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Heavy metal removal from waste waters by phosphonate metal organic frameworks

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Abstract: The increase attention in the area of phosphonate metal organic framework is exemplified with a variety of applications and a rich chemistry of these compounds. Water pollution caused by heavy metal ions is a major concern due to their toxicity to many life forms. In order to decrease the heavy metals impact upon the environment various technologies of water treatment such as: chemical sedimentation, ion exchange, redox process are studied. The tendency is to find a versatile and economical method of heavy metals removal from waste waters. Phosphonate metal organic frameworks were obtained by the reaction of $Ni(CH_3COO)_2 \cdot 4H_2O$, phosphonic acid (phosphonoacetic (CP), vinyl phosphonic acid (VP) and N,N-bis(phosphonomethyl)glycine (Gly)) in hydrothermal conditions. Coordination polymers synthesized were characterized by FTIR, XRD, scanning electron microscopy (SEM) and thermal gravimetric analysis (TGA). The adsorption processes represent a very good alternative for heavy metals removal due to low costs and ease of operation. In the present paper the adsorption performance of the mentioned materials in the removal process of heavy metals from aqueous solutions, was studied using the batch method. The adsorption conditions were investigated by varying the initial pH, contact time and adsorbate initial concentration for chromium metal ions removal from aqueous solutions. It was found that the adsorption efficiency of the studied materials in the removal process of Cr(VI) ions from aqueous solutions is in the following order: Ni-CP < Ni-Gly ≤ Ni-VP.

Keywords: adsorption; ICGC-6; phosphonate metal organic frameworks; waste waters.

Dedicated to: the 150th anniversary of the Romanian Academy.

Introduction

Heavy metal contamination in aqueous environment has turn out to be a serious warning due to the rapid increase of industrial and removal activities being highly toxic to living organisms even at low concentrations [1, 2]. Among numerous heavy metal ions, chromium is known to be a typical heavy metal contaminant and significantly damages ecosystems. Hexavalent chromium (Cr(VI)) is generally more toxic than Cr(III) and can be easily absorbed and accumulated in human body. The efficient elimination of chromium from wastewater released after industrial and mining processes is required.

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The main sources chromium release are from industrial production processes such as electroplating, leather tanning, textile industries metal finishing, nuclear power plant, and chromate preparation [3, 4]. Solid wastes from chromate-processing facilities, can be sources of pollution for groundwater, where the chromium deposit time might be several years. For this reason heavy metal ions are tending to accumulate in the environment thus employing the negative affect on the environments and ecosystems.

A variety of methods for chromium removal from wastewater have been explored over the past decade. The conventional methods of chromium removal from water include reduction and precipitation, ion exchange, adsorption, etc. Some of those sorbents exhibit moderate affinity/selectivity for Cr(VI), which have mainly limited their effectiveness and efficiency for the removal of Cr(VI) from aqueous solutions. Adsorption technique has been extensively applied to take away heavy metal ions from waste water. Numerous materials have been used as adsorbents for the removal of Cr(VI) processes including activated carbon, modified activated charcoal, activated neem leaf powder, wheat bran, and groundnut shell powder were used as adsorbents for effective removal of Cr (VI), biogenic iron based nanoparticles, biopolimers, magnetic nanoparticles, metal organic frameworks [5–14].

Metal– organic frameworks (MOFs), a new type of porous materials with fascinated structure and topology have gained considerable attention in the last period. They are form from inorganic metal ions linked by organic ligands through coordination bonds. Several research groups explored the utilization of MOFs for the removal of heavy metal ions from aqueous solutions [15–18].

In our previous work we described the synthesis and characterization of materials of phosphonates metal organic frameworks [19–22]. Starting from various ligands with one phosphonate moiety – vinyl phosphonic acid, a carboxy-diphosphonate ligand – N,N-bis(phosphonomethyl) glycine and a carboxy-phosphonate ligand – phosphonoacetic acid with $Ni(CH_3COO)_2 \cdot 4H_2O$, three phosphonate metal organic frameworks were synthesized [23–25]. The structure, morphology and properties of materials were investigated by FTIR, XRD, scanning electron microscopy (SEM) and thermal gravimetric analysis (TGA).

The adsorption performance of nickel phosphonates materials is described. The effect of pH, chromium initial concentrations and contact time upon the adsorption properties.

All synthesized compounds were not studied as adsorbants till now and this is an attractive investigation also due to their possible further utilization of the exhausted adsorbant as catalyst [26].

Experimental

Synthesis of phosphonate metal organic frameworks

A 100 mL round-bottomed flask was charged with $Ni(CH_3COO)_2 \cdot 4H_2O$ (50.0 mmol), phosphonoacetic, N,N-bis(phosphonomethyl)glycine or vinylphosphonic (50.0 mmol), urea (50.0 mmol), and distilled water (100 mL). The pH was adjusted to 4.5 in the case of Ni-CP and Ni-Gly and 2.8 in the case of Ni-VP with an aqueous solution of NaOH (0.1 M). The solution was heated in an oil-bath at 80 °C for 75 h. The resulting crystals were collected by filtration, washed with distilled water and dried in air (yield: 52–75 %) [19, 22–25].

Instrumentation

Thermal analysis (TG-DTA) data were recorded on an SDT-Q600 analyzer from TA instruments. A Perkin Elmer Diamond thermogravimetric analyzer was used applying temperatures between 30 and 650 °C under a flow of N_2 with a heating rate of 10 °C/min. FTIR spectra were recorded on a Jasco-FT/IR-4200 instrument in the range 400–4000 cm^{-1} using the KBr pellet method. Using a pH HI 2221 Calibration Check pH/ORP Meter by Hanna Instruments, solutions pH was measured.

The X-ray diffraction patterns were recorded by using a Rigaku Ultima IV X-ray diffractometer (40 kV, 40 mA) with CuKα radiation ($\lambda = 0.15406$ nm).

SEM images were recorded using a Quanta FEG 250 microscope, equipped with a ZAF type EDAX quantifier.

Adsorption studies

The studied materials were used in the removal process of different metal ions (Pb(II), Cd(II) and Cr(VI)) from aqueous solutions. The adsorption process was conducted in batch mode using an initial concentration of metal ions of 30 mg/L and a S:L ratio of 2 g/L. The samples were stirred for 1 h at 200 rpm using a Julabo SW23 shaker bath. After elapsed time the residual concentration of the metal ions were analyzed using a Varian SpectrAA 280 FS atomic adsorption spectrophotometer.

A detailed adsorption study was conducted in the case of Cr(VI) removal from aqueous solutions. Effect of pH, Cr(VI) initial concentration and shaking time upon the adsorption efficiency was investigated. For these purposes a stock solution of 1 g/L of Cr(VI) was prepared by dissolving calculated amount of potassium dichromate ($K_2Cr_2O_7$)in distilled water. This was then used as a stock solution.

In order to investigate the influence of the initial pH of Cr(VI) solution, upon the adsorption capacity of Ni(II) based phosphonate metal organic frameworks, 25 mL of synthetic water sample containing 30 mg/L Cr(VI)and different initial pH (range: 1–7) was added to a calculated amount of adsorbent in order to have a solid:liquid (S:L) ratio of 2 g/L. The pH adjustment of the solution was done using 1.0 M NaOH and 1.0 M HCl. The samples were stirred for 1 h at constant speed (200 rpm). After the time elapsed the samples were filtered and the residual concentration of Cr(VI) ions was analyzed in the filtrate.

In order to study the effect of contact time upon the adsorption capacity of the studied materials, the experiments were carried out using a S:L ratio of 2 g/L and a 30 mg/L Cr(VI) solutions, varying the contact times (15–180 min) between the adsorbents and adsorbate.

The effect of Cr(VI) initial concentration was investigated using 0.05 g of adsorbent suspended in 25 mL of Cr(VI) solution of different concentration (range: 2.5–250 mg/L). The suspensions were stirred for 1 h at room temperatures, after the completion of experiment, the suspensions were filtered and analyzed for Cr(VI) residual concentration.

The amount of pollutant adsorbed onto Ni(II) based phosphonate metal organic frameworks was calculated from equation (1):

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \tag{1}$$

where: q_e is the amount of the pollutant adsorbed on the studied materials (mg/g); C_o and C_e represents the initial and equilibrium concentration of the pollutant in the solutions (mg/L), respectively. V is the volume of the solution (L) and m is the mass of the adsorbent (g) used in the experiments.

Modeling

To evaluate the maximum adsorption capacity of the studied materials developed in the removal process of Cr(VI) from aqueous solutions and the adsorption mechanism, the experimental data were fitted with the Langmuir and Freundlich adsorption models and with the pseudo-first order and pseudo-second order kinetic models.

Adsorption isotherm describes the relationships between adsorbent and adsorbate. For single solute systems, Langmuir and Freundlich isotherm are the most widely used adsorption models [27–29].

The Langmuir isotherm assumes that the adsorbent has a uniform surface with a finite number of adsorption sites and the adsorption take place only on one layer. When the monolayer is saturated, the maximum adsorption occurs. In addition the model assumes that the adsorbate molecules cannot migrate on the adsorbent surface, the energy of adsorption being constant [27–29]. The linear form of Langmuir isotherm is described by the Equation (2):

$$\frac{C_e}{q_e} = \frac{1}{K_L \cdot q_m} + \frac{C_e}{q_m}, \tag{2}$$

where: q_e is the amount of Cr(VI) adsorbed per gram of adsorbent, i.e. metal uptake (mg/g), and C_e is the equilibrium concentration of adsorbate in the bulk solution after adsorption (mg/L). q_m is the measure of the monolayer sorption capacity (mg/g) and K_L denotes the Langmuir isotherm constant related to the affinity between adsorbent and the adsorbate (L/mg). The values of q_m and K_L can be determined by plotting C_e/q_e versus C_e.

Contrary the Freundlich isotherm assumes the heterogeneity of the surface and the exponential distribution of active sites and their energies [28]. The linear form of Freundlich isotherm is expressed as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e, \tag{3}$$

where: K_F and n are Freundlich constants, which represent adsorption capacity (mg/g) and adsorption intensity, respectively. The values can be calculated from the intercept and slope of logarithmic plot of q_e against C_e.

Adsorption kinetics describes the adsorption mechanism of metals on adsorbents and the metal adsorption rate which controls the contact time of metals at the solid-liquid interface [28].

The pseudo-first-order kinetic model can be expressed linearly as [27–29]:

$$\ln(q_e - q_t) = \ln q_t - k_1 \cdot t, \tag{4}$$

where: q_e and q_t are the amount of the Cr(VI) adsorbed onto the studied materials (mg/g) at equilibrium and after time t, respectively. t is the contact time (min), k_1 is the specific sorption rate constant (min^{-1}). The values of the adsorption rate constant (k_1) were determined from the $\ln(q_e - q_t)$ in terms of t.

The pseudo-second order model is based on the solid phase adsorption and assumes that the chemisorption is the rate controlling step. The model can be expressed in its linear form as [29]:

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e}, \tag{5}$$

where: q_e and q_t are the amount of the Cr(VI) adsorbed onto the studied materials (mg/g) at equilibrium and at time t, respectively. t is the contact time (min), k_2 is the pseudo-second-order adsorption rate constant [g/(mg · min)]. From the slope and intercept of (t/q_t) versus t plot can be determined q_e and k_2 parameters.

Results and discussion

Materials characterization

The structure, morphology, and properties of phosphonates metal organic frameworks were investigated by FTIR, XRD, scanning electron microscopy (SEM) and thermal gravimetric analysis (TGA).

The FT-IR spectrum of Ni-Gly ($Ni(C_4H_9O_8NP_2) \cdot 2H_2O$) shows strong absorptions for the active groups. Symmetric and antisymmetric vibrations for the carboxylate group of the coordinated N,N-bis(phosphonomethyl) glycine ligand dominated the spectrum. Antisymmetric stretching vibrations were present for the deprotonated

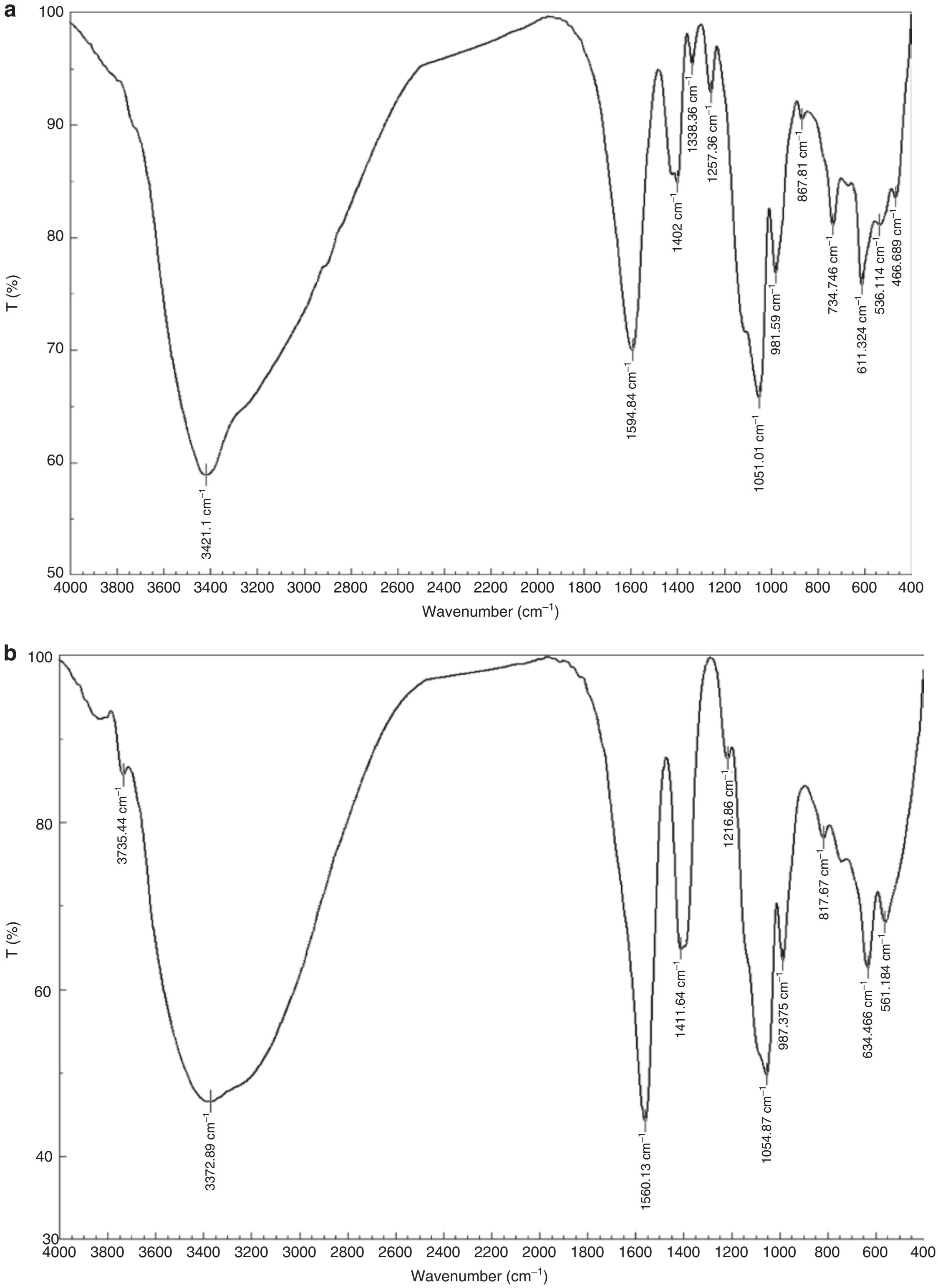

Fig. 1: The IR spectra of the obtained materials: (a) Ni-Gly, (b)Ni-CP.

carboxyl group around 1560 cm^{-1}. Symmetric vibrations for the same group appear at 1411 cm^{-1}. The presence of a broad band at 3372 cm^{-1} is due to the stretching vibration of the water molecule OH coordinated to the central nickel atom, (Fig. 1a) [24]. The Ni-CP $[\mathrm{Ni(O_2C{-}CH_2PO_3)_2 \cdot 2H_2O}]$ spectrum shows the asymmetric and symmetric

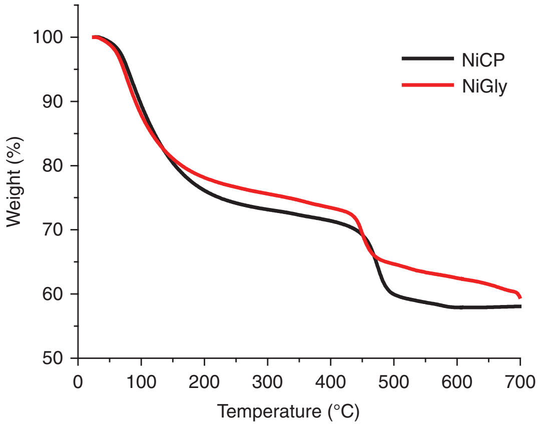

Fig. 2: Thermal behaviour of Ni-CP and Ni-Gly.

vibrations of the carboxylate group at 1594 and 1402 cm^{-1}, respectively, the vibrations of the phosphonic group in the region 1000–1100 cm^{-1} and the typical broad band of the coordinated water around 3421 cm^{-1}. The absence of a band in the region 1800–2600 cm^{-1} (the O–H vibration of a COOH group) is in agreement with a deprotonated carboxyl group (Fig. 1b). The FTIR spectra of Ni-VP (Ni($C_2H_3PO_3$) · H_2O) confirms the formation on Ni(II)

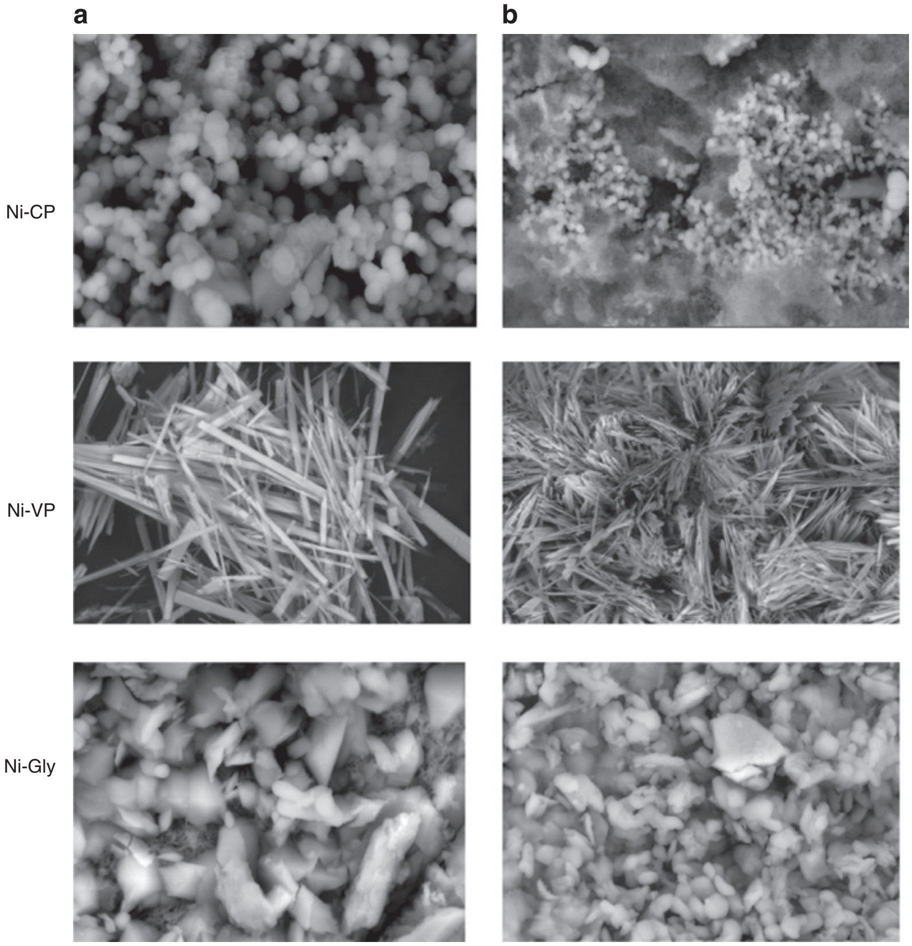

Fig. 3: SEM images of the studied materials before (a) and after (b) adsorption of Cr(VI).

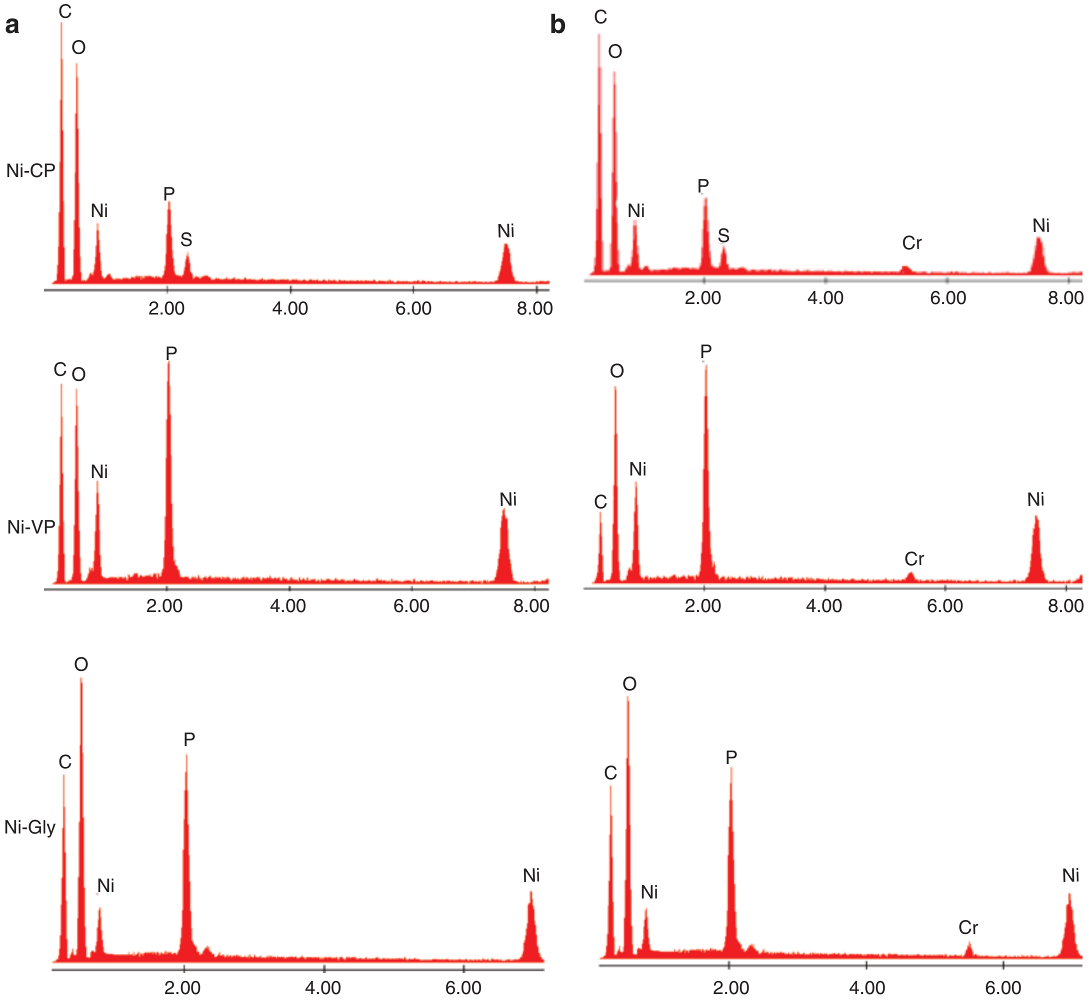

Fig. 4: EDX spectra of the studied materials before (a) and after (b) adsorption of Cr(VI).

based phosphonate metal organic framework due to the absence of the peak at 2300–2900 cm^{-1} attributed to P-OH vibrations. Detailed charaterization of Ni-VP compound was previously described [20].

Thermogravimetric analysis of Ni-CP compound shows a first weight loss in mass before 100 °C and a loss between 100 and 250 °C that marks the expulsion of water molecules of crystallization. This process was simultaneous with P–C bond scission and the decomposition of the compound. In the case of Ni-Gly ($Ni(C_4H_9O_8NP_2) \cdot 2H_2O$) removal of water starts immediately upon heating in and is lost slowly between until 300 °C, followed by decomposition at ~400 °C. The total weight loss caused by decomposition of all the organic composition of Ni-CP and Ni-Gly is around 41 % and is reached at approximately 700 °C, suggesting an endothermic process. The small number of detected TGA peaks reflects simple mechanisms of decomposition for both compounds (Fig. 2).

The morphology of the obtained materials before and after adsorption of Cr(VI) can be observed from the SEM images presented in Fig. 3. It can be observed that Ni-CP particles are presented as fluffy spheres. These spherical particles have tendency to adhere together and form chains during the adsorption of Cr(VI) process. This tendency lead to the decreasing of the specific surface area and from this reasons it is expected that the Ni-CP particles to develop the lowest adsorption capacity in the removal process of Cr(VI) from aqueous solutions. Ni-VP particles are present as thin, irregular, acicular plate shapes and Ni-Gly particles are present as flakes-like porous structures and after adsorption of Cr(VI) a significant change was observed in their structure. The surfaces appear to be rough due to they are covered with the Cr(VI) ions.

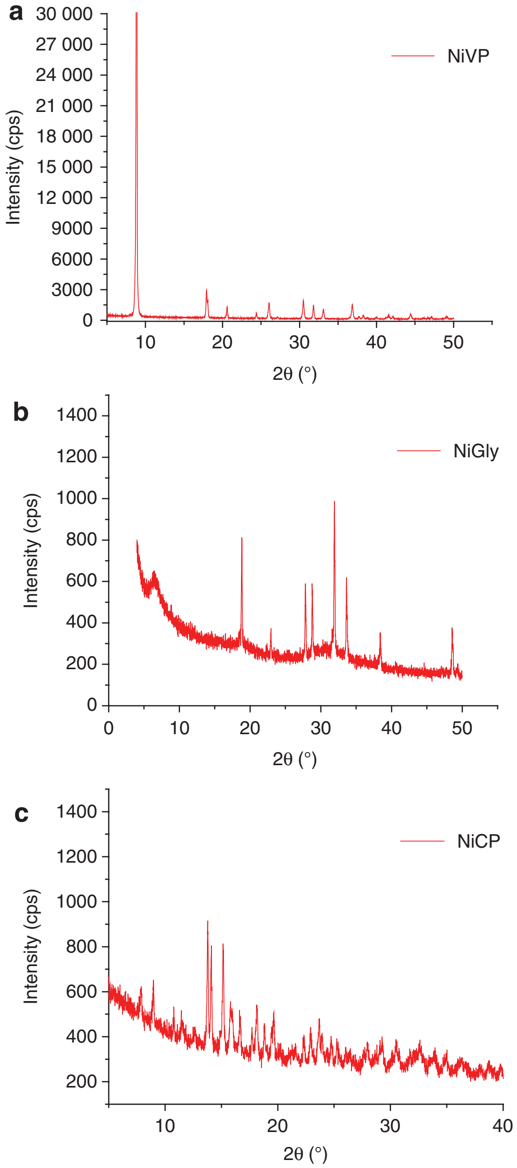

Fig. 5: The X Ray powder diffractograms of the obtained materials: (a) NiVP; (b) NiGly; (c) NiCP.

The adsorption of Cr(VI) onto the studied materials is also confirmed by the EDX spectra of the samples (Fig. 4). From the EDX spectra of selected zone of studied materials before and after adsorption can be observed the new chromium peak along with the bearing groups of elements specific for the Ni(II) based phosphonate metal organic frameworks.

The compounds showed good crystallinity with well-defined peaks in the X-Ray powder diffraction, judging from the intensity of the peaks in the 2θ region. The patterns give a good indication that this nickel compounds are layered structures (Fig. 5). The XRD data of all compounds are comparable with the theoretical one.

Adsorption studies on phosphonates metal organic frameworks

The adsorption capacities developed by the studied materials in the removal process of different metal ions from aqueous solutions are presented in Fig. 6.

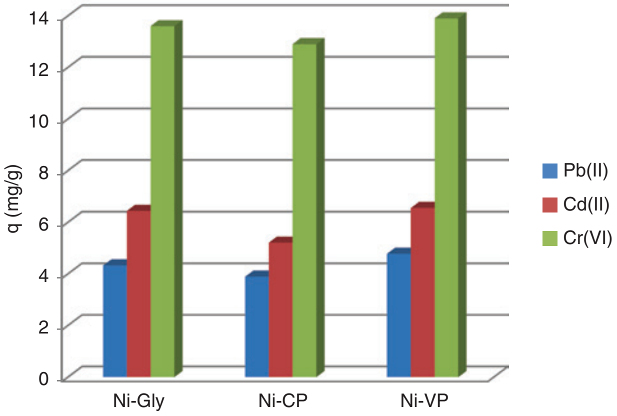

Fig. 6: The adsorption capacity of the studied materials in the removal process of different metal ions from aqueous solutions. $C_i = 30$ mg/L, S:L = 2 g/L, t = 60 min, v = 200 rpm.

It can be observed that the Ni(II) based phosphonate metal organic frameworks developed a doubled or even higher adsorption capacity in the removal process of Cr(VI) from aqueous solutions compared with the adsorption capacities developed in the removal process of the studied divalent metal ions. From this reasons the detailed adsorption studies were carried out in the removal process of Cr(VI) from aqueous solutions.

Effect of pH on the adsorption capacity

The solution pH has an influence on both surface properties of the adsorbent and also on the ionic form of the chromium solutions. From this reason it is the most important parameter while assessing the adsorption capacity of an adsorbent for metal ion removal from aqueous solution. Adsorption experiments were carried out in the pH range of 1–7, keeping all other parameters constant. The effect of initial pH on the adsorption capacity of the studied materials in the removal process of Cr(VI) ions from aqueous solutions is illustrated in Fig. 7.

It can be observed that the highest adsorption capacity is obtained for all the studied materials at pH 2.5. With an increase of pH at values higher than 2.5 the adsorption capacities of the studied material decrease. At lower pH the predominant species of chromium ions is $HCrO_4^-$ and the adsorbent surface present an increase in H^+ ions [27, 28]. The strong electrostatic attraction between positively charged adsorbent surface and

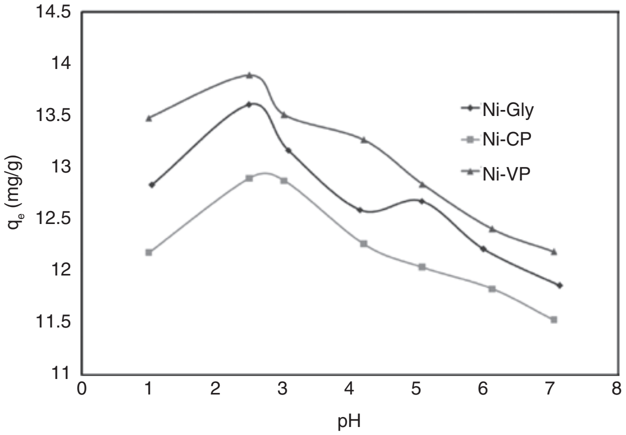

Fig. 7: Effect of initial pH on the adsorption capacity of the studied materials in the removal process of Cr(VI) ions from aqueous solutions. $C_i = 30$ mg/L, S:L = 2 g/L, t = 60 min, v = 200 rpm.

chromate ions can be the explanation of the increasing of the adsorption capacity of the studied materials at lower pH values. This is in accordance with previous studies that reported the removal of Cr(VI) by different adsorbents [30].

Effect of contact time on the adsorption efficiency

The contact time also significantly influences the adsorption rate of the target ions. In order to achieve the saturation uptake capacity, the effects of contact time on the adsorption were investigated in the range of 15–180 min. As shown in Fig. 8, there is no significant change in the removal efficiency of Cr(VI) after 60 min contact time. Compared with other reported adsorbents, Ni(II) based phosphonate metal organic frameworks show a fast adsorption rate for Cr(VI) ions.

Adsorption kinetic studies enable determination of adsorption capacity in different times. Fitting of experimental data to pseudo-first and pseudo-second order kinetic equations is shown in Fig. 9. Parameters of the kinetic equations are given in Table 1.

As seen in the table, calculations revealed that kinetics of sorption of Cr(VI) onto Ni(II) based phosphonate metal organic frameworks corresponds to pseudo-second order kinetic model ($R^2 > 0.999$). Also, the calculated value of q_e was very close to that obtained experimentally. In contrast, for the pseudo-first order reaction, R^2 value was low and q_e differed markedly from the experimental value.

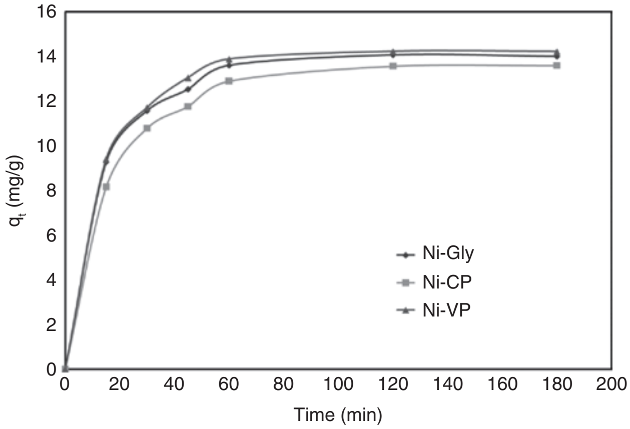

Fig. 8: Effect of contact time on the adsorption capacity of the studied materials in the removal process of Cr(VI) from aqueous solutions. $C_i = 30$ mg/L, S:L = 2 g/L, pH = 2.5, v = 200 rpm.

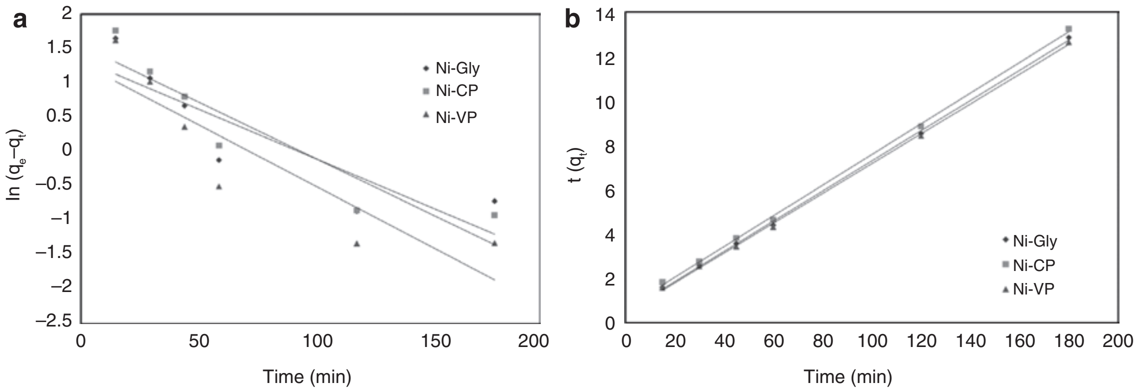

Fig. 9: Pseudo-first order (a) and pseudo-second order (b) kinetic models for Cr(VI) adsorption onto the studied materials.

Table 1: Kinetic parameters for Cr(VI) sorption onto the studied materials.

Adsorbent material	$q_{e,exp}$ mg Cr(VI)/g	Pseudo-first-order model			Pseudo-second-order model		
		$q_{e,calc}$ (mg/g)	k_1 (min^{-1})	R^2	$q_{e,calc}$ (mg/g)	k_2 (min/(mg/g))	R^2
Ni-Gly	14.0	3.83	0.0141	0.7722	14.7	0.00924	0.9992
Ni-CP	13.6	4.71	0.0161	0.8563	14.5	0.00698	0.9992
Ni-VP	14.2	3.62	0.0175	0.7958	14.9	0.00962	0.9992

Effect of Cr(VI) initial concentration on the adsorption capacity

The effects of initial concentration on adsorption capacity developed by the studied materials are presented in Fig. 10. It was observed that the adsorption capacity of the studied materials increase with the increase in initial Cr (VI) concentration, until it reach a constant value. This behavior can be explained by the fact that all the adsorbents had a limited number of active sites, which would have become saturated above a certain concentration [31]. At lower concentration almost all the metal ions could interact with binding sites facilitating maximum adsorption. As the initial concentration increases, there is an increase in number of metal ions competing for available binding sites. At higher concentration more chromium ions are left unabsorbed in the solution due to saturation of adsorption sites [31].

In order to gain further understanding of the behavior and mechanisms involved in the Ni(II) based phosphonate metal organic frameworks and chromium interactions, the linearized Langmuir and Freundlich plots are studied as indicated in Fig. 11. The values of parameters calculated from the slope and intercept of Fig. 11 are tabulated in Table 2.

The values of the correlation coefficient (R^2) for all the studied materials are higher than 0.99 for the Langmuir isotherm, higher than for the Freundlich isotherm, which indicates that the uptake occurs on a homogenous surface by monolayer adsorption and can be described in terms of chemisorption as the formation of an ionic or covalent bonds between adsorbent and adsorbate [32]. Moreover, the maximum adsorption capacity of the studied material obtained from the Langmuir plot is very close to that obtained experimentally. The essential characteristics of the Langmuir isotherm may also be expressed in terms of a dimensionless separation factor of equilibrium (R_L) which may be calculated from equation [33]:

$$R_L = \frac{1}{1 + K_L C_0}, \tag{6}$$

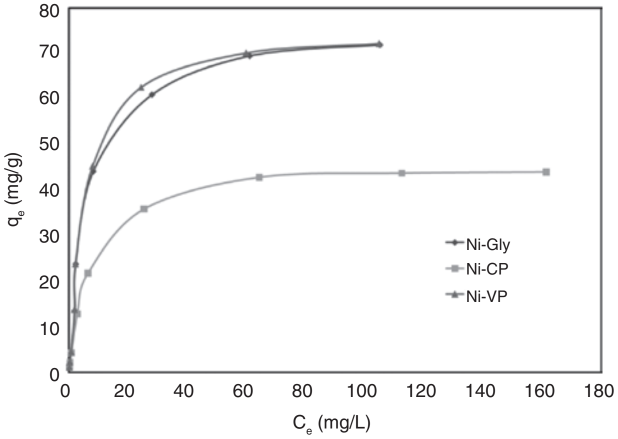

Fig. 10: Equilibrium isotherm of Cr(VI) adsorption onto the studied materials. $C_i = 2.5–250$ mg/L, S:L = 2 g/L, t = 60 min, pH = 2.5, v = 200 rpm.

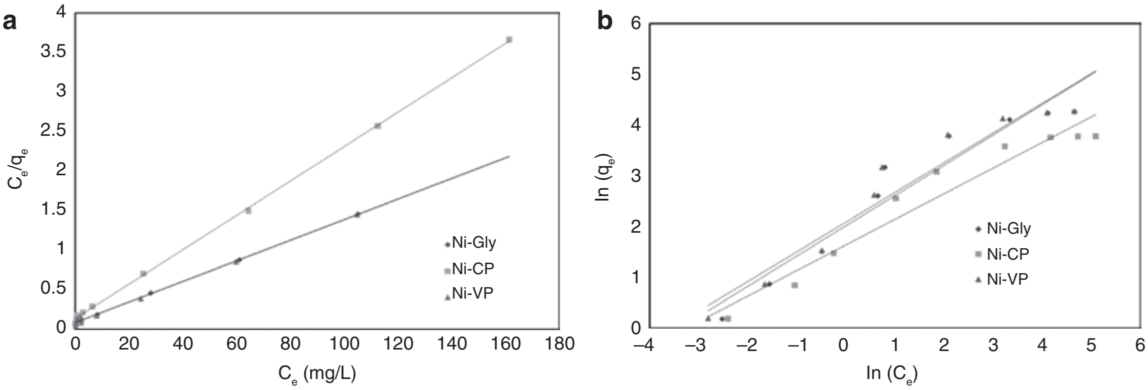

Fig. 11: Langmuir (a) and Freundlich (b) isotherms for Cr(VI) adsorption onto the studied materials.

Table 2: Parameters of Langmuir and Freundlich isotherms for Cr(VI) adsorption onto the studied materials.

Adsorbent material	$q_{m, exp}$ mg Cr(VI)/g	Langmuir isotherm			Freundlich isotherm		
		K_L (L/mg)	$q_{m, calc}$ (mg/g)	R^2	K_F (mg/g)	1/n	R^2
Ni-Gly	72	0.145	76.9	0.9981	7.54	0.5965	0.9324
Ni-CP	44	0.162	45.9	0.9994	5.18	0.5039	0.9426
Ni-VP	72.2	0.164	77.0	0.9978	8.12	0.5847	0.9931

Table 3: Maximum adsorption capacities develop by various adsorbent in the removal process of Cr(VI) from aqueous solutions.

Adsorbent	q_m (mg/g)	pH	Reference
Beech sawdust	16.1	1	[34]
Sugarcane bagasse	13.4	2	[34]
Neem leaves	63	2	[35]
Black tea leaves	45.5	2	[36]
OS-Sulfuric acid AC	71	1.5	[29]
Ni-CP	45.9	2.5	This work
Ni-Gly	76.9	2.5	
Ni-VP	77.0	2.5	

The parameter (R_L) is related to the shape of the isotherm according to the following characteristics: the value of R_L indicates the shape of the isotherm: unfavorable, $R_L > 1$; linear, $R_L = 1$; favorable, $0 < R_L < 1$; and irreversible, $R_L = 0$. R_L values were found to be between 0 and 1 for all the concentration of Cr(VI) for all the studied materials, which indicate that the Ni(II) based phosphonate metal organic frameworks are good adsorbents for Cr(VI) ion removal.

The adsorptive capacities of Ni(II) based phosphonate metal organic frameworks were compared with other adsorbents described in the literature as Cr(VI) ions removal, under similar conditions to those employed in the present work. These have been tabulated in Table 3. It is clearly seen that the studied materials exhibited considerably higher adsorption capacity when the removal of Cr(VI) was undertaken at very low pH values.

Conclusions

Ni(II) based phosphonate metal organic frameworks were synthesized by hydrothermal method and characterized by FTIR, XRD, scanning electron microscopy (SEM) and thermal gravimetric analysis (TGA). These materials are found to be able to adsorb Cr(VI) from aqueous solutions under various experimental conditions. The adsorption was found to be strongly dependent on pH, initial hexavalent chromium concentration and stirring time. The uptake of Cr(VI) by the studied materials was maximal at acidic medium, follows a pseudo-second-order kinetics and shows good fits with Langmuir ($R^2 > 0.99$) isotherm model. It was found that the adsorption efficiency of the studied materials in the removal process of Cr(VI) ions from aqueous solutions is in the following order: Ni-CP < Ni-Gly ≤ Ni-VP. It can be concluded that Ni(II) based phosphonate metal organic frameworks represent a good adsorption properties in the removal process of Cr(VI) from aqueous solutions, developing adsorption capacities comparable or even higher than some adsorbents reported in literature. This is a follow-up on our ongoing research studies on phosphonate metal organic framework as adsorption materials.

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