added to 40% acetic acid and stirred for 24 h. Then, 100 mg of SPIONs was added and was sonicated for 30 min. The sample was then lyophilized in vacuum.

Characterization of SPIONs

The prepared SPIONs were characterized for further studies. Absorbance spectrum of SPIONs was recorded at UV–Vis spectrometer. Fourier transform infrared spectroscopy (FTIR) of prepared SPIONs was analysed using IR Affinity-1s, Shimadzu, Japan, for wave number range of 4000–400 cm^{-1}. Microscopic analysis was investigated using transmission electron microscope (TEM) (TEECNAI G2 Spirit Biotwin—120 kV) and atomic force microscopy (AFM) (Bruker, Germany). X-ray diffraction (XRD) patterns of the SPIONs were recorded by Smartlab X-ray diffractometer (Rigaku, Japan). The XRD patterns were taken in the 2θ range of 20°–80° in a fixed-time mode at room temperature. To determine the stability of the SPIONs, zeta potential value was recorded (Brookhaven Zeta-PALS). Raman spectroscopy was also performed using LabRam HR 800 model of Horiba Jobinyvon.

Chromium metal removal

Adsorption studies were carried out according to the procedure quoted by Sureshkumar et al. (2016) with some modifications. 5 mM potassium dichromate was dissolved in 90 ml of distilled water which contains 450 ppm of chromium metal Cr(VI) and was divided into three portions in which 10 mg/10 ml, 20 mg/10 ml and 30 mg/10 ml of chitosan-coated SPIONs in distilled water were added in each portion of solution separately. It was stirred continuously at 400 rpm at 22 °C for 3 h, and the pH was maintained acidic at 5.7 (Anah and Astrini 2017; Namasivayam and Ranganathan 1993). 1 ml of sample was withdrawn from each solution every 15 min for about 3 h. Chitosan-coated SPIONs were made to settle under the magnetic field, and the solution above the settled residue was then analysed for absorbance at 350 nm (Shimadzu, Japan). The concentration of the chromium was determined against the standard graph and % removal was determined by the following formula:

$$\%\ \text{removal} = \frac{C_0 - C_t}{C_0} \times 100$$

To determine the adsorbent's ability and other constants, Langmuir isotherm (Kumar and Sivanesan 2006), Freundlich isotherm (Dada et al. 2012) and Temkin isotherm (Piccin et al. 2011) were carried.

Results and discussion

Characterization of SPIONs and chitosan-coated SPIONs

UV–Vis analysis was performed and their respective peaks near 225 nm and 360 nm indicated the synthesis of SPIONs and chitosan-coated SPIONs (Fig. 1a, b), where

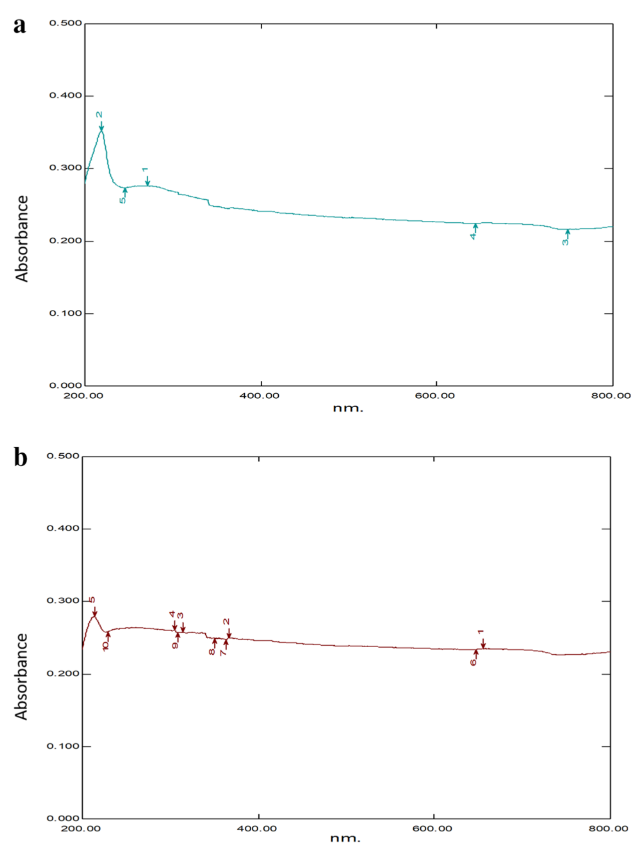


Fig. 1 UV–Vis analysis of **a** SPIONs, **b** chitosan-coated SPIONs

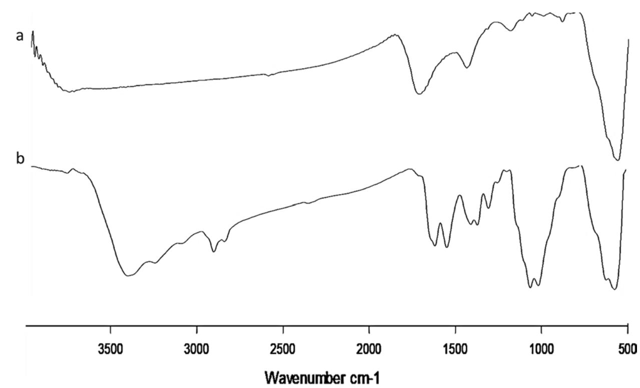


Fig. 2 FTIR analysis of **a** SPIONs, **b** chitosan-coated SPIONs

Samrot et al. (2017) also found magnetite nanoparticles to have absorbance maximum around 230–250 nm. In FTIR, the presence of strong absorption bands at around 569 and 575 cm^{-1} showed the formation of magnetic nanoparticles (Fe–O stretching vibration of tetrahedral sites of spinel structure) (Fig. 2a, b) (Inbaraj and Chen 2012). The peak at 2920 cm^{-1}, 1627 cm^{-1}, 1416 cm^{-1} and 1069 cm^{-1} was the stretching vibrations of –CH, N–H, C–N vibration of amino group and C–O in the ether group of chitosan, respectively (Fig. 2b). TEM analysis of both SPIONs and chitosan-coated SPIONs showed it is spherical in shape (Fig. 3a, b). AFM analysis of SPIONs showed that the nanoparticles were well dispersed and size below 20 nm (Fig. 4a) and below 35 nm in case of chitosan-coated SPIONs (Fig. 4b). The SPIONs and chitosan-coated SPIONs were crystalline in nature as they have shown reflection pattern in XRD at 220, 311, 400, 511 and 440, and the shape was cubic spinel structure of Fe_3O_4 (JCPDS 85-1436) (Marquez et al. 2012) (Fig. 5a, b). The zeta potential value of the SPIONs was found to be −38.10 mV and that of chitosan-coated SPIONs to be 3.34 mV suggesting that the SPIONs were stable than the latter (Figs. 6a, b) (Bhattacharjee 2016). In Raman spectroscopy, the minor peak at 600 cm^{-1} was corresponding to the A1 g mode of magnetite where peaks at 220 and 280 for Eg mode (Fig. 7a), these similar peaks were already reported (Justin et al. 2017; Mitchell et al. 2015; Panta and Bergmann 2015; Pham et al. 2016). There is a shift in Raman spectrum due to chitosan coating (Fig. 7b), which was also seen by Mai et al. (2012) where they coated chitosan on to magnetite.

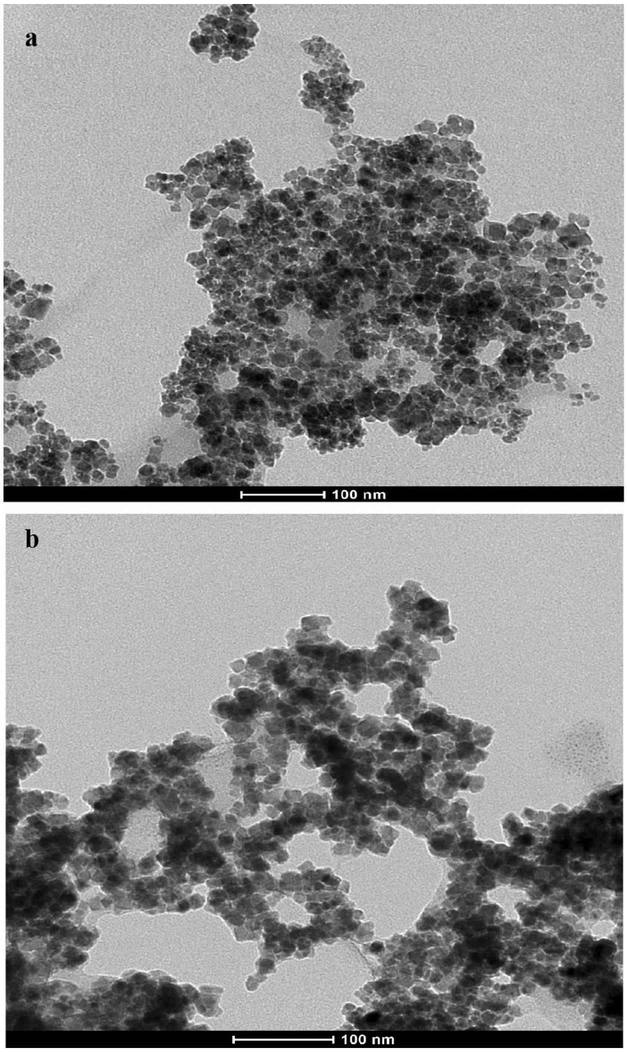


Fig. 3 TEM analysis of **a** SPIONs, **b** chitosan-coated SPIONs

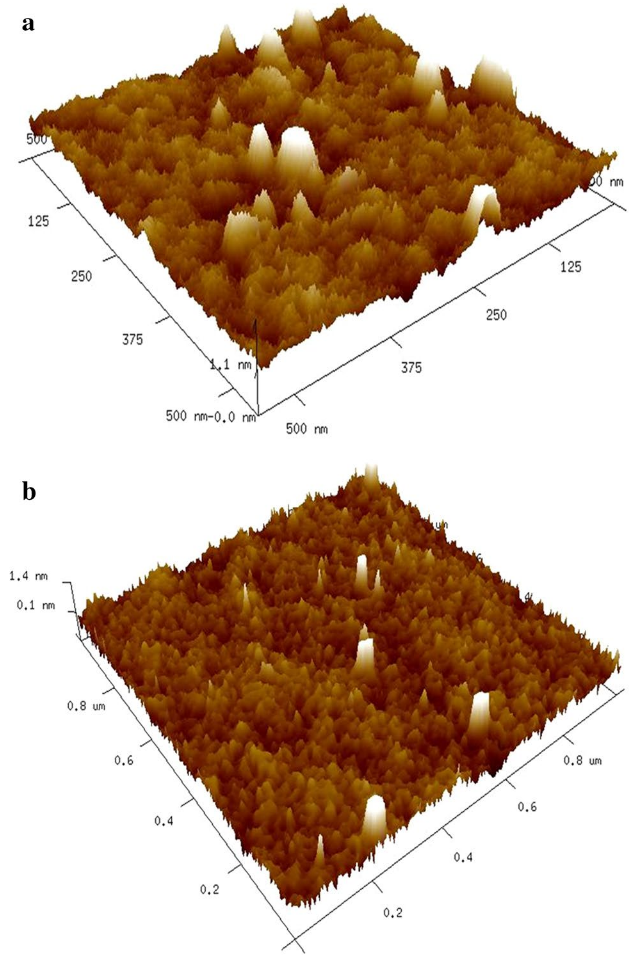


Fig. 4 AFM analysis of **a** SPIONs, **b** chitosan-coated SPIONs

Chromium metal adsorption studies

Chitosan-coated SPIONs have proven to be more efficient in the removal of chromium ions [Cr(VI)] from the solution (Fig. 8). The interaction between the amine groups of chitosan with the heavy metal had been already explained (Yavuz et al. 2006; Sarkar and Sarkar 2013), where the amines covalently bonds with heavy metal ions, thereby acting as an electron pair

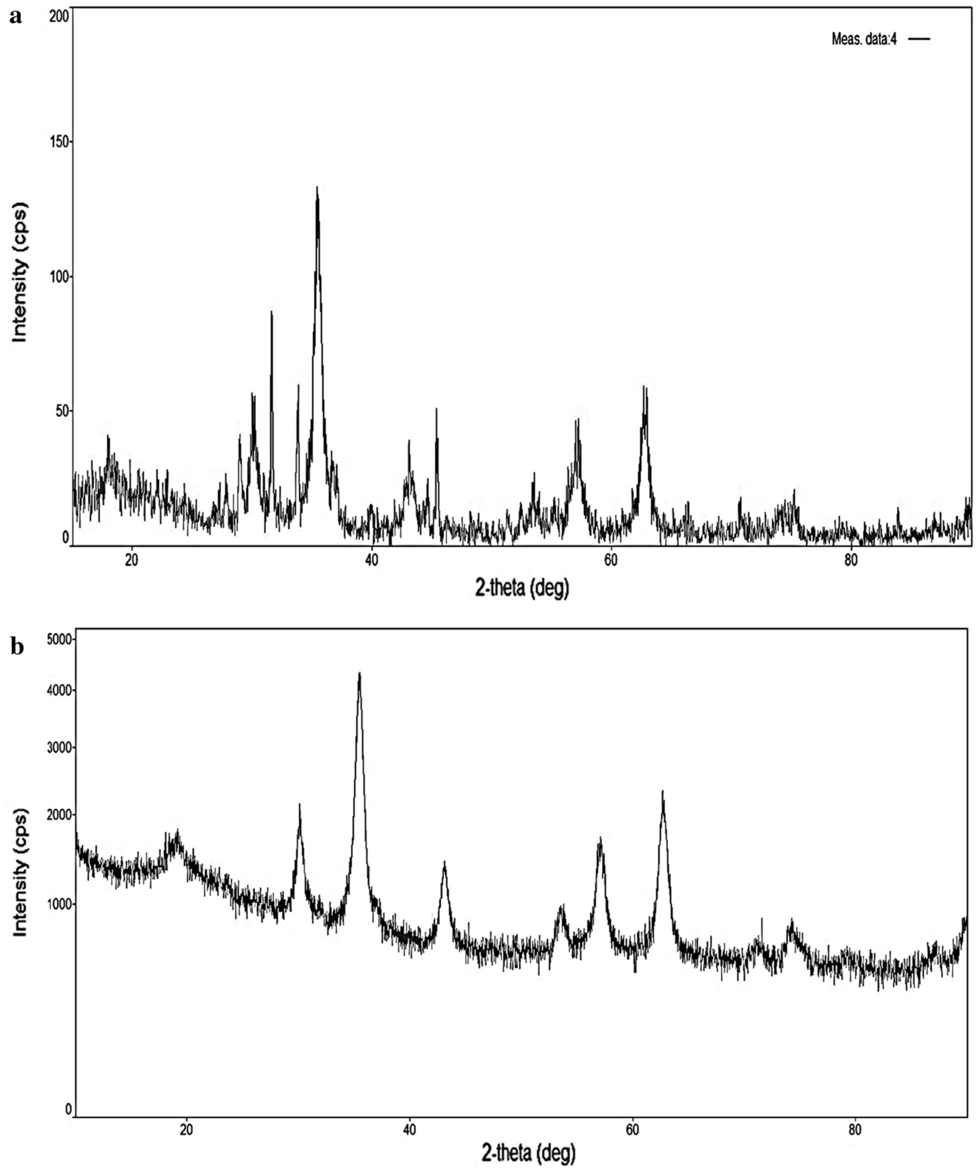


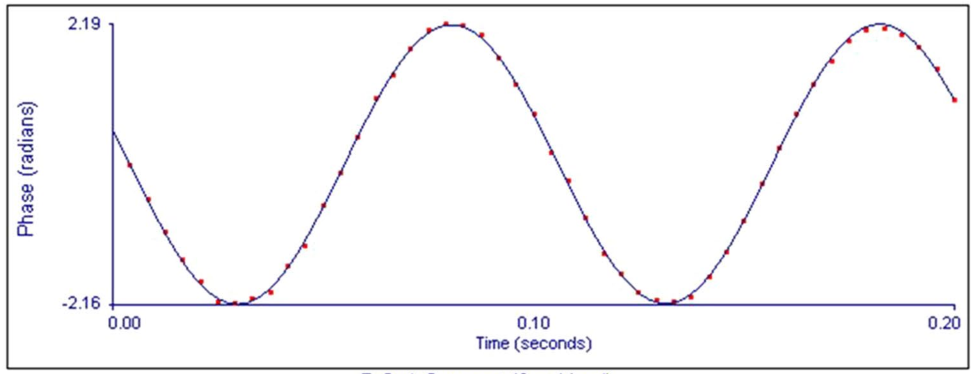
Fig. 5 X-ray diffraction analysis of **a** SPIONs, **b** chitosan-coated SPIONs

donor. Even the nanoparticles also adsorbs chromium; thus, chitosan-coated nanoparticles showed greater efficiency than the control. Even the applied acidic pH has its role in adsorption and removal of heavy metal from wastewater (Alzaidi et al. 2016; Shalaby et al. 2014).

In order to study the performance of adsorbent, which was chitosan-coated SPIONs, in the process of adsorption, different adsorption isotherms were plotted by deriving adsorption constants and analysing the R^2 values of each isotherm. The

Fig. 6 Zeta potential analysis of **a** SPIONs, **b** chitosan-coated SPIONs

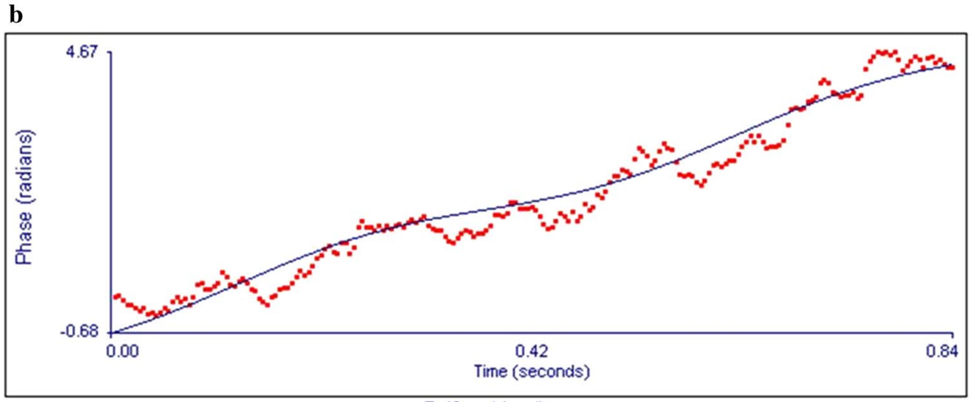
a



Fe3o4_2_repeat (Combined)

Run	Mobility	Zeta Potential (mV)	Rel. Residual
1	-2.98	-38.10	0.0060
2	-2.98	-38.19	0.0087
Mean	-2.98	-38.15	0.0073
Std. Error	0.00	0.05	0.0014
Combined	-2.98	-38.14	0.0051

b



P (Combined)

Run	Mobility	Zeta Potential (mV)	Rel. Residual
1	0.26	3.34	0.0285
2	0.37	4.70	0.0176
Mean	0.31	4.02	0.0230
Std. Error	0.05	0.68	0.0055
Combined	0.11	1.39	0.0145

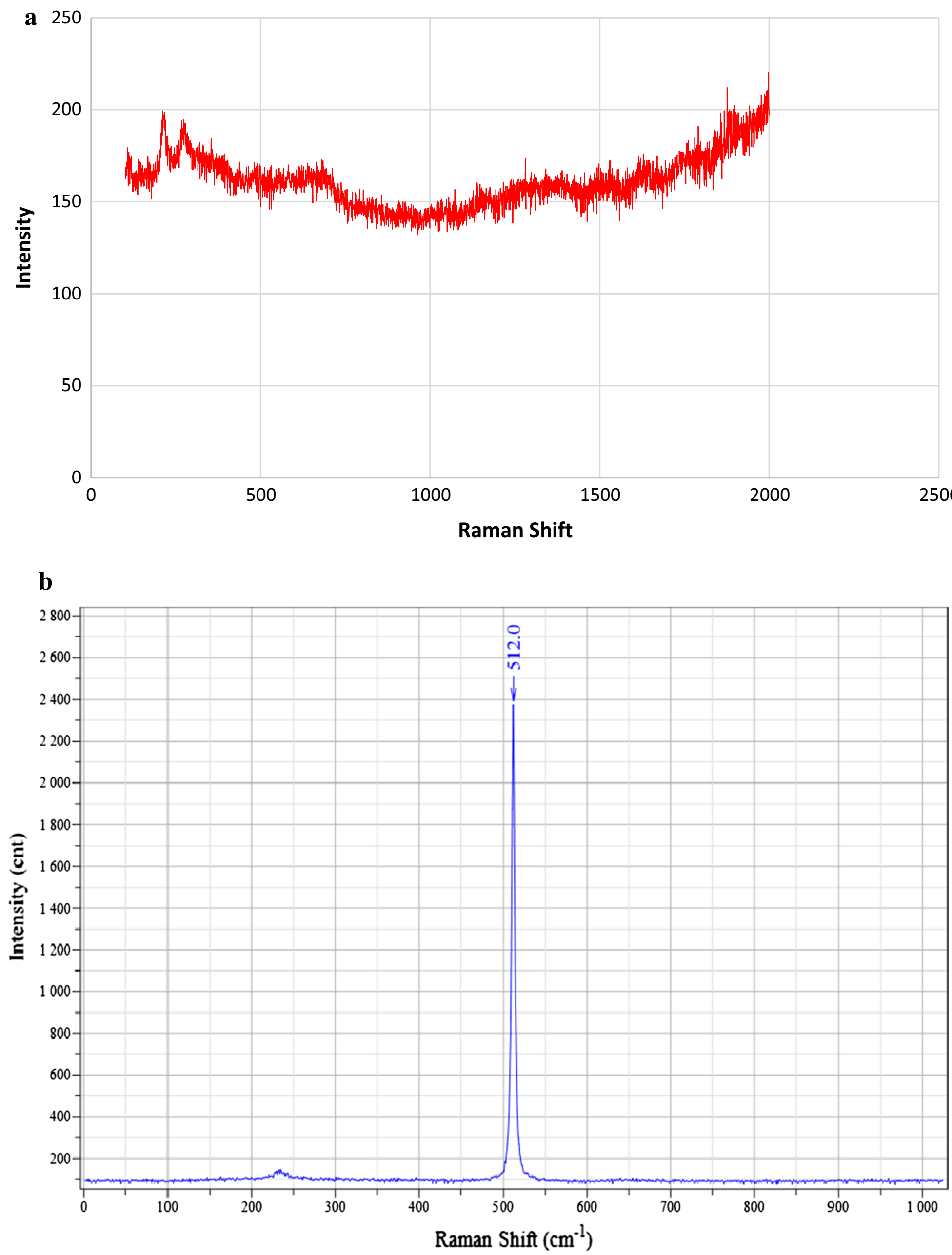


Fig. 7 Raman spectroscopy analysis of **a** SPIONs, **b** chitosan-coated SPIONs

different isotherms plotted were Langmuir, Freundlich and Temkin isotherms. The comparison of R^2 of the linearized form of all the three adsorption equations indicated that the Freundlich model yields a better fit for the experimental equilibrium adsorption data with a value of 0.992 when compared to the other two (Fig. 9a–c). This suggested that the binding sites on the adsorbent were heterogeneous and multilayer adsorption of chromium could occur (Jiang et al. 2013; Shalaby et al. 2014).

Summary and conclusions

The chemical structure and the morphology of SPIONs and chitosan-coated SPIONs had been investigated. SPIONs coated with chitosan were interacting better with chromium and improved the heavy metal adsorption. The major reason must be the interaction between amine of chitosan and heavy metal leading to covalent bonding. Once the bonding is happening between the chitosan-coated SPIONs and heavy metal, removal of these SPIONs out of the water is easier as it

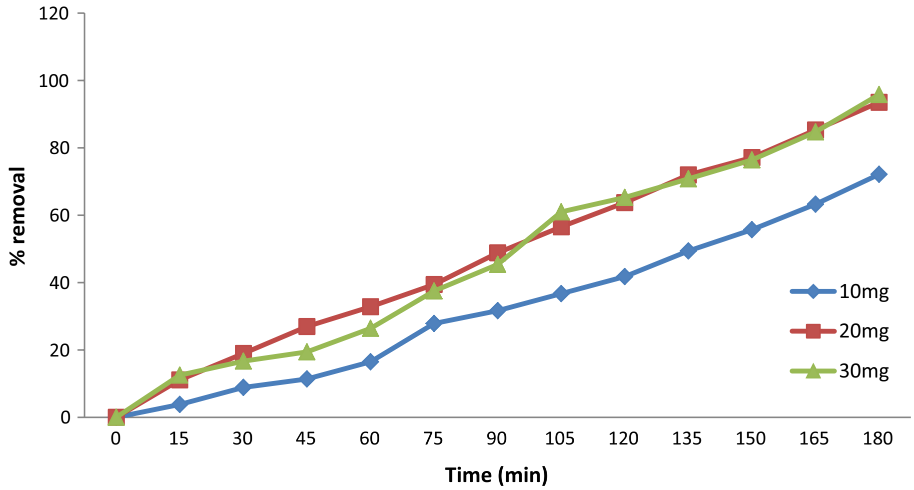


Fig. 8 Percentage chromium removal efficiency of chitosan-coated SPIONs at regular intervals of time

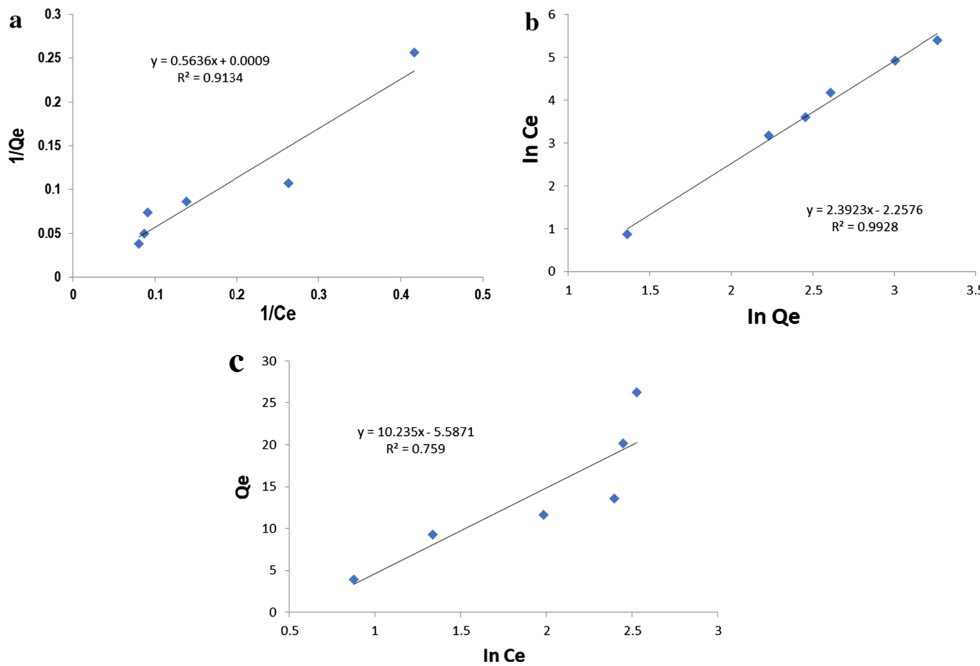


Fig. 9 Adsorption isotherm for chromium removal. **a** Langmuir isotherm. **b** Freundlich isotherm. **c** Tempkin isotherm

can be removed by applying external magnetic field. Thus, it can be employed for efficient removal of chromium ion from wastewater.

Compliance with ethical standards

Conflict of interest The authors declare no conflict of interest.

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