Magnetic Schiff’s base sorbent based on shrimp peels wastes for consummate sorption of chromate
Khalid Z. Elwakeel, Ahmed M. Elgarahy and Samya H. Mohammad

ABSTRACT
Magnetic Schiff’s base chitosan composite has been prepared starting from shrimp peels as a raw material. Chitosan extraction involved three main stages as preconditioning, demineralization deproteinization and deacetylation. Chitosan modification process took place through the reaction between chitosan and polymeric Schiff’s base of thiourea/glutaraldehyde in the presence of magnetite. The synthetic hybrid composite was characterized by Fourier transform infrared spectroscopy and scanning electron microscopy-energy dispersive X-ray analyses and tested as sorbent for Cr(VI) recovery from aqueous solution. The performance of the sorbent was systematically evaluated by batch sorption experiments, followed by equilibrium and kinetic studies with different mathematical models. The isotherm study demonstrate that the sorbent achieved 99.1% (sorption capacity; 252.45 mg g\(^{-1}\)) removal efficiency in Cr(VI) solution with concentrations up to 400 mg/L. Experimental data gave better mathematical fitting towards pseudo-second-order kinetic model and Langmuir isotherm model. The distribution coefficient was obtained at different temperatures and the thermodynamic parameters have been calculated: the sorption is endothermic, spontaneous and contributes to increase the randomness of the system. The sorbent could be recycled for three cycles of sorption/desorption.

Key words | Cr(V) sorption, desorption, magnetic sorbent, Schiff’s base chitosan, sorption isotherm

INTRODUCTION
Chromium is a contaminant commonly discharged into the environment as a result of wastewater from a range of industries such as tanning, paint, electroplating, printed circuit boards, metal processing, steel fabrication wood preservative industries (Chakraborty et al. 2015). This has resulted in soil and water pollution as well as changes in structure of natural communities and ecosystems. Chromium occurs in aqueous systems in trivalent and hexavalent forms, but the latter form is of particular concern due to its greater toxicity and mobility in the environment (Liu et al. 2016). Contact with chromium can cause severe health problems from simple skin irritation to cancer (Duranoglu et al. 2012; Proctor et al. 2015). The discharge limit of chromium from industries is 1,000–2,000 μg/L (Song et al. 2015a), chromium is hazardous to health when its limit in drinking water reaches 50 μg/L (Dokou et al. 2015). The most common treatment for Cr in industrial wastewater involves the reduction of Cr(VI) to the less toxic Cr(III), the precipitation of Cr(III) into Cr(OH)\(_3\) at high pH values, and the separation of the precipitate (Barrera-Díaz et al. 2012). This procedure has been found to be expensive and produces significant amounts of contaminated waste (sludge) that requires controlled landfill disposal. Sorptive removal as an alternative has received considerable attention due to the possibility to overcome the problem of safe disposal of generated sludge (Maleki et al. 2011; Sharma et al. 2011). Sorption refers to removal of solute from aqueous phase from an environmental matrix to the surface of a solid. Sorption is a promising technique for reducing pollutants in natural and industrial systems to improve increasingly serious environmental and public problems (Elwakeel 2009a; Elwakeel & Guibal 2016). A great diversity of materials of biological origin have been investigated for chromium recovery from dilute solutions, including agricultural waste and by-products (Mahvi et al. 2008), fungal biomass (Sargın et al. 2016), algal biomass (Hegde et al. 2016), or biopolymers issued from marine resources such as alginate (Geetha et al. 2016) and chitosan (Dima et al. 2015). On the other hand, the application of
long-chain backbone comprised of natural, inexpensive, and nontoxic polysaccharide with a more importantly, Fe₃O₄ is introduced to the sorbent matrix to make obtained by the alkaline partial deacetylation of chitin (Dima et al. 2015). Chitosan has drawn particular attention as an effective biosorbent due to its low cost compared with activated carbon and its high contents of amino and hydroxyl functional groups showing high adsorption potential for various metal ions (Li et al. 2016).

The cost of adsorbents is also an important parameter. Chitosan is easily obtained from the wastes of the seafood processing industry. One of the major drawbacks of the raw chitosan is associated with the poor acid resistance which could be largely improved by crosslinking with chemical agents such as epichlorohydrin and glutaraldehyde. However, the crosslinked polymer network makes the functional groups on chitosan surface more impassable; therefore, its sorption ability decreases (Donia et al. 2007). To solve this problem, some active functional groups are grafted on the crosslinked chitosan (Elwakeel 2010). So the efforts have been directed towards chitosan modification by functionalized crosslinker to improve both the sorption capacity and acid resistance. Herein, we reported the development of chemically modified chitosan abstracted from shrimp peels wastes with Schiff’s base cross-linker to remove Cr(VI) from aqueous solution, moreover, Fe₃O₄ is introduced to the sorbent matrix to make its phase separation using an external magnetic field possible. The effects of several parameters on the sorption process, including the initial pH of the solution, the sorbent dose and the effect ionic strength were studied. The regeneration of the loaded materials for the repeated use was carried out.

**MATERIALS AND METHODS**

**Chemicals**

Shrimp peels collected from local shops in Port Said, Egypt, glutaraldehyde, thiourea were Sigma-Aldrich products. Diphenylcarbazide was a Hach product, USA. All other chemicals were Prolabo products and were used as received. Potassium dichromate (K₂Cr₂O₇) was used as a source of Cr(VI). FeSO₄·7H₂O and FeCl₃·6H₂O were used for preparing magnetite particles as reported earlier using the modified Massart method (Elwakeel & Guibal 2004). Schiff’s base sorbent for chromate removal from water

**Preparation of chitosan**

Chitosan was prepared from shrimp peels according to the previously reported procedure (Islam et al. 2011). The process involves demineralizations of peels. In this step, the peels were suspended in 4% HCl at room temperature in the ratio of 1:14 (w/v). After 36 h, the peels were quite squasy and were rinsed with water to remove acid and calcium chloride. The demineralized peels were then treated with 5% NaOH at 90 °C for 24 h with a solvent to solid ratio of 12:1(v/w). The residue was then collected and washed to neutrality in running tap water. Then it was dried in sun and the product is chitin. The preparation of chitosan is simply deacetylation of chitin (Guibal 2004). Removal of acetyl groups from the chitin was achieved by using 70% NaOH solution with a solid to solvent ratio of 1:14 (w/v) at room temperature for 72 h. The mixture was stirred after some times for homogenous reaction. The resulting chitosans were washed to neutrality in running tap water and rinsed with distilled water. Then filtered and dried in sun. The deacetylation degree (DD) of the prepared chitosan is 78.6% obtained from Fourier transform infrared spectroscopy (FTIR) analysis. The DD was calculated from the following relationship:

$$\text{DD} = 100 \left( \frac{A_{1660} \text{cm}^{-1} / A_{3450} \text{cm}^{-1}}{1.33} \right)$$

where A₁660 cm⁻¹ and A₃450 cm⁻¹ are the absolute heights of absorption bands of amide and hydroxyl groups, respectively.

**Preparation of Schiff’s base modified magnetic chitosan**

Schiff’s base modified magnetic composite was prepared according to the previously reported method (Scheme 1) (Elwakeel & Atia 2014). One gram of chitosan was dissolved in 50 mL of 25% aqueous acetic acid solution. Three grams of thiourea (39.47 mmol) were dissolved in 100 mL distilled water. 18 mL (25%) glutaraldehyde solution (46.8 mmol) was added to thiourea solution in a round flask. The mixture was stirred on a water bath for 5 h at 50 °C. After completion of the reaction, 3 g of magnetite was added while stirring. The contents of the flask were then added to the chitosan solution and stirred until the solution become homogenous then heated up to 70 °C for 6 h. A large quantity of gel was formed, washed repeatedly with 0.5 NaOH solution then water and dried at 70 °C for 8 h. The dried gel (8.89 g) was referred by (M-Schiff’s-Ch).
Characterization of the sorbent

In order to confirm the functionalization of the sorbent Schiff’s base modified magnetic chitosan (M-Schiff’s-Ch) material was examined in dried KBr powder by recording the infrared spectra over the range of 4,000–400 cm⁻¹ using a FTIR spectrophotometer (FT/IR4100 Jasco-Japan). The morphology and the elemental distribution of Cr(VI) in the Schiff’s base modified magnetic chitosan were analyzed with scanning electron microscope (SEM) coupled with an energy dispersive X-ray (EDX) analysis system (JEOL JSM-6510LV).

Preparation of solutions

Stock solution (500 mg L⁻¹) of potassium dichromate (K₂Cr₂O₇) as Cr(VI) was prepared in distilled water. HCl (0.5 M) and NaOH (0.5 M) were used to change the acidity of the medium. 2 M of NaCl (in 0.5 M NaOH) was used as the desorbing agent for chromate anions from the sorbent. The Cr(VI) concentration of all samples was determined by the spectrophotometry method. The pink complex formed between 1,5-diphenylcarbazide and Cr(VI) was measured at 540 nm using photometer 7100, Palintest, USA.

Sorption experiments

The Cr(VI) solutions were obtained by dilution of the stock solution with distilled water just prior experiments. For the study of pH effect 20 mL of 50 mg L⁻¹ of Cr(VI) solution at different pH values (in the range 2–11) were mixed with 0.05 g of sorbent (dried weight) for 3 h, and the stirring speed was maintained at 40 rpm using a reciprocal agitator, Rota bit, J.P. Selecta (Spain). The pH values were adjusted by addition of 0.01–0.5 M HCl and 0.01–0.5 M NaOH solutions and measured by using a pH meter (Aqualytic AL15). Samples were collected and filtrated through magnetic separation and the filtrate was analyzed for residual Cr(VI) concentration. The pH was not controlled during the sorption but the final pH was systematically recorded.

For sorption isotherms 0.05 g of sorbent (m) was mixed with 20 mL of Cr(VI) at different initial concentrations (C₀, ranging between 40 and 1,000 mg/L) for 3 h. The pH of the solutions was initially set at 5.37. After solid/liquid separation, the residual concentration of Cr(VI) (mg Cr(VI) L⁻¹) was determined and the sorption capacity (qₑ, mg g⁻¹) was determined by the mass balance equation:

\[
qₑ = \frac{(C₀ - Cₑ)\cdot V}{m} \tag{2}
\]

where C₀ and Cₑ are the initial and equilibrium concentration of metal ion in solution (M), respectively, V is the volume of solution (L) and m the mass of sorbent (g).

For uptake kinetics, 0.45 g of sorbent was mixed with 180 mL of Cr(VI) solution (C₀: 50 mg L⁻¹) at pH 5.37. Samples (5 mL) were collected (the sorbent being magnetically separated) at fixed times and the residual concentrations were determined. The agitation speed was set at 40 rpm while the temperature was maintained at 25 ± 1 °C. The sorbed amount of Cr(VI) per unit weight of the sorbent at time t (q(t), mg Cr(VI) g⁻¹), was calculated from the mass balance equation (taking into account the decrement in the volume of the solution) according:

\[
q(t) = \frac{\sum_{i=1}^{n} (C(t)_{i, t} - C(t)_{i, 0}) \times V(t)_{i, t}}{m} \tag{3}
\]

where C(t)₀ (M) is the Cr(VI) concentration of the withdrawn sample number i at time t and C(t)₀ = C₀, V(t)₀ (mL) is the volume of the solution in the flask at sample number i and time t, and m is the mass of the sorbent in the flask. Here V(t)₀×V(t)₂ equals 5 mL (the sample volume).

The effect of temperature on the sorption of Cr(VI) was carried out in the 20 mL of Cr(VI) solutions (50 mg L⁻¹, pH 5.37) with 0.05 g of sorbent for 60 min at various temperatures.

The effect of sorbent dose on Cr(VI) removal was carried out in the 20 mL of Cr(VI) (50 mg L⁻¹, pH 5.37) at 25 ± 1 °C for 60 min.

Regeneration experiments were performed by contact of 0.3 g of the sorbent with 20 mL of 50 mg L⁻¹ Cr(VI) (at pH 5.37 for 100 min. The amount of Cr(VI) sorbed (and the sorption capacity) was determined by the mass balance equation (Equation (1)). The solution was magnetically decanted and the sorbent was washed by distilled water. The loaded sorbent was mixed with 20 mL of 2 M of NaCl (in 0.5 M NaOH) for 30 min. The regenerated sorbent was magnetically decanted, then carefully washed by distilled water for reuse in the second run. The regeneration efficiency (RE, %) was calculated according to the following equation:

\[
RE\% = \frac{\text{Amount of sorbed Cr(VI)(mg)at run(n + 1)}}{\text{Amount of sorbed Cr(VI)(mg)at run(1)}} \times 100 \tag{4}
\]

where n is the number of regeneration cycle.
RESULTS AND DISCUSSION

Sorbent characterization

FTIR spectrometry was used to characterize the structure of the sorbent (Figure S1, see supplementary data section, available with the online version of this paper). Chitosan, being a heteropolymer made up of glucosamine and acetylglucosamine units, is characterized in FTIR spectra by several bands: (a) amine band (free form) which is observed at 1,545-1,445 cm\(^{-1}\); (b) 1,638 cm\(^{-1}\); amide I band; and (c) 1,545 cm\(^{-1}\); amide II band. The reaction between aldehyde groups and amine moieties on glutaraldehyde and chitosan, respectively, involves the formation of ceto-imine linkage: \( >C = N - \) bands, identified by band (1,638 cm\(^{-1}\)). Guibal et al. cited some thiourea derivatives of chitosan characterized with FTIR techniques (Guibal et al. 2000), the spectra of these thiourea derivatives are similar to that of raw chitosan. Spectra of the compounds in which the \( >C = S \) group is attached to a nitrogen atom show an absorption band in the general \( >C = S \) stretching region (1,050 ± 1,300 cm\(^{-1}\)). Other bands in the broad region, 1,545-614 cm\(^{-1}\), can be attributed to (a) vibrations involving interaction between \( >C = S \) stretching and \( >C = N - \) stretching (1,638–1,445 cm\(^{-1}\)) and (b) the \( >C = S \) group. These bands are superimposed to amine/amide bands and the glucose ring, respectively. So, the sulfur type vibrations are difficult to detect, and the changes in the spectra resulting from Schiff’s base modification of chitosan are observed mainly on amine/amide regions.

The surface morphology of the M-Schiff’s-Ch (before and after sorption) is shown in Figure 1. The SEM micrographs reveal that the surface of sorbent is smooth with some pores, which can be clearly seen in the magnified view of the SEM micrographs, and the sorption of Cr(VI) changed the surface of M-Schiff’s-Ch sorbent to be more darker.

The EDX analysis of the M-Schiff’s-Ch sorbent before and after sorption evaluated that the surface of sorbent contains various elements such as carbon, oxygen, sulfur, copper and iron (Figure 2). Although a quantitative analysis of Cr loaded on the sorbent by SEM-EDX would not be accurate, the level of Cr is high enough to demonstrate qualitatively the homogeneous distribution of the metal on the surface of the sorbent. The mass percentage of Cr(VI) element at and after sorption evaluated that the surface of sorbent contains 10.5%. This is a first evidence of the high affinity of the sorbent for Cr(VI). It is noteworthy that the peaks of Fe element (representative of magnetite core) are significantly decreasing probably due to the coating of the sorbent with Cr deposition: this is confirmed by the relative decrease of the relative intensities of C and O elements; the relative intensity of Fe element decreases in the thin analyzed layer at the surface of the sorbent (electron beam does not penetrate more than the micron unit).

Biosorption performance evaluation

Effect of pH

Batch sorption experiments were performed at different initial pH (pH\(_i\)) ranging from 2 to 11. The variation in the uptake of chromate as a function of equilibrium pH (pH\(_{eq}\)) is shown in Figure 3(a). The Cr(VI) removal efficiency by the studied biosorbent was strongly depended on variations of the solution pH, which affects the surface charge of the adsorbent and the degree of ionization, and the chromate species. The highest amounts of Cr(VI) uptake (19.46-19.87) occurred at pH\(_{eq}\) values ranging from 5.37-7.02, then Cr(VI) slightly declines with further increase in pH to 11. Although the surface charge of the sorbent becomes more positive at lower pH (Elwakeel 2009b; Elwakeel & Guibal 2009b), the Cr(VI) uptake slightly decreases at pH\(_{eq}\) values ranging from 2.25-3.7, this may be attributed to the higher concentration of Cl\(^{-}\) which compete the chromate anions for interaction with the protonated active sites, in addition some of the chromate anions may be found in the neutral form as H\(_2\)CrO\(_4\), resulting in decreasing the adsorption capacity of adsorbent. It is known that chromate exists in different species, which include (H\(_2\)CrO\(_4\), HCrO\(_4\), CrO\(_4^{2-}\), HCr\(_2\)O\(_7\) and Cr\(_2\)O\(_7^{2-}\)) depending upon the chromium concentration and the solution pH (Dima et al. 2015). The main Cr(VI) species in equilibrium in the acidic pH range in diluted solution are the anions HCrO\(_4\) and CrO\(_4^{2-}\). They interact with the protonated amine groups of modified sorbent. The species such as Cr\(_2\)O\(_7^{2-}\) and HCr\(_2\)O\(_7\) coexist at high total chromium concentrations, above 1.000 mg L\(^{-1}\). At pH between 2 and 6, Cr\(_2\)O\(_7^{2-}\) and HCrO\(_4\) ions exist in equilibrium, and under alkaline conditions (pH > 8) it exists predominantly as chromate anion (Tan et al. 2012).

At pH\(_i\) 3.55 (equivalent to pH\(_{eq}\) 5.37), a large quantity of hydronium ions (H\(^+\)) existed and made the surface of M-Schiff’s-Ch more positively charged. Thus, M-Schiff’s-Ch was effective for sorption of negatively charged chromate anions by electrostatic attraction. As a result, the uptake of Cr(VI) was then increased in the acidic condition. However, in alkaline conditions, the OH\(^-\) anion was increased with the increasing pH. Then the increasing OH\(^-\) anion brought a competitive adsorption with chromate ions and slightly
decreased the sorption capacity of M-Schiff's-Ch towards Cr(VI) ions (Song et al. 2015a, 2015b).

Meanwhile, after sorption equilibrium, final solution pH was also determined and results are shown in Figure 3(b). For experiments performed at pH<7.3, the equilibrium pH (pH_{eq}) tended to increase, probably due to the sorption of protons alongside Cr(VI) onto the sorbent surface. In contrast, the sorption at higher pH (pH>7.3) caused a pH_{eq} decrease. At higher pH values, OH^- ions might be sorbed onto the surface of M-Schiff's-Ch leading to decreasing solution pH_{eq}.

**Kinetics**

Information regarding the kinetics of metal ions uptake is required to select the optimum condition for large-scale
metal removal processes. The time required for reaching the equilibrium has been evaluated by the plot of the sorption capacity (obtained by mass balance) as a function of time (Figure 4(a)) and the relative residual concentration (C/C₀) as a function of time (Figure 4(b)) under selected experimental conditions (reported in the caption of Figure 4). The sorption process can be described by three steps: (a) the initial step lasting for a few minutes (less than 10 min) that counts for 26% of total sorption of Cr(VI) ions; (b) a second step, standing between 10 and 270 min that corresponds to the progressive saturation of the sorbents; and (c) the saturation plateau with a negligible residual sorption (which counts for less than 3.5% of total sorption). This last section is probably associated with the progressive and slow swelling of biopolymer layer with limited effect of resistance to intraparticle diffusion. The fast sorption compared with other sorption systems based on other chitosan based sorbents can be attributed to the fast chemical reaction between Schiff’s base and the chromate anions. The second stage is probably controlled by the combination of reaction rate and the swelling effect of M-Schiff’s-Ch layers. As the sorption sites become progressively covered,
the rate of sorption decreased. Basically, 270 min of contact appears to be sufficient for roughly achieving equilibrium.

The uptake kinetics has been modelled using four models: the so-called pseudo-first-(PFORE) (Lagergren 1898) and pseudo-second-(PSORE) order rate equations (Ho & McKay 1999), the simplified model of resistance to intraparticle diffusion (Weber & Morris 1963) and Elovich model (Zeldowitsch 1934). These models and their linear forms are reported in Table S1 (see supplementary data section, available with the online version of this paper), where \( k_1 \) is the pseudo-first-order rate constant (min\(^{-1}\)) of sorption and \( q_e \) and \( q_t \) (mg g\(^{-1}\)) are the amounts of Cr(VI) sorbed at equilibrium and time \( t \), respectively, \( k_2 \) is the pseudo-secondary-order rate constant (g mg\(^{-1}\) min\(^{-1}\)), \( K_i \) is the intraparticle diffusion rate (mg g\(^{-1}\) min\(^{0.5}\)), \( \alpha \) the initial sorption rate (mg g\(^{-1}\) min\(^{-1}\)) and \( \beta \) the desorption constant (g mg\(^{-1}\)).

The validity of each model is checked by the correlation coefficient associated to linear fit. Accordingly, and as shown in Table 1, the analysis of its correlation coefficients shows that the PSORE gives a best fit of experimental data for Cr(VI) sorption on M-Schiff’s-Ch sorbent. The lines in Figure 4(a) show the modeling of kinetic profiles with the PSORE, Weber and Morris and Elovich models: the models fit well the kinetic data, though some discrepancies can be observed in the curvature zone. The good fit of experimental data with PSORE model confirms that the chemical reaction is the rate-controlling step for uptake kinetics. As expected, designing Schiff’s base modified magnetic chitosan particles contributes to significantly reduce the sorption time compared with, for example, β-cyclodextrin – chitosan modified biochars which reaches to Cr(VI) sorption capacity after 2,700 min of contact time (Huang et al. 2016).

The intraparticle diffusion model provides a more comprehensive approach for defining of sorption mechanism, and the plot generally allows identifying different successive steps in the global process (Markovski et al. 2014). The Weber and Morris shows multi-linear sections (Figure S3(a), see supplementary data section, available with the online version of this paper), i.e. three linear sections (on the plot \( q_t \) vs. \( t^{0.5} \)) with fast kinetics in first step followed by the gradual attainment of equilibrium, and a pseudo saturation plateau. The multi-linear plot does not pass through the origin suggesting that the resistance to intraparticle diffusion is not the sole rate-limiting step: other steps, e.g. resistance to film diffusion and/or reaction rate, are probably involved in the control of uptake kinetics (Table 1). The second section is characterized by a much lower kinetic rate and leads to a slow approach to equilibrium with the control by the resistance to intraparticle diffusion (into internal macroporous and mesoporous network). From the second region of the plot, which intra-particle diffusion related micro-pore diffusion occurs; \( K_{i2} \), \( X \) and \( R^2 \) values were calculated and given in Table 1. A significant difference of \( K_i \) values (Table 1) indicates the availability of the functional groups is primary controlled by diffusional transport through pores system in second and third steps, structure of the porous sorbent, i.e. pores network, consists from macropores which extends into particle interior and branched into tree like system of meso and micropores. The Cr(VI) ions must diffuse through whole pore systems to reach total surface area within the particles, where the intra-particle diffusion, resistance due to diffusional transport inside pores, slow down overall process contributing to formation of time-dependent concentration gradient due to fast kinetic process at the surface, until saturation of all available surface sites was achieved. \( X \) represents the boundary layer diffusion effects (external film resistance). As the value of \( X \) decreases, the effect of boundary layer diffusion on the reaction rate decreases. The obtained values of \( X \) (Table 1) indicate that the boundary layer diffusion effect (external film resistance) has significant effect on the diffusion rate. The last step is very slow and represents only a small percentage of the total sorption: this phase can be associated to the resistance to diffusion in the microporous network of the sorbent. In addition, the progressive saturation of available and accessible sorption sites influences the local equilibrium on the surface between surface sorption and desorption.

Elovich’s equation is another rate equation based on the sorption capacity. In 1934, the kinetic law of chemisorptions was established through the work of Zeldowitsch

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**Table 1 | Kinetic parameters for Cr(VI) sorption**

<table>
<thead>
<tr>
<th>PFORE</th>
<th>PSORE</th>
<th>Weber and Morris model</th>
<th>Elovich equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 ) (d)</td>
<td>( q_e, \text{calc} ) (b)</td>
<td>( R^2 )</td>
<td>( k_i ) (d)</td>
</tr>
<tr>
<td>0.011</td>
<td>10.735</td>
<td>0.9428</td>
<td>0.0017</td>
</tr>
<tr>
<td>0.349</td>
<td>11.256</td>
<td>0.9399</td>
<td>0.184</td>
</tr>
</tbody>
</table>

Units: (d): min\(^{-1}\); (b): mg g\(^{-1}\); (c): g mg\(^{-1}\) min\(^{-1}\); (d): mg g\(^{-1}\) min\(^{0.5}\); (e): mg g\(^{-1}\) min\(^{-1}\); (f): g mg\(^{-1}\).
(Zeldowitsch 1934). It has commonly been called the Elovich equation. The values of α and β were determined from the intercept and slope, respectively, of the linear plot of $q_t$ vs $\ln t$ (Figure S3(b), see supplementary data section). The value of α for the sorption of Cr(VI) ions on the M-Schiff-Ch sorbent is 1.66 (mg g$^{-1}$ min$^{-1}$). This value indicate that the initial sorption rate of Cr(VI) ions is relatively high compared with the previous studies of Dima et al. (Dima et al. 2015; El-Korashy et al. 2016), in that work, reticulated chitosan micro/nanoparticles was prepared from shrimp peels. The high initial sorption rate of Cr(VI) onto M-Schiff’s-Ch sorbent may be attributed to the high concentration of active sites on the sorbent surface allowed for reacting with Cr(VI) ions. The value of β (desorption constant) is found to be 0.28 g mg$^{-1}$. This is consistent with the levels reached with reticulated chitosan micro/nanoparticles obtained from shrimp peels (Dima et al. 2015).

**Equilibrium sorption isotherm**

Figure 5 shows Cr(VI) sorption isotherm at initial pH 5.37 (initial pH shifted to 5.7 ± 0.2 and 7 ± 0.2 after metal sorption) using the M-Schiff’s-Ch. The isotherm study was conducted to establish equilibrium between the amount of Cr(VI) bound on the surface of the sorbent as a function of that remaining in solution at a constant temperature of 25 °C. The isotherm study demonstrate that M-Schiff’s-Ch achieved 99.1% removal efficiency in Cr(VI) solutions with concentrations up to 400 mg/L. The equilibrium sorption isotherms are some of the most important data for determining the mechanism of Cr(VI) sorption on the sorbent. Several isotherm models have been used to describe experimental data for sorption isotherms. However, among these, four different appropriate isotherm models were selected for this work for the analysis of the equilibrium data: the Langmuir (Langmuir 1918), Freundlich (Freundlich 1906), Dubinin-Radushkevich (Dubinin et al. 1947) and Temkin (Temkin & Pyzhov 1940) isotherm models.

The linear and nonlinear forms of the isotherm models are shown in Table S2 (see supplementary data section, available with the online version of this paper) of the additional material, and their parameters are shown in Table 2, where $q_e$ the adsorbed value of Cr(VI) at equilibrium concentration (mg g$^{-1}$), $q_L$ is the maximum sorption capacity or the saturation of the monolayer (mg g$^{-1}$) and $K_L$ is the Langmuir binding constant which is related to the energy of sorption (L mg$^{-1}$), $C_e$ is the equilibrium concentration of Cr(VI) in solution (mg L$^{-1}$). $K_F$ (mg g$^{-1}$) (L mg$^{-1}$)$^{1/n}$ and n are the Freundlich constants related to the sorption capacity and intensity, respectively. $K_{DR}$ (J mol$^{-2}$) is a constant related to the sorption energy, $Q_{DR}$ (mg g$^{-1}$) is the theoretical saturation capacity, $\varepsilon$ (J$^2$ mol$^{-2}$) is the Polanyi potential, T is the temperature where the sorption occurs, $A_T$ (kJ mol$^{-1}$) is the Temkin isotherm constant, $b_T$ (L g$^{-1}$) is Temkin constant in relation to heat of sorption.

The Langmuir model is the simplest theoretical model for monolayer sorption onto a surface with a finite number of identical sites. It was originally developed to represent chemisorption on a set of distinct sorption sites. The isotherm fitting was plotted on the basis of the nonlinear equations using the model constant parameters obtained from the linear equation plot analysis (Figure S4(a), see supplementary data section, available with the online version of this paper). Via comparison of the R$^2$ values, the Langmuir isotherm resulted in very good fitting, with R$^2$ values of >0.999. In addition, the $q_e$ calculated from the Langmuir isotherm was close to the experimental $Q_{max}$. The asymptotic shape of the sorption isotherm (Figure 5) confirms that the Langmuir equation is probably more appropriate for fitting experimental data than the other equations (e.g. the exponential trend of the Freundlich equation is not consistent with the profile of the curve). The Langmuir model is based on the assumption that sorption sites are identical and energetically equivalent, and that sorption occurs at monolayer coverage (Elwakeel & Yousif 2010). Furthermore, the Langmuir parameters can be used to predict the affinity between the sorbate and sorbent using the dimensionless separation factor $R_L$.

$$R_L = \frac{1}{1 + K_L C_0}$$  (5)
where \( K_L \) is the Langmuir equilibrium constant and \( C_0 \) is the initial concentration of Cr(VI) ions. Values of \( 0 < R_L < 1 \) indicates the ‘suitability’ of the process. In this study, the values of \( R_L \) of the M-Schiff’s-Ch for the sorption of Cr(VI) ions lie between 0.0051 and 0.072 for all concentration and temperature ranges at 25°C. This means much smaller than 1.0, and that the sorption is very favorable whatever the concentrations range.

The Freundlich isotherm model is based on the assumption of a heterogeneous distribution of the sorption sites (basically corresponding to heterogeneous material in terms of reactive groups) (Freundlich 1906), as well as possible multilayer accumulation. In this study, the values of \( n \) and \( K_F \) were determined from the slope and intercept, respectively, of the linear plot of \( \log q_e \) vs \( \log C_e \) (Figure S4(b), see supplementary data section) of Freundlich equation given in Table 2. The correlation coefficients \( (R^2) \) of the linear form for the Langmuir model were higher (and closer to 1.0) than the values obtained for the Freundlich equation (Table 2). This was expectable based on the shape of sorption isotherms: the saturation plateau is consistent with the asymptotic trend associated to the Langmuir equation (Table S2, see supplementary data section). This isotherm was expected based on the shape of sorption isotherms: the saturation plateau is consistent with the asymptotic trend associated to the Langmuir equation, while the Freundlich equation means an exponential trend. This suggests that metal sorption occurs through monolayer sorption onto a surface, with a finite number of identical sites, which are homogeneously distributed over the sorbent surface.

Another popular equation for the analysis of isotherm is that proposed by Dubinin and Radushkevich isotherm (Table S2, see supplementary data section). This isotherm was developed in accounting for the effect of the porous structure of the sorbents, and the energy involved in the process. The Polanyi potential \( (\epsilon) \) given as Equation (6) (Dubinin et al. 1947):

\[
\epsilon = RT \ln \left( 1 + \frac{1}{C_0} \right)
\]

\( R \) is the universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)) and \( T \) is the absolute temperature (K). The slope of the plot of \( \ln q_e \) vs \( \epsilon^2 \) (Figure S5(a), see supplementary data section, available with the online version of this paper) gives \( K_{DR} \) and the intercept yield \( Q_{DR} \) (Table 2). The D-R constant \( (K_{DR}) \) can give the valuable information regarding the mean energy of sorption by Equation (7):

\[
E_a = \frac{1}{(2K_{DR})^{0.5}}
\]

where \( E_a \) (J/mol) is the mean sorption energy; in the range 1–8 kJ mol\(^{-1}\), \( E_a \) describes a physical sorption, while chemical sorption corresponds to a mean energy higher than 8 kJ mol\(^{-1}\). The value of the mean sorption energy \( (E_a) \) is in the range of 1–8 kJ mol\(^{-1}\) (Table 2). The uptake can be described in terms of chemisorptions as the chemical interaction between Schiff’s base and chromate anions. However, this interpretation is not consistent with the low value of the free energy of sorption (i.e., \( E_a \)) found to be close to 1.03 kJ mol\(^{-1}\); this means below the limit value of chemical sorption processes, which is generally set at 8 kJ mol\(^{-1}\). It was not possible to find a clear explanation to this unexpectedly low value of \( E_a \); the dispersion of experimental data in the figure representing the D-R isotherm model (which serves to calculate \( E_a \)) is not sufficient to explain this low value.

The Temkin equation was also used to model the sorption isotherm (Table S2, see supplementary data section). The Temkin isotherm takes into account the interactions between sorbent particles and sorbate assuming that the free energy of sorption is a function of the surface coverage (Temkin & Pyzhev 1940). The constant \( A_T \) reflects the initial sorption heat of the sorbent: the greater \( A_T \) value the higher the sorption heat and the greater the affinity of the sorbent for the sorbate. The obtained values confirm the strong interaction between Cr(VI) and the reactive groups at the surface of the M-Schiff’s-Ch sorbent.

Mechanism of chromium sorption

Sorption mechanism is probably due to high affinity between Cr(VI) ions and Schiff’s base of thiourea and glutaraldehyde in the composite structure. According to the
published literature, the Cr(VI) sorbed onto the Fe(III) modified chitosan was partially reduced to relatively non-toxic Cr(III) based on the surface chemical compositions of the Cr(VI) adsorbed during the fast and highly efficient Cr(VI) removal process (Shen et al. 2015). Dambies et al. (2003) confirmed that Cr(VI) ions are chemically reduced in acidic solution by chitosan light exposure or free aldehyde groups. Peterson et al. (Peterson et al. 1997) using EXAFS simulation for Cr₂O₃ and Na₂CrO₄ compounds, shows that Cr(III) is octahedrally coordinated, with six oxygen atoms at approximately 2.0 Å, and that Cr(VI) is tetrahedrally coordinated, with four oxygen atoms at approximately 1.6 Å. So a significant fraction of the Cr(VI) may be reduced to Cr(III) in loaded M-Schiff’s-Ch sorbent, most likely due to the presence of both magnetite and Schiff’s base groups.

**Influence of temperature**

The sorption of Cr(VI) onto the surface of the M-Schiff’s-Ch sorbent reach to an equilibrium state then no further tendency to change the concentrations of Cr(VI) onto the sorbent surface and also in aqueous solution. At equilibrium, the rate of sorption Cr(VI) onto the sorbent surface is equal to the rate of desorption of Cr(VI) from the surface of the sorbent. The concentration of Cr(VI) onto sorbent surface and in aqueous solution becomes practically constant. The ratio of effective concentration of Cr(VI) onto solid sorbent to the liquid aqueous solution is constant called equilibrium constant, $K_c$ of the sorption process.

$$K_c = \frac{C_s}{C_e}$$

where $C_s$ and $C_e$ are equilibrium concentrations of Cr(VI) onto the sorbent surface and in aqueous solution, respectively.

Classic van’t Hoff reaction isotherm equation correlates between free energy change ($\Delta G$), standard free energy change ($\Delta G^o$) and equilibrium constant ($K_c$) at constant temperature (T) as:

$$\Delta G = \Delta G^o + RT\ln K_c$$

At equilibrium, free energy change ($\Delta G$) is zero; hence Equation (9) reduces as:

$$\Delta G^o = -RT\ln K_c$$

This is the most important equation used in sorption thermodynamics to predict the feasibility of sorption process. The standard free energy change is the free energy change of the sorption process at unit concentrations of sorbate and unit active sites of the sorbent.

To predict standard enthalpy change ($\Delta H^o$) and standard entropy change ($\Delta S^o$), Equation (10) rearranged in the form of equilibrium constant ($K_c$) as:

$$\ln K_c = \frac{\Delta G^o}{RT}$$

According to classic thermodynamic, the thermodynamic parameters standard free energy change ($\Delta G^o$) is also related to standard enthalpy change ($\Delta H^o$) and standard entropy change ($\Delta S^o$) at constant temperature by the equation:

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

Therefore, the van’t Hoff equation becomes:

$$\ln K_c = \frac{-\Delta H^o}{RT} + \frac{\Delta S^o}{R}$$

The values of standard enthalpy change ($\Delta H^o$) and standard entropy change ($\Delta S^o$) for the sorption of Cr(VI) onto the M-Schiff’s-Ch are determined from the slope and intercept for the plot of lnK versus 1/T and listed in Table 3. The positive values of $\Delta H^o$ confirm the endothermic nature of sorption process. The negative values of $\Delta G^o$ (Table 3) indicate that the sorption reaction is spontaneous, the increase in the negativity of $\Delta G^o$ with increasing temperature confirm that the sorption is favorable at higher temperatures.

**Effect of sorbent dose**

The sorption of Cr(VI) on the M-Schiff’s-Ch sorbent was studied by changing the quantity of sorbent range of (0.01 to 0.1 g for 20 mL of Cr(VI) solution), with the

<table>
<thead>
<tr>
<th>$\Delta H^o$ (kJ mol⁻¹)</th>
<th>$\Delta S^o$ (J mol⁻¹ K⁻¹)</th>
<th>308 K</th>
<th>318 K</th>
<th>328 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.99</td>
<td>40.50</td>
<td>-6.41</td>
<td>-6.82</td>
<td>-7.22</td>
</tr>
</tbody>
</table>
Cr(VI) concentration of 50 mg/L at 25 °C and pH of 5.37. Sorptive removal of Cr(VI) from aqueous solution showed dose-dependent manner. The results in Figure 6(a) show the Cr(VI) sorption capacity as a function of sorbent amount. It has been found that the sorption capacity decreases from 94 mg g\(^{-1}\) to 9 mg g\(^{-1}\) when the mass of the M-Schiff's-Ch increases from 0.01 to 0.1 g, respectively. The influence of sorbent doses on sorptive capacity is mainly related to increased surface area, which leads to unsaturation of binding sites through sorption process. On the other hand, Figure 6(b) shows the effect of dose on the relative residual concentration (C/C\(_0\)) of Cr(VI) by the M-Schiff's-Ch sorbent. As the dose increases, the relative residual concentration of Cr(VI) is decreased. This is more than likely attributed to the increased sorbent surface area and availability of more binding sites resulting from an increase in sorbent doses. The results shown indicate that the removal efficiency increases up to C/C\(_0\) = 0.0011 at sorbent dose of 0.1 g for 20 mL Cr(VI) solution. According to the result, the dose of 0.01 g for 20 mL of Cr(VI) solution will achieve the maximum loading capacity for the sorbent. On the opposite hand with a sorbent dosage of 0.1 g for 20 mL of Cr(VI) solution, it is possible to remove about 99.98% of Cr(VI) from the solution (achieving environmental target). The sorbent dosage to be used depends on the target of the sorption process: concentration effect or maximum decontamination.

**Effect of ionic strength (addition of NaCl)**

The effect of chloride ions on Cr(VI) removal was examined, by addition of increasing concentrations of NaCl (from 5 to 45 g L\(^{-1}\); C\(_0\): 50 mg/L; sorbent dosage: 0.05 g 20 mL\(^{-1}\)) (Figure 7). For the studied sorbent, increasing the amount of NaCl affects the sorption capacity: the sorption capacity decreases by 32%, when NaCl concentration reaches 45 g L\(^{-1}\). This is probably due to the competitor effect of chloride anions against Cr(VI) anions for interaction with the sorption sites; it is possible to make profit of this effect for promoting the desorption of Cr(VI) anions and the recycling of the sorbent using alkaline NaCl solutions (see below).

**Comparison of sorption performance for Cr(VI) ions with various sorbents**

Table 4 shows a comparison of the maximum sorption capacities of materials found in the recent literature; the best operating conditions are also presented. The strict comparison is difficult since maximum sorption capacities were not obtained under similar experimental conditions; however, these data are sufficient to show that the M-Schiff's-Ch sorbent has a sorption capacity of the same order of
magnitude as other sorbents (and in some cases better). The critical point that confirms the interest of these materials is the relatively fast sorption compared to other systems. The design of magnetic core coated by a thin layer of chemically-modified Schiff’s base chitosan allows reduction of the contribution of the resistance to intraparticle diffusion and makes the sorbent for Cr(VI) binding very efficient kinetically. The high sorption capacity of the M-Schiff’s-Ch sorbent towards Cr(VI) ions reveals that sorbents could be promising for practical application in Cr(VI) ions removal from wastewater.

Regeneration

Desorption of Cr(VI) anions is generally performed by pH change. In most cases, desorption is performed under basic conditions. Regeneration of the M-Schiff’s-Ch sorbent was carried out by contacting 20 mL of an alkaline saline solution (i.e. 2 M of NaCl in 0.5 M NaOH) with M-Schiff’s-Ch sorbent for 30 min. After regeneration, the sorbent was again carefully washed with distilled water to become ready for the second run of uptake. The RE for each adsorption/desorption cycle was found to be 98.5, 98.1, and 97.2%. The sorbent shows quite good stability in both sorption and desorption performance along the four sorption/desorption cycles. A slight decrease of sorption performance is observed but, even at the fourth step, the decrease in sorption efficiency is less than 2.78%. The Schiff’s base modified magnetic chitosan material can thus be used for repeated sorption/desorption cycles with high efficiency.

Table 4  Comparison of sorption performance for Cr(VI) with various sorbents appeared in the literature

<table>
<thead>
<tr>
<th>Adsorbent material</th>
<th>Initial pH</th>
<th>Contact time (min)</th>
<th>Temperature (°C)</th>
<th>Initial concentration (mg/L)</th>
<th>Sorbent dosage (g L⁻¹)</th>
<th>Sorption capacity (mg g⁻¹)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surfactant modified zeolite</td>
<td>3</td>
<td>1,200</td>
<td>25</td>
<td>400</td>
<td>100</td>
<td>6.31</td>
<td>Song et al. (2015b)</td>
</tr>
<tr>
<td>Ferri hydroxide (Fe(OH)₃)</td>
<td>7</td>
<td>120</td>
<td>25</td>
<td>20</td>
<td>2.0</td>
<td>7.68</td>
<td>Yu &amp; Zhang (2014)</td>
</tr>
<tr>
<td>Chitosan-Fe(III) complex</td>
<td>5</td>
<td>10</td>
<td>30</td>
<td>400</td>
<td>5.0</td>
<td>173.1</td>
<td>Shen et al. (2013)</td>
</tr>
<tr>
<td>Chitosan/multiwalled carbon nanotubes/Fe composite nanofibers</td>
<td>2</td>
<td>60</td>
<td>25</td>
<td>1,000</td>
<td>0.5</td>
<td>335.6</td>
<td>Beheshti et al. (2016)</td>
</tr>
<tr>
<td>Polypyrrole wrapped oxidized multiwalled carbon nanotubes nanocomposites</td>
<td>2</td>
<td>100</td>
<td>25</td>
<td>500</td>
<td>0.5</td>
<td>294.1</td>
<td>Bhaumik et al. (2016)</td>
</tr>
<tr>
<td>MnO₂</td>
<td>5.9</td>
<td>30</td>
<td>20</td>
<td>6.24</td>
<td>0.2</td>
<td>0.83</td>
<td>Gheju et al. (2016)</td>
</tr>
<tr>
<td>Carbonaceous nanofibers</td>
<td>5</td>
<td>–</td>
<td>30</td>
<td>10.4</td>
<td>0.2</td>
<td>122.71</td>
<td>Cheng et al. (2016)</td>
</tr>
<tr>
<td>β-Cyclodextrin- chitosan modified biochars</td>
<td>2</td>
<td>2,700</td>
<td>25</td>
<td>800</td>
<td>2.0</td>
<td>206</td>
<td>Huang et al. (2016)</td>
</tr>
<tr>
<td>Magnetic Schiff’s base chitosan composite</td>
<td>5.3</td>
<td>150</td>
<td>25</td>
<td>850</td>
<td>2.5</td>
<td>252.4</td>
<td>This work</td>
</tr>
</tbody>
</table>

CONCLUSION

Schiff’s base magnetic chitosan composite has been prepared based on shrimp peel wastes. The composite is characterized by a fast and a higher sorption towards Cr(VI) ions from aqueous solution at a broad range of pH values. Significant differences are also detected on SEM-EDX analyses after Cr(VI) sorption: the typical signals of Cr element strongly appears after Cr(VI) sorption. The sorption isotherm is described by the Langmuir equation and the process is endothermic, spontaneous and with increased randomness. The uptake kinetics are described by the pseudo-second-order rate equation and the particles, being magnetic, can be readily recovered. Increasing the concentration of NaCl decreases the sorption capacity. Finally, the Cr(VI) ions can be efficiently desorbed from loaded sorbent with alkaline solution of 2 M of NaCl in 0.5 M NaOH and the sorbents can be reused for a minimum of four sorption/desorption cycles with a limited loss in efficiency (less than 2.78%) at the fourth sorption cycle.

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