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Synthesis, adsorption and selectivity studies of N-propyl quaternized magnetic poly(4-vinylpyridine) for hexavalent chromium

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ABSTRACT

The ability of solid N-propyl quaternized magnetic poly(4-vinylpyridine) for the extraction of chromium (VI) in aqueous solutions was investigated. For the synthesized Cr(VI) magnetic polymers, the optimum pH obtained was 4 for both the magnetic ion imprinted polymer (IIP) and the corresponding non-ion imprinted polymer NIP. The amount of the adsorbent which gave the maximum adsorption was determined to be 20 and 65 mg for the magnetic IIP and NIP, respectively. A Cr(VI) concentration which was adsorbed maximally was 5 mg L^{-1} which was therefore taken as the optimum. The maximum adsorption capacities for the magnetic polymers were 6.20 and 1.87 mg g^{-1} for the magnetic IIP and NIP, respectively. The optimum time for the adsorption of the Cr(VI) analyte was determined as 40 min. The prepared magnetic ion imprinted polymer showed good selectivity towards Cr(VI). The order of selectivity of the investigated anions followed the sequence: $Cr_2O_7^{2-} > SO_4^{2-} > F^- > NO_3^-$.

1. Introduction

Pollution of water bodies due to the indiscriminate disposal of heavy metals has been a concern for a long time. The rapid increase in the levels of environmental pollution over recent decades has resulted in increasing concern for people's well-being and for global ecosystems [1]. Inorganic pollutants of great physiological concern are heavy metals [2], because of their toxicity [3], towards aquatic-life, human beings and the environment [4].

One of these toxic heavy metals is chromium and is considered a priority pollutant [5]. Chromium has many industrial applications, for example, its compounds can be added to cooling water to inhibit corrosion [6]. Chromium and its compounds are also employed in the manufacturing of inks, industrial dyes and paint pigments [7]. Other uses of chromium include stainless steel production, leather tanning, wood preservation, fertilizers, chrome tanning, textile, photography, *etc*. [8]. Chromium metal is also extensively used in ferrous alloys, mostly due its resistance to ordinary corrosive agents. The dichromate anions oxidize various functional groups like the aldehydes and alcohols and are used as catalysts in this regard [9].

Just like other metals, chromium enters the environment as a result of effluents discharged from industries [10]. Once it enters the natural water system, chromium exists primarily in trivalent and hexavalent forms [11]. Many water bodies around the world have set Cr(VI) maximum allowed limit in order to reduce harm caused by this ion. In the case of USA, Canada, WHO and South Africa, this is regulated to 50 μg L^{-1} [12–14].

The need to study chromium speciation emanates from drastic differences in biochemical properties of Cr(III) and Cr(VI) compounds [15]. For instance, Cr(III) is an essential element for humans and animals and plays an important role as the glucose-tolerance factor (GTF) in insulin metabolism [16,17]. Also Cr(III) is considered a micro-nutrient for many living organisms while Cr (VI) is an irritant to plants and animal tissues. The hexavalent form of chromium is also known to be very toxic to humans and causes chronic adverse effects [16]. Cr(VI) is carcinogenic because of its high oxidation potential and its ability to penetrate biological membranes [18,19]. The toxicity of Cr(VI) is as a result of its properties as an oxidant [20]. Trivalent chromium has a low solubility in aqueous medium in alkaline and neutral pH [21,22]. Low solubility of chromium(III) means it will be retained and adsorbed to solid particles or it precipitates [23], thereby making it relatively immobile in the aquatic systems. On the other hand, Cr (VI) is highly soluble and can be transported over a great distance before it is reduced back to the trivalent state. In aqueous solution, the hexavalent chromium species may exist in a variety of oxo-species, namely, dichromate ($Cr_2O_7^{2-}$), hydrochromate ($HCrO_4^-$) or chromate (CrO_4^{2-}) depending on concentration and pH [24–26].

Many sorbent based extraction of chromium have been reported [27–29]. However, very few have been reported on the use of magnetic ion imprinted polymers for the selective removal of Cr(VI) [30–32]. Further, most of the reported studies have not done any detailed selectivity studies on the prepared magnetic ion

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imprinted polymers. This work therefore proposes the use a magnetic polymeric adsorbent, N-propyl quaternized magnetic poly(4-vinylpyridine) for the removal of a hexavalent form of chromium from aqueous solutions. The selectivity and adsorption kinetics of the prepared magnetic ion imprinted polymers is well studied.

2. Experimental

2.1. Chemicals and equipment

2.1.1. Chemicals

For the synthesis of magnetite, $FeCl_2•4H_2O$ and $FeCl_3•6H_2O$, of analytical grades were co-precipitated in the presence of NH_4OH. All chemicals were purchased from Sigma Aldrich (Steinheim, Germany). For the synthesis of the magnetic polymers, the following chemicals were used; ethylene glycol dimethacrylate (EDGMA), benzoyl peroxide, 1-bromopropane, 4-vinylpyridine (4-VP), dimethylformamide (DMF), methanol, surfactant for coating magnetite, γ-methacryloxypropyltrimethoxysilane (γ-MPS) all purchased from Sigma Aldrich (Steinheim, Germany). The imprint, $Na_2Cr_2O_7 \cdot 2H_2O$ was purchased from BDH Chemical Ltd, (Poole, England). All other chemicals used were of the highest analytical grades and were from Sigma Aldrich (Steinheim, Germany).

2.1.2. Preparation of stock solutions

A 1000 mg L^{-1} stock solution of chromium(VI) was prepared by dissolving an appropriate amount of sodium dichromate, $Na_2Cr_2O_7 \cdot 2H_2O$ (analytical reagent grade) in deionized water. Stock solutions of 1000 mg L^{-1} (for selectivity of Cr(VI)-magnetic ion imprinted polymers) were also prepared by dissolving appropriate amounts of the following dried salts in 1 L volumetric flasks: NaF, $NaNO_3$, Na_2SO_4 and $Na_2Cr_2O_7 \cdot 2H_2O$. All salts were purchased from Sigma Aldrich (Steinheim, Germany). Working solutions were prepared daily from the stock solution through serial dilutions. The stock solutions were stored at 4 °C when not in use.

2.1.3. Equipment

Atomic absorption spectroscopy measurements were performed using a PG-990 AAS model from PG Instruments Limited (Leicestershire, UK). Argon was used as a purge gas. All pH measurements were performed on 766 Calimatic pH meter equipped with a Shott N61 pH electrode from Knick (Berlin, Germany). In batch adsorption studies, a Laser Photo/Contact Tachometer DT-1236L from Lutron (Taipei, Taiwan) was used to measure the rotational speed of the magnetic stirrer. Solvent evaporation was done on a Rotavapour II (Buchi, Switzerland). Deionized water was prepared from Millipore instrument (Massachusetts, USA) and was used in preparation of all aqueous solutions. Metrohm 762 Compact Ion Chromatograph (Leonberg, Germany) with a Metrosep A Supp 5 (6.1006.520) 150 × 4.0 mm analytical column was used for the determination of fluoride, nitrate, sulfate and phosphate anions. The eluent solution was made of 1.0 mM $NaHCO_3$ and 3.2 mM Na_2CO_3. The eluent was pumped at 0.7 mL min^{-1}. The suppressor solution was 50 mM H_2SO_4 and deionized water. All the solutions, including eluents used were degassed by ultrasonication and filtered through a 0.45 μm filter paper before being used in the IC.

2.2. Synthesis of magnetic imprinted polymers for Cr(VI) recovery

2.2.1. Synthesis of magnetite

Synthesis *via* the co-precipitation of ferrous and ferric salts in an alkaline medium was used [33]. A volume of 180 mL of an aqueous solution containing 11.2 mmol Fe^{3+} and 5.6 mmol Fe^{2+} was heated to 50 °C. After heating, 12.5 mL of ammonia was added under vigorous stirring. After 30 min, the reaction was heated and kept at 90 °C for 30 min again. An inert atmosphere of N_2 was used for the whole experiment. After completion of the reaction, the black precipitate was collected by an external magnetic field, washed with water and ethanol and dried under vacuum.

2.2.2. Coating of magnetite

Kan et al. [34] approach was used to modify the magnetic nanoparticles with a double bond. In this method, 4 mL γ-MPS was dropwisely added into the mixture of solvents of ethanol and water (1:1, *v*/*v*) containing dispersed Fe_3O_4 nanoparticles and the reaction was carried out for 12 h at 40 °C under N_2 gas. The product was then separated and washed by ethanol for several times and dried under vacuum

2.2.3. Synthesis of magnetic poly(4-vinylpyridine)

Prior to the synthesis of poly(4-vinylpyridine), the monomer, 4-vinylpyridine was distilled at 65 °C to remove the inhibitor, hydroquinone. An amount of 2.5 mg of γ-MPS-coated magnetite was added to a volume of 28 mL of the distilled 4-vinylpyridine. This mixture was then transferred to a 50 mL volumetric flask to which 50 mg benzoyl peroxide was added with magnetic stirring. The flask was then placed into an oil bath at 85 °C for 2 h and then the temperature was elevated to 135 °C were it was maintained for an hour. The whole reaction was performed under an inert atmosphere of nitrogen. The polymerization was then stopped by cooling it to 0 °C. The unreacted 4-vinylpyridine monomers was removed by washing the poly(4-vinylpyridine) with 35 mL of methanol. The free bulk magnetic poly(4-vinylpyridine) polymer was recovered by heating off the methanol solvent at 30 °C by use of a rotary evaporator.

2.2.4. Preparation of magnetic and poly(n-propyl-4 vinylpyridinium) bromide

Quaternization of magnetic poly(4-vinylpyridine) was achieved by refluxing 11.34 g of magnetic poly(4-vinylpyridine) in 40 mL of DMF with a slight stoichiometric excess of 1-bromopropane (10 mL). This reaction was carried out for 42 h at 60 °C.

2.2.5. Preparation of magnetic poly(n-propyl-4-vinylpyridinium) dichromate

Magnetic poly(n-propyl-4-vinylpyridinium) bromide was dissolved in 50 mL of DMF containing 0.34 g of dissolved sodium dichromate. This solution was stirred at room temperature for 2 h. Magnetic poly(n-propyl-4-vinylpyridinium) dichromate was then obtained by driving off the excess solvent by use of a rotary evaporator at 47 °C. The corresponding magnetic NIP was similarly synthesized except that the dichromate imprint was excluded.

2.2.6. Leaching of chromium

After polymerization has ceased, the synthesized magnetic IIP and NIP of chromium were ground and sieved to a particle size range of 27–53 μm range. The particles were then washed repeatedly with de-ionized water to remove all unreacted pre-polymerization reagents. The chromium imprint was then removed by stirring 5 g of the magnetic polymers in 100 mL of 1 mol L^{-1} HCl for 6 h. Magnetic IIP and NIP particles were filtered through a 0.45 μm filter paper. The filtrate was analyzed for chromium content and the residue was subjected to a fresh HCl leachant for the same period of time. This cycle was repeated several times until the chromium content in the filtrate was almost non-detectable.

2.3. Characterization

Surface area of the magnetic polymers was determined by weighing 0.2 g of the sample which was degassed in N_2 at 150 °C for 4 h prior to analysis with the Micromeritics Flow Prep 060 instrument (Aachen, Germany). Fourier-transform infrared spectra were recorded in the frequency range of 400–4000 cm^{-1} using a Bruker FTIR spectrometer, Model Tensor 27 (Ettlingen, Germany) and the spectra were recorded in the solid state. Thermogravimetric analysis for the prepared materials was performed with Perkin Elmer Pyris 1 TGA Thermogravimetric Analyzer (Massachusetts, USA) using nitrogen as the purge gas, at a flow rate of 20 mL min^{-1} and a heating rate of 5 °C/min from 0 to 1000 °C.

2.4. Optimization of parameters for Cr(VI) uptake

Sample pH (2–10), magnetic polymer amount (5–120 mg), contact time (10–75 min) and initial U(VI) concentration (1–20 mg) were optimized. Optimization was achieved by varying one parameter while keeping the others constant. All experiments were carried out in triplicates in batch modes. The influence of these parameters was evaluated by calculating the extraction efficiency or recovery as shown in Eq. (1) below:

$$\text{Extraction efficiency}(\%) = \frac{(C_o - C_e)}{C_o} x\ 100 \tag{1}$$

where C_o (mg L^{-1}) is the initial concentration and C_e (mg L^{-1}) represents the final equilibrium concentration after adsorption. The adsorption capacity, q (mg g^{-1}), is defined as the mass of substrate bound on a gram of adsorbent. Eq. (2) below shows the mathematical equation for the calculation of the adsorption capacity in which C_o (mg L^{-1}) and C_e (mg L^{-1}) are as described for Eq. (1) and V(L) is the volume of the sample solution and W(g) the mass of the adsorbent [35–37].

$$q = \frac{(C_o - C_e)V}{W} x\ 100 \tag{2}$$

3. Results and discussion

3.1. Synthesis and characterization of magnetic Cr(VI) polymers

3.1.1. Synthesis and coating of magnetite

The synthesis of magnetite by co-precipitation of the ferrous and ferric salts produced a black precipitate upon increasing of pH by addition of ammonia. The widely used stober–sol–gel method for coating nanoparticles with silica was used. It relies on the use of silicon alkoxides as the source of silica matrix [34]. These silica matrices were formed through hydrolysis of γ-MPS in basic alcohol/water mixtures. The resultant silanol groups then bonded covalently with the hydroxyl groups around the magnetite.

3.1.2. Synthesis of magnetic poly(4-vinylpyridine)

Poly(4-vinylpyridine) has been prepared, but in most cases, it is non-magnetic. For example, Toral et al. [38], synthesized poly-(4-vinylpyridine) with an average molecular weight 60,000 g mol^{-1}. Bicak and Gazi [39] also synthesized this polymer in their study of quantitative quaternization of poly(4-vinylpyridine). In both cases, their proposed structure of the homopolymer was similar to the one depicted in Fig. 1. The expanded structure of 4-vinylpyridine copolymerized with γ-MPS-functionalized magnetite is shown in Fig. 1.

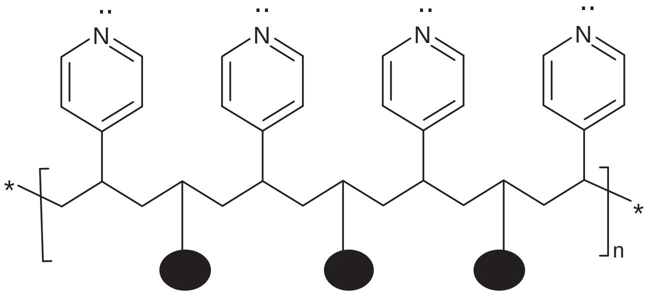

Fig. 1. Structure of magnetic poly(4-vinylpyridine) where the black dots represent γ-MPS-functionalized magnetite.

3.1.3. Quaternization of magnetic poly(4-vinylpyridine) and FTIR characterization

In order to remove metallic oxy-anions in aqueous environments, a positive charge has to be introduced by contacting poly (4-vinylpyridine) particles with acids such as hydrochloric acid [40]. However, in order to introduce a permanent positive charge in the polyelectrolyte, a reaction with an alkyl group was chosen in this study. N-propyl reacted with the pyridine nitrogen to give quaternized magnetic poly(4-vinylpyridine). In order to have a high positive charge building up in the polymer, a solvent of high dielectric constant should be used [41]. In this work, DMF was used as a solvent and the bromide ions formed diffused away from the pyridinium ions of the cationic polyelectrolyte. Due to the neighboring group effect, quaternization of the poly(4-vinylpyridine) does not occur with quantitative conversions and typically, 65–70% quaternization are most common with most alkyl halides [42]. However, in their research, Bicak and Gazi [39] found out that methyl iodide is likely to give high quaternization yields of up to 95%. Another reason of not achieving 100% quaternization was discussed by Sonmez and Bicak [43]. They pointed out that some small percentages of pyridine groups remain embedded deep in the polymer matrix and may remain unreacted. Hence the reaction to introduce a charge on the polyelectrolyte only represents quantitative quaternization of the pyridine rings in accessible positions of the cross-linked matrix.

Fourier-transform infrared analysis was carried out to estimate the degree of quaternization. During alkylation of magnetic poly (4-vinylpyridine) with N-propyl bromide, aliquots of the solutions were withdrawn at 14 h intervals and purged with nitrogen to form a viscous solution. This was then FTIR analyzed to check the shift of the band at 1600 cm^{-1}. In quaternization of magnetic poly (4-vinylpyridine), a C=N band in pyridine, usually at 1600 cm^{-1}, was displaced to higher wavenumbers to 1636 cm^{-1}, Fig. 2. These results were consistent with those obtained by Li et al. [44] who obtained a shifted value of 1636 cm^{-1}. This was also in agreement with reports of the quaternization reaction by the introduction of a positive charge to form a pyridinyl ring in the polymer structure [45,46]. Additionally, the intensity of the band at about 1560 cm^{-1}, as shown in Fig. 2 corresponds to positively charged nitrogen atoms.

3.1.4. Addition of the dichromate imprint to the quaternized magnetic poly(4 vinylpyridine)

The dichromate displaced the smaller bromide anion from the magnetic polymer backbone and that was the start of the formation of micro-cavities that were specific for the dichromate ion. Evidence of the embedding of dichromate into the magnetic polymer is shown by the resonance peak of the Cr–O and Cr=O bonds at 943 cm^{-1} in the spectra in Fig. 3. In two separate studies

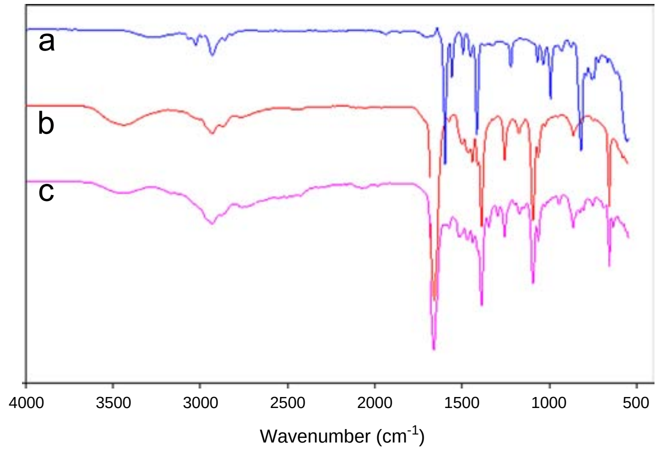

Fig. 2. FTIR spectra of quaternized magnetic poly(4-vinylpyridine) after (a) 0 h, (b) 14 h and (c) 42 h.

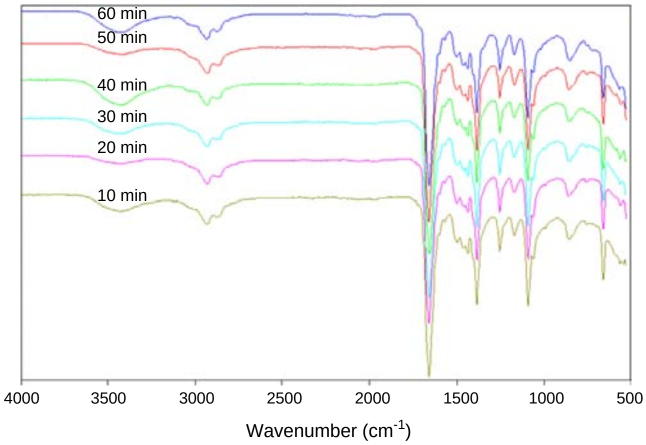

Fig. 3. FTIR spectra of quaternized magnetic poly(4-vinylpyridine) after addition of $Na_2Cr_2O_7$.

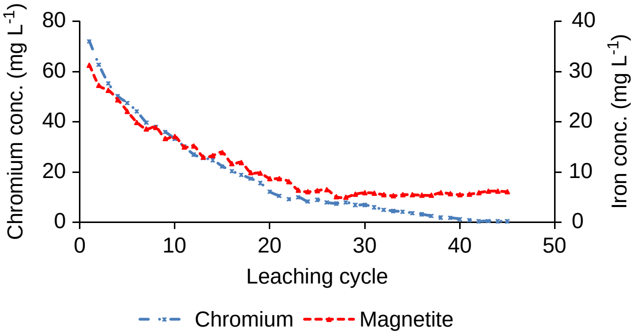

Fig. 4. Leaching of chromium and iron from the magnetic IIP.

Table 1
BET areas and constants for the magnetic polymers.

Magnetic polymer	BET surface area (m² g^{-1})	v_m	c
Unleached	1.0	0.23	8.71
Leached	16.8	7.7	124

by Arslan et al. and Ortiz-Palacios [47,48] these resonance peaks were assigned to 943 and 934 cm^{-1} respectively.

3.1.5. *Cross-linking and leaching of dichromate from the magnetic polymers*

For structural rigidity, EGDMA cross-linking monomer was used. This ensured that the magnetic polymers were not dissolved in solution during their applications in adsorption studies. After cross-linking, the magnetic polymers were leached with HCl for many cycles as illustrated in Fig. 4. Leaching was only stopped after the chromium content was not detected. The magnetic polymers were then conditioned with deionized water in order to remove all the excess chloride ions from HCl leachant and dried in the oven at 50 °C for 12 h.

The magnetite was observed washing away from the polymeric matrix. This was in parallel with the leaching of the chromium to form pores within the magnetic polymer matrix. However, it is important to note that the magnetite was not totally washed away otherwise it would have defeated the whole purpose of the project of making the polymers magnetic.

3.1.6. *Brunauer, Emmett and Teller (BET) surface analysis*

The adsorption data in the relative pressure (p/p_o) range 0.05–0.35 was fitted to the BET model and gave good linear plots. As for the unleached magnetic poly(n-propyl-4-vinylpyridinium) dichromate polymer, c was 8.71 and v_m was 0.23. The surface area for the unleached magnetic poly(n-propyl-4-vinylpyridinium) dichromate polymer was found to be 1.00 ± 0.02 m^2 g^{-1}. After leaching of the chromium from the magnetic IIP, there was an increase in the surface area to 16.8 ± 1 m² g^{-1} which corresponded to 16.8% increase. The BET constants, c and v_m for the leached magnetic NIP were found to be 124 and 7.7 respectively. All the BET surface areas and constants for the magnetic polymers are summarized in Table 1. This was consistent with the findings of other studies, like that from Bayramoglu and Arica [49] who found that the specific surface area of the IIP and the corresponding NIP particles to be 34.5 m^2 g^{-1} and 21.7 m^2 g^{-1}, respectively, which indicated the presence of microporous on the surface of the Cr(VI)-imprinted particles.

3.1.7. *Thermo-gravimetric analysis (TGA)*

In order to gain insight into the structural information for the magnetic polymers, the thermal stability was probed with TGA (data not shown). The maximum weight loss occurred at 425 °C, corresponding to degradation of the polymer backbone, and a small peak that occurred at around 220 °C was attributed to the loss of moisture from the magnetic polymers. It was also observed from the TGA spectrum of the Cr(VI) loaded magnetic polymer that the maximum weight loss due to the decomposition of the backbone occurred at a slightly lower temperature. This indicated that the unleached magnetic polymer was slightly more stable than the leached one. It was also observed that the leached and unleached Cr(VI) magnetic polymers had total weight losses of 82.5% and 59.2%, respectively. The remaining mass corresponded to the presence of Cr(VI) and magnetite in the unleached magnetic polymer and magnetite in the leached magnetic polymer. In almost similar studies by Toral et al. [38], where they quaternized the polymer with an octyl moiety, the stability of the Cr(VI) loaded polymer was also stable as compared to the leached one. The decomposition of the two polymers occurred at around 500 and 400 °C respectively. However, in terms of the residual weight of the leached polymer, they found it to be close to 100%. In this work it was observed to be 59.2% because of the embedded magnetite in the polymer matrix.

3.2. *Optimization for maximum adsorption*

3.2.1. *Effect of sample pH*

The effect of pH on the removal of Cr(VI) was investigated in the pH range of 2–10 at room temperature. The experimental results are presented in Fig. 5 where it was observed that the maximum adsorption occurred in the pH range 2–6. The optimum pH for the uptake of Cr(VI) was then chosen to be 4 which corresponded to 90% and 73% Cr(VI) removal for the magnetic IIP and NIP, respectively. The Cr(VI) extraction efficiency decreased at pH values greater than 6 for both the magnetic IIP and its control polymer. Beyond this pH, there was an anticipated strong competition between hydroxyl ions and the dichromate ions in solution. These two anions compete for the fabricated active adsorption sites on the magnetic polymers.

Similar results were obtained by Bayramoglu and Arica [49] who showed that at high acidic pH of 2–4, adsorption was very high and decreased rapidly after pH 5. However, they did not quaternize their polymers but rather used 4-VP as a functional monomer. Their Cr(VI)-ion imprinted poly(4-vinyl pyridine-co-2-hydroxyethyl methacrylate) particles were prepared by bulk polymerization. On poly(4-vinylpyridine) coating onto a granular activated carbon Fang et al. [50] observed a 90% Cr(VI) removal at a pH of 2 which was almost maintained but decreased sharply at pH 6–8 and no apparent sorption was observed when pH was above 9. After firstly forming a linear copolymer from 4-VP and styrene, Pakade et al. [51] prepared an IIP selective of Cr(VI) by quaternizing the linear copolymer with 1,4-dichlorobutane. The pH trend they got did not show a drop in Cr(VI) absorption after pH 4–5 because the pH they used only ranged from 1 to 4.

3.2.2. *Effect of the amount of the adsorbent*

The removal of chromium by magnetic polymers at different adsorbent doses (5–120 mg) from a Cr(VI) concentration of 5 mg L^{-1} was investigated. The results (Fig. 6) showed that, initially, the extraction efficiency of Cr(VI) increased with the increase in the dose of magnetic polymers due to the greater availability of the adsorption sites within the adsorbent. For the magnetic IIP, the increase in adsorbent dosage from 5 to 20 mg resulted in an increase from 47% to 95% in extraction efficiency of Cr(VI) ions whilst an increase from 83% to around 90% was observed for the dose from 5 to 65 mg for the magnetic NIP. The optimum amounts of the magnetic polymers were then chosen to be 20 and 65 mg for the magnetic IIP and NIP, respectively as there was no significant increase beyond these weights. Considering an initial volume of 25 mL for both the magnetic IIP and NIP, the normalized volume became 0.8 g L^{-1} and 2.6 g L^{-1}, respectively. Magnetic NIP required more sorbent amount because it had no specific binding cavities for Cr(VI) adsorption.

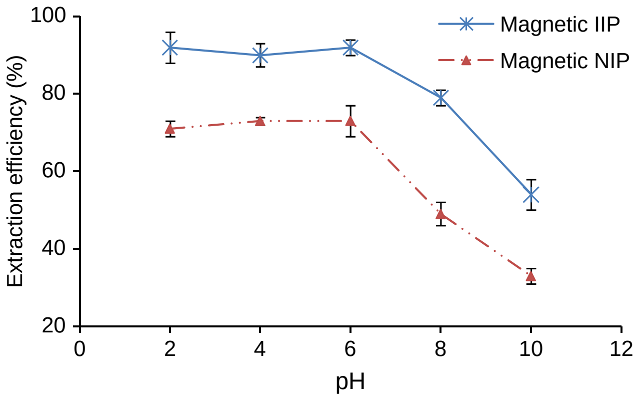

Fig. 5. Effect of sample pH. Experimental conditions: polymer amount, 20 mg; sample volume, 25 mL; chromium concentration, 5 mg L^{-1}; contact time, 45 min; stirring speed, 600 rpm; temperature, room temperature.

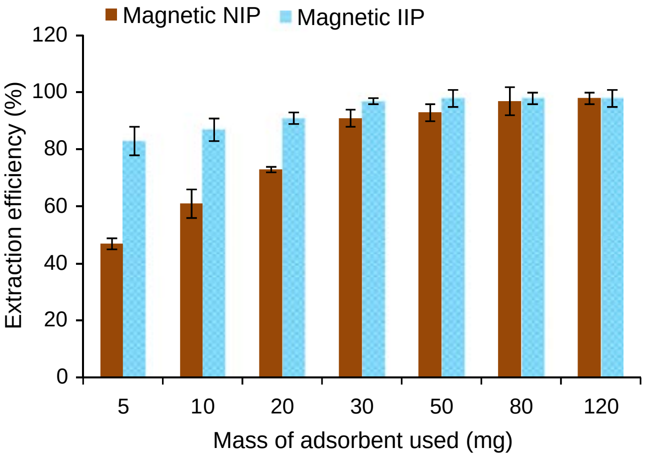

Fig. 6. Chromium extraction efficiency obtained by varying the mass of magnetic polymers. Experimental conditions: sample pH, 4; sample volume, 25 mL; chromium concentration, 5 mg L^{-1}; contact time, 45 min; stirring speed, 600 rpm; temperature, room temperature.

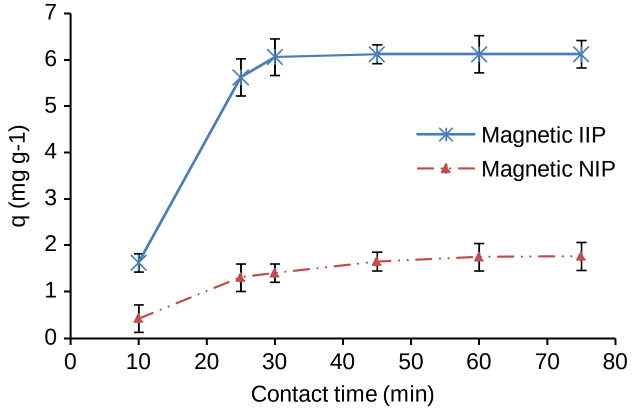

Fig. 7. Effect of contact time on the uptake of chromium by magnetic polymers. Experimental conditions: sample pH, 4; sample volume, 25 mL; chromium concentration, 5 mg L^{-1}; polymer weight, (20 mg for magnetic IIP and 65 mg for magnetic NIP); stirring speed, 600 rpm; temperature, room temperature.

Investigating the effect of polypyrrole embedded with Fe_3O_4 nanocomposite dosage on adsorption of Cr(VI) from aqueous solution showed that Cr(VI) extraction efficiency increased with an increase in Fe_3O_4 endowed polypyrrole dose [52]. The extent of Cr(VI) removal from 50 mL of 200 mg L^{-1} Cr(VI) solution changed from 16.3% at a dose of 25 mg to 100% at a dose of 100 mg which is equivalent to an optimum of 2 g L^{-1} of Fe_3O_4 embedded polypyrrole. In the study by Hadjmohammadi et al. [53], who used pine needles powder as a biosorbent, the uptake of Cr(VI) from 50 mL of 50 mg L^{-1} solutions, the adsorbent dose reached a plateau at 0.5 g of sorbent which translated to a normalized volume of 10 mg L^{-1}. Using tetraethylenepentamine on Fe_3O_4 magnetic polymer adsorbent, Yao et al. [54] found a proportion of 20 mg per 250 mL (0.8 mg L^{-1}) water sample would ensure efficient pre-concentration of Cr(VI).

3.2.3. *Effect of contact time*

Cr(VI) removal by magnetic polymers as a function of contact time is shown in Fig. 7. The rate of $Cr_2O_7^{2-}$ uptake was average and the maximum uptake was observed within 30–35 min for both the magnetic IIP and NIP. Before this time, there was a high rate of

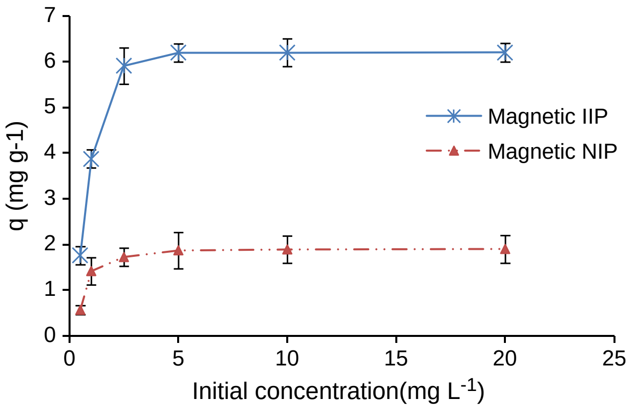

Fig. 8. Effect of initial concentration on the uptake of chromium by magnetic IIP and NIP.

accumulation of the analyte in the adsorption sites within the magnetic polymer matrix. After reaching equilibrium, there was no further increase of adsorption of Cr(VI) as all the adsorption sites were saturated. A similar trend was observed by Yao et al. [54] who used tetraethylenepentamine on Fe_3O_4 magnetic polymer as an adsorbent. Their results showed that the rate of Cr(VI) uptake was initially high, followed by a much slower subsequent adsorption quantity leading gradually to an equilibrium condition. A contact time of 35 min of stirring was considered enough to reach maximum values of separation and pre-concentration of Cr (VI) ions [54]. This short extraction time meant that the prepared magnetic ion imprinted polymer displayed a fast mass transfer for chromium.

3.2.4. *Effect of initial Cr(VI) concentration*

The results obtained for the effect of initial concentration on the uptake of chromium by magnetic IIP and NIP are presented in Fig. 8. An initial chromium concentration of 1–20 mg L^{-1} was investigated. In this experiment, the magnetic polymer dose was fixed as well as the contact time and solution pH of which the values are indicated in the caption of Fig. 8. It was observed that the magnetic polymers' Cr(VI) removal roughly increased significantly from 1 to 2.5 mg L^{-1} and 1 to 1.5 mg L^{-1} for the magnetic IIP and NIP, respectively. An initial Cr(VI) concentration of 5 mg L^{-1} was taken to the optimum. After this value, equilibrium was attained as there was no appreciable increase in the amount of the analyte adsorbed on the magnetic polymers. The maximum adsorption capacities for the magnetic polymers corresponding to the considered optimum Cr(VI) concentration of 5 mg L^{-1} were 6.20 and 1.87 mg g^{-1} for the magnetic IIP and NIP, respectively.

3.3. *Kinetic and adsorption modeling*

3.3.1. *Pseudo-first and second order kinetics*

The correlation coefficients values for the pseudo-first and second order kinetics were calculated from the plots like the one shown in Fig. 9. From the graphs, it was observed that correlation coefficients values of the pseudo-second order kinetics produced better quality of linearization compared to the pseudo-first order kinetics.

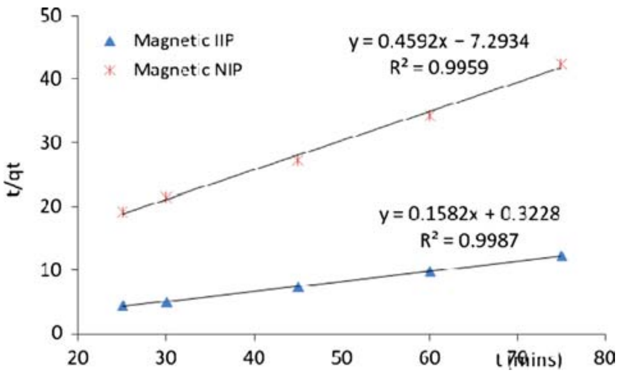

Fig. 9. Pseudo second-order plots for the adsorption of chromium onto magnetic polymers.

Table 2
Calculated kinetic parameters of pseudo-first and pseudo-second orders for initial Cr(VI) concentration of 5 mg L^{-1}.

Polymer	Pseudo first-order			Pseudo second-order		
	R^2	k_1 (L min^{-1})	q_e (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1})
IIP	0.9114	0.121	11.256	0.9987	0.078	3.098
NIP	0.9808	0.083	3.682	0.9959	0.029	2.178

Table 3
The Langmuir and Freundlich constants for adsorption of Cr(VI) on magnetic polymers.

Magnetic polymer	Langmuir isotherm				Freundlich isotherm		
	b (L g^{-1})	q_m (mg g^{-1})	R_L	R^2	n	K_f (L g^{-1})	R^2
Cr-IIP	4.23	3.8	0.05	0.881	2.23	2.90	0.841
Cr-NIP	1.67	2.3	0.11	0.992	2.59	0.78	0.911

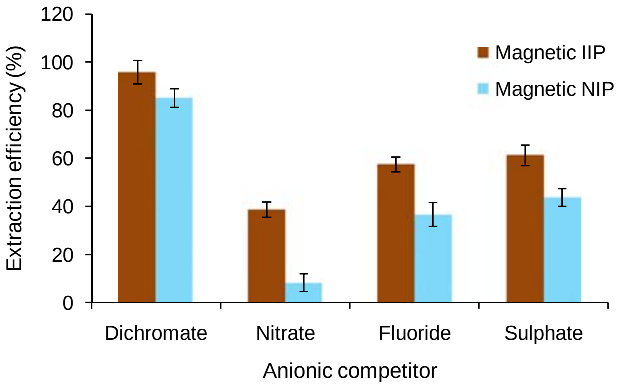

Fig. 10. Extraction efficiencies of anions extracted by the magnetic Cr(VI) IIP and NIP from 2 mg L^{-1} spiked binary mixtures of solutions.

From Table 2, the adsorption capacity values obtained by this method were much closer to those reported before in this work (6.20 and 1.87 mg g^{-1} for the magnetic IIP and NIP, respectively). A pseudo-second order further suggests that the type of interaction between the target template and the adsorbent surface was chemisorption as a rate controlling step [24]. This interaction was probably due to the exchange of electrons on the dichromate and the quaternized nitrogens.

3.3.2. *Freundlich and Langmuir isotherm modeling*

In order to find out whether Cr(VI) adsorption on the surface of the prepared magnetic polymer was monolayer or multilayer,

Table 4
K_d, K and K' values for the magnetic Cr(VI) IIP and NIP in binary mixtures.

$Cr_2O_7^{2-}$ ion competitor	K_d (L g^{-1})				K		K'
	$Cr_2O_7^{2-}$ IIP	$Cr_2O_7^{2-}$ NIP	Magnetic IIP	Magnetic NIP	Magnetic IIP	Magnetic NIP	Magnetic NIP
SO_4^{2-}	11.70	3.06	1.98	0.30	5.91	10.20	0.58
F^-	23.50	1.90	1.69	0.22	13.91	8.64	1.61
NO^{3-}	33.00	5.53	0.79	0.035	41.77	158	0.26

Freundlich and Langmuir isotherm modeling were done on the adsorption data. The results, summarized in Table 3, indicated that neither model was perfectly followed. The reason for this is unclear, perhaps other isotherm models not tested were followed, like the Elovich kinetic model, intraparticle diffusion, the Weber–Morris kinetic model, the film diffusion model according to the Reichenberg equation, the film diffusion model according to Vermeulen's approximation [55–57].

3.4. Selectivity of Cr(VI)

Competing anions are known to influence Cr(VI) uptake. However, because HCl was used as a leachant, it was likely that the chloride ion would have interfered with the selectivity studies, hence it was not used. The other ions selected, such as the sulfate and phosphate ions were selected as potential competitors because of their chemical similarities to the dichromate ion with respect to charge and oxy-ionic nature. The selectivity performances of the magnetic polymers are summarized in Fig. 10 and Table 4. The order of selectivity of the investigated anions followed the sequence $Cr_2O_7^{2-} > SO_4^{2-} > F^- > NO_3^-$.

Pakade et al. [51] investigated the influence of coexisting ions on the uptake of Cr(VI) onto 1,4-dichlorobutane quaternized linear copolymer. Their findings were that the selectivity order was $Cr_2O_7^{2-} > SO_4^{2-} > F^- > PO_4^{3-} > NO_3^- > Cl^-$. After considering two Cr(VI) competitors, Neagua and Mikhalovsky [24] found that there was also a rather remarkable selectivity towards hexavalent chromium over the sulfate anion. The full order of selectivity was $Cr_2O_7^{2-} > SO_4^{2-} > Cl^-$ which was almost what was obtained in this study. However, the same authors reported that the adsorption selectivity for the common anions onto commercial styrene anion exchangers and it followed the order $SO_4^{2-} > I^- > Cr_2O_7^{2-} > Br^- > Cl^-$. Fang et al. [50] also performed some selectivity studies on three competitor ions for Cr(VI) and found the selectivity order of $Cr_2O_7^{2-} > PO_4^{2-} > SO_4^{2-} > NO_3^-$. For the two Cr(VI) competitors investigated by Bayramoglu and Arica [49], it was demonstrated that (4-vinyl pyridine-co-hydroxyethyl methacrylate) particles showed excellent selectivity for Cr(VI) and the adsorption capacity of IIP particles for Cr(VI) anions was 13.8 and 11.7 fold greater than those of the Cr(III) and Ni(II) ions, respectively.

3.5. Reusability of Cr magnetic polymers

Since the reusability of the magnetic polymers is an important factor, six adsorption–desorption cycles were performed (data not shown). What was observed is that the magnetic polymers maintained their stability as well as their chromium abstraction capacity of 98.5% and 89% for the magnetic IIP and NIP, respectively. This high robustness of the imprinted polymers has the significance that they can be cleaned, thereby regenerating their adsorption capabilities. For up to 5 cycles, the IIP synthesized by Pakade et al. [51] was still stable as it showed 96% extraction efficiency.

4. Conclusions

Quaternization enabled the preparation of magnetic ion imprinted polymers for Cr(VI). Both magnetic IIP and NIP showed potential in the uptake of uranium and chromium from aqueous solutions. Magnetic IIPs always expectedly showed a higher dichromate uptake as compared to their corresponding magnetic NIPs.

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