

Evaluation of iron-based hybrid materials for heavy metal ions removal

Dorota Kołodyńska · Maciej Kowalczyk ·
Zbigniew Hubicki

Received: 2 September 2013 / Accepted: 2 December 2013 / Published online: 18 December 2013
© The Author(s) 2013. This article is published with open access at Springerlink.com

Abstract The article presents in detail the results of the sorption of heavy metal ions such as Cu(II), Zn(II), Cd(II), and Ni(II) in the presence of ethylenediamine-*N,N'*-disuccinic acid as well as chromium(VI) on Purolite Arsen X^{np} and Lewatit FO36. Factors affecting the sorption equilibrium (sorbent dose, contact time, temperature, pH, and the presence of interfering ions) were studied. To compare the surface morphologies of the studied ion exchangers, scans using atomic force microscope were also recorded, and attenuated total reflectance infrared spectroscopy was applied to establish the adsorption mechanism. The main parameters affecting sorption are initial concentration of the solution, pH, and phase contact time. Temperature has only a slight influence. The kinetic data were fitted using the pseudo-first-order and pseudo-second-order models. In the case of Cr(VI) adsorption, the equilibria on Purolite Arsen X^{np} and Lewatit FO36 were established within 60 min, in the case of Cu(II) and Zn(II) within 30–40 min and for Cd(II) and Pb(II) even less than 30 min. Moreover, it was found that the effectiveness of adsorption in the case of Cr(VI), Cu(II), Zn(II), Cd(II), and Pb(II) on Purolite ArsenX^{np} was higher than that on Lewatit FO36.

Introduction

Removal of heavy metal ions from various types of waters and waste waters is an essential problem in environmental protection and has a result on human health. On the other

hand, stricter requirements concerning the quality of waste waters lead to more refined and complex chemical processes used in their purification. Therefore, the search for new methods and novel materials for heavy metal ions removal, particularly of As(V) and Cr(VI) ions, is very important [1–8]. Some of them are hybrid ion exchangers (HIX) based on nanosized metal oxides (NMOs) such as ferric, manganese, aluminum, titanium, magnesium, and cerium oxides. For example, the addition of hydrated iron oxides to the polymers (PS and DVB, less frequently polyacrylic, with a macroporous or gel matrix, containing cation or anion exchange functional groups) leads to the obtaining of adsorbents characterized by very good adsorption, mechanical, and hydraulic properties [9, 10]. The quality of the sorbents obtained depends on: (i) the quantity, structure, crystallinity, and degree of dispersion of the iron oxides introduced; (ii) physical form of the base polymer; and (iii) the type of functional groups involved in the preparation of hybrid polymers as well as influence on the process of adsorption. For example, Qiu et al. [11] found that the hybrid sorbent based on the hydrous iron oxide and neutral polystyrene matrix (PS) without an attached functional group (HFO–PS) and based on the negatively charged HFO–PS–SO₃[−] matrix had totally different adsorption properties toward Cu(II) ions in the presence of sulfate(VI) ions. The adsorption of Cu(II) on HFO–PS was promoted in sulfate solutions; however, when influenced by covalently attached sulfonic acid groups, Cu(II) adsorption on HFO–PS–SO₃[−] was inhibited by the added sulfates.

As described by Sarkar et al. [12], the first step in the preparation of HIX based on iron oxides and polystyrene–divinylbenzene copolymers (PS–DVB) includes loading of Fe(III) onto the functional groups of ion exchanger, then desorption and simultaneous precipitation of Fe(III) hydroxides using a solution containing NaCl and NaOH,

D. Kołodyńska (✉) · M. Kowalczyk · Z. Hubicki
Department of Inorganic Chemistry, Faculty of Chemistry,
Maria Curie Skłodowska University, Maria Curie Skłodowska
Sq. 2, 20-031 Lublin, Poland
e-mail: kolodyn@poczta.onet.pl

and finally rinsing and washing the resin with an ethanol–water mixture followed by a mild thermal treatment. The high concentration of the functional groups allowed high and fairly uniform loading of hydrous iron oxide particles (~9–12 % of Fe by mass) within the polymeric matrix. Such ions as Cl^- , SO_4^{2-} , and HCO_3^- exhibit only weak affinities for hydrous iron oxides and are characterized by a smaller selectivity. Cumbal and SenGupta [5] reported the preparation of two classes of polymer-supported nanoparticles containing iron for As(III,V) removal: (i) hydrated Fe(III) oxides dispersed in an ion exchange resin, and (ii) polymeric particles with magnetic properties.

Increasing the amount of iron oxide introduced into the polymer increases the adsorption capacity of the sorbent, but after crossing saturation of the polymer matrix followed by the blocking of pores, a significant decrease in adsorption capacity is observed. Typically, the iron oxide content in the copolymer is equal to 100–200 mg Fe g^{-1} of sorbent. The best adsorption properties of hybrid polymers are found for those in which the inner surfaces of the pores are coated with a thin layer of iron oxides. This effect can be achieved by proper selection of the polymer matrix, the amount of iron placed in a single cycle of synthesis, and by performing appropriate treatment. These factors also affect the degree of dispersion of the introduced iron oxides. The introduction of smaller agglomerates provides a greater surface area and thus a more effective adsorbent.

In this article, the HIX Purolite Arsen X^{np} (Purolite) and Lewatit FO36 (Lanxess) were used to remove Cu(II), Zn(II), Cd(II), and Pb(II) ions in the presence of ethylenediamine-*N,N'*-disuccinic acid (EDDS) which belongs to a group of readily biodegradable complexing agents. The metals for the evaluation were chosen due to their occurrence in waste water streams. Optimal conditions of adsorption were based on the speciation distribution of the studied heavy metal complexes with EDDS. The adsorption properties of the above-mentioned sorbents were also evaluated in the case of arsenic and chromium.

Investigations were carried out using the static method, based on which adsorption parameters were calculated in single versus multicomponent systems at different pH values and temperatures as well as in the presence of interfering ions. To compare the surface morphologies of the studied ion exchangers before and after the adsorption process, scans using atomic force microscope (AFM) were also recorded, and infrared spectroscopy (ATR/FT-IR) was applied to establish the adsorption mechanism.

Materials and methods

Purolite Arsen X^{np} also known as FerriIXTM A33E is a strongly acidic macroporous cation exchanger based on a

polystyrene-divinylbenzene skeleton with attached sulfonic acid groups and containing hydrated iron oxide nanoparticles. The resin has the bead size of 0.3–1.2 mm; adsorption capacity 1.56 meq L^{-1} ; and iron oxide content not exceeding 42 %. It is also characterized by an enormous capacity for As(V) [13].

Lewatit FO36 is a weakly basic, macroporous anion exchanger also based on PS–DVB and containing the weak amine functional groups and iron oxide nanoparticles. It has the bead size 0.34–0.38 mm, adsorption capacity 1.5 eq L^{-1} (30 BV h^{-1} , 0.1 mg L^{-1} As(V), 6 mg L^{-1} SiO_2 , and 60 mg L^{-1} PO_4^{3-}), and iron oxide content not exceeding 23 % [14]. The following salts were used: $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, ZnCl_2 , $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, and $\text{Pb}(\text{NO}_3)_2$ as a source of metal ions, and the *S,S*-isomer of EDDS (Innospec Speciality Chemicals, UK) used as supplied to react with these metal ions in solution without pH adjustment. In addition, a Cr(VI) working stock solution was prepared by dissolving $\text{K}_2\text{Cr}_2\text{O}_7$ in deionized water. Experiments were carried out in multicomponent systems containing Cr(VI), Cu(II), and Zn(II) ions, with or without the complexing agent (EDDS) as well as in the presence of accompanying ions Cl^- , NO_3^- , and SO_4^{2-} . In the investigations mixtures of Cd(II) and Pb(II), with and without EDDS were also used. In these systems, metal ions are complexed in the form of $[\text{M}(\text{edds})]^{2-}$ ions, whereas, Cr(VI) is not complexed.

Batch kinetic experiments were conducted in 250-mL conical flasks containing ion exchanger (2 g) to which a solution of metal ions (200 mL) was added, with and without EDDS and with the initial pH values of 4.5 and 10.0. The flasks were shaken on a rotary shaker at 180 rpm. Batch studies were carried out to investigate the effects of phase contact time (1–180 min), initial metal concentration (1–5 mmol L^{-1}), solution pH (4–12), temperature (20–60 °C), and the presence of other ions (Cl^- , NO_3^- , SO_4^{2-}). Solution pH was adjusted with 0.1-mol L^{-1} HNO_3 or 0.1-mol L^{-1} NaOH.

A laboratory shaker Elpin type 357, (Elpin-Plus, Poland) was used for agitation. The pH values were measured with a PHM 84 pH meter (Radiometer, Denmark) with glass REF 451 and calomel pHG 201-8 electrodes. The accuracy of the pH meter is ± 0.01 pH units. Concentrations of the heavy metals were measured with an AAS spectrometer SpectrAA 240FS (Varian, Australia). Measurements were performed using the following parameters: wavelength Cu(II): 324.70 nm, Zn(II): 213.90 nm, Cd(II): 228.80 nm, and Pb(II): 217.00 nm with slit width = 0.50 nm. Cr(VI) ions in the effluent were determined colorimetrically using 1,5-diphenyl-carbazide method at 546 nm with a Specord M42 (Carl Zeiss, Jena) UV–Vis spectrophotometer. The morphology of the hybrid sorbent samples was analyzed with AFM Digital Instruments (USA) NanoScope III. The

infrared spectra were recorded by a Nicolet-380 Fourier transform infrared spectrometer using the ATR method. All experiments were made in triplicate, and the results were taken as the average value.

The amounts of metal ions adsorbed at time “*t*” of hybrid sorbents (*q_t*, mg g⁻¹) were calculated from the mass balance equation:

$$q_t = (c_0 - c_t)V/m,$$

where *c₀* is the initial concentration of a metal ion (mg L⁻¹); *c_t* is the concentration of metal ion at time *t* (mg L⁻¹), *V* is the volume of the solution (L); and *m* is the mass of HIX (g).

The equilibrium data were analyzed using the Langmuir and Freundlich isotherms and the characteristic parameters for each isotherm determined. The linear form of the Langmuir model can be expressed as [15]

$$c_e/q_e = c_e/q_0 + 1/K_L q_0,$$

where *c_e* is the equilibrium concentration of metal ions (mg L⁻¹) and *q_e* is the amount of the metal ions adsorbed on the hybrid sorbent (mg g⁻¹), and *q₀* and *K_L* are the Langmuir constants related to the adsorption capacity (mg g⁻¹) and the equilibrium constant (L g⁻¹), respectively.

The adsorption equilibrium data were also applied to the Freundlich model [16]:

$$\log q_e = \log K_F + (1/n)\log c_e,$$

where *K_F* and *n* are the Freundlich constants related to the adsorption capacity and the adsorption intensity, respectively.

The pseudo-first-order model (PF-order) was presented by Lagergren and expressed as follows [17]:

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)t$$

where *q_t* is the amount of metal ions adsorbed on the hybrid sorbents at time *t*, and *k₁* is the rate constant (min⁻¹). The rate constant, *k₁*, was obtained from the slope of linear plots of log(*q_e - q_t*) against *t*.

The adsorption data were also analyzed in terms of the pseudo-second order mechanism (PS-order) [18, 19]:

$$t/q_t = (1/h) + (1/q_e)t,$$

and the initial rate of adsorption *h* is

$$h = k_2 q_e^2,$$

where *k₂* is the rate constant of PS-order adsorption (g(mg min)⁻¹), and *h* is the initial rate of adsorption (mg(g min)⁻¹).

The constants *q_e*, *h*, and *k₂* can be determined from the plots of *t/q_t* against *t*.

Results and discussion

The study showed that the hybrid sorbents, including Purolite Arsen X^{np} and Lewatit FO36, can be used to remove Cu(II), Zn(II), Cd(II), Pb(II), and Cr(VI) under appropriate conditions. The effectiveness of the adsorption process depends on the initial concentration of solution, pH, phase contact time, addition of a complexing agent EDDS and presence of accompanying ions.

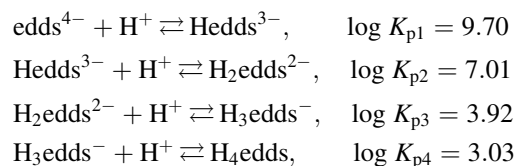
It was found that the optimal pH values for the adsorption of Cu(II), Zn(II), Cd(II), Pb(II), and Cr(VI) ions on Purolite Arsen X^{np} and Lewatit FO36 are above 4.5 (Fig. 1).

Under these conditions, Cu(II), Zn(II), Cd(II), and Pb(II) ions are coordinated to the goethite phase. It should be mentioned that, for example, Cu(II) at pH between 2 and 6.5 occurs predominantly as the aqueous Cu²⁺ cation. With increasing pH, the following hydroxoions occur Cu(OH)⁺, Cu(OH)₂, Cu(OH)₃⁻, and Cu(OH)₄²⁻. At pH values >7, the major hydrolysis product is Cu₂(OH)₂²⁺. Therefore, at pH values >4.5, Cu(II) is likely to sorb as the aqueous cation. Under analogous conditions, other ions are also in the form of cations or hydroxoions. Numerous studies show that the Cu(II) ions are sorbed on goethite as the surface complexes ≡FOCu⁺ and ≡FOCuOH or a combination of both [20, 21].

However, as complexing agents are present, these are adsorbed specifically on metal oxides and hydroxides to form inner sphere complexes. It is also known that they are responsible for increase, decrease, or no change in the adsorption of metal ions, for example on soils. Some authors confirm that the adsorption of metals in systems containing organic ligands increases at pH values below the adsorbent point of zero charge (PZC) and increases at higher pH [22]. However, other authors showed that the addition of organic substances decreases the adsorption even under acid conditions below the PZC [23].

In the present article, ethylenediamine-*N,N'*-disuccinic acid (H₄edds) consists of four isomers: *S,S*- (25 %), *R,R*- (25 %), *R,S*- (50 %), and *S,R*- (50 %); however, only the *S,S*-isomer of EDDS is readily biodegradable. It was proved that 83 % of it is converted to CO₂ within 20 days [24]. The other isomers are either partly or completely nonbiodegradable [25, 26]. It follows from the EDDS speciation profile at pH 10 that the predominant form is the anion (edds)⁴⁻ (Fig. 2).

EDDS has four ionisable protons with the following protonation constants:



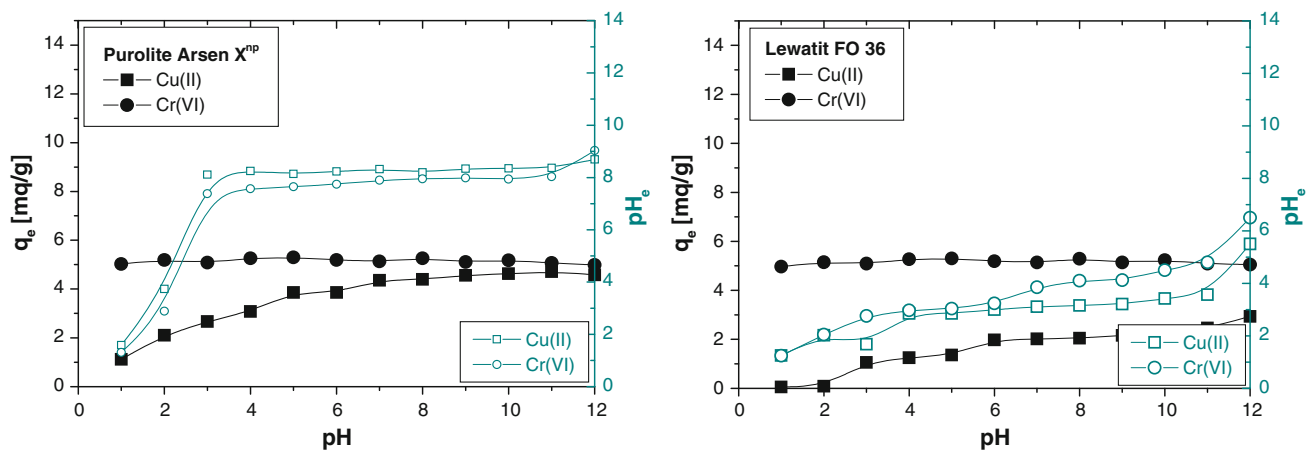


Fig. 1 Effect of pH on the adsorption of Cu(II) and Cr(VI) on Purolite Arsen X^{np} and Lewatit FO36

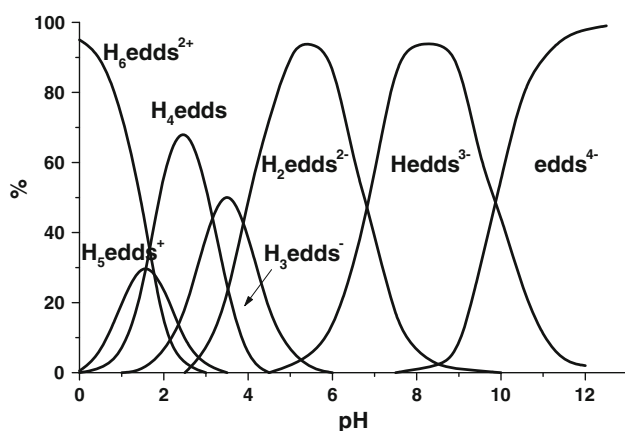
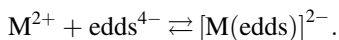


Fig. 2 Speciation profile of EDDS versus pH

and ($\sum \log K_{pi} = 23.66$, $i = 1-4$) [27, 28].

According to the literature data, EDDS showed good complexing properties toward heavy metal ions, and the reaction is characterized by the formation of stable 1:1 metal to ligand complexes as the major species:



For the Cu(II), Zn(II), Cd(II), and Pb(II) complexes with EDDS, the stability constants are as follows: 13.1, 13.4, 16.4, and 12.7, respectively.

According to the literature data, metal capacity on the goethite surface increases with metal electronegativity: Cu(II) > Pb(II) > Cd(II) [29]. In addition, the behavior of the metals in the three-component system consisting of metal solution; organic ligand and hybrid sorbent can be controlled by several processes: (i) the adsorption of the free metal cations on the sorbent surface, (ii) the adsorption of the metal cations by the sorbent surface modified by interaction with the anions of dissolved EDDS, (iii) the formation of metal complexes with EDDS in solution, (iv)

the adsorption of free and charged metal complexes with EDDS on the sorbent surface, and finally (v) the interaction of anionic complexes with the functional groups of the hybrid sorbents.

To establish which of the above-mentioned steps has decisive influence on the sorption process in the next stage, the effect of the phase contact time on the effectiveness of Cu(II), Zn(II), Cd(II), Pb(II), and Cr(VI) ions' adsorption at different initial concentrations (1–5 mmol L⁻¹) was studied, and the examples of results for Purolite Arsen X^{np} are presented in Fig. 3.

It was found that in the case of Cr(VI) adsorption, the equilibrium on Purolite Arsen X^{np} was established within 60 min, in the case of Cu(II) and Zn(II) within 30–40 min. (at low concentrations), and for Cd(II) and Pb(II) even <30 min. For Lewatit FO36, the equilibrium times were almost analogous. Moreover, it was found that the effectiveness of adsorption for these ions on Purolite ArsenX^{np} was higher than on Lewatit FO36.

Based on the kinetic analysis, it was found that the rate constants k_1 decreased with increase in the initial metal ion concentrations (data not presented for the concentrations 3 and 5 mmol L⁻¹). The correlation coefficients were high, ranging from 0.8253 to 0.9284 for Purolite Arsen X^{np} and from 0.9562 to 0.9982 for Lewatit FO 36. However, the calculated equilibrium capacities (q_1) according to the Lagergren pseudo-first order rate expression were in disagreement with the experimental capacities ($q_{e,exp}$) for solutions with initial concentrations 1–5 mmol L⁻¹. Better results were obtained using the pseudo-second order equation (Table 1).

In addition, studies on the effect of ethylenediamine-*N,N'*-disuccinic acid (EDDS) addition clearly showed that the influence of complexing agent is different depending on the system (Figs. 4, 5). For Purolite ArsenX^{np}, addition of EDDS had a negative impact on the adsorption of Cu(II)

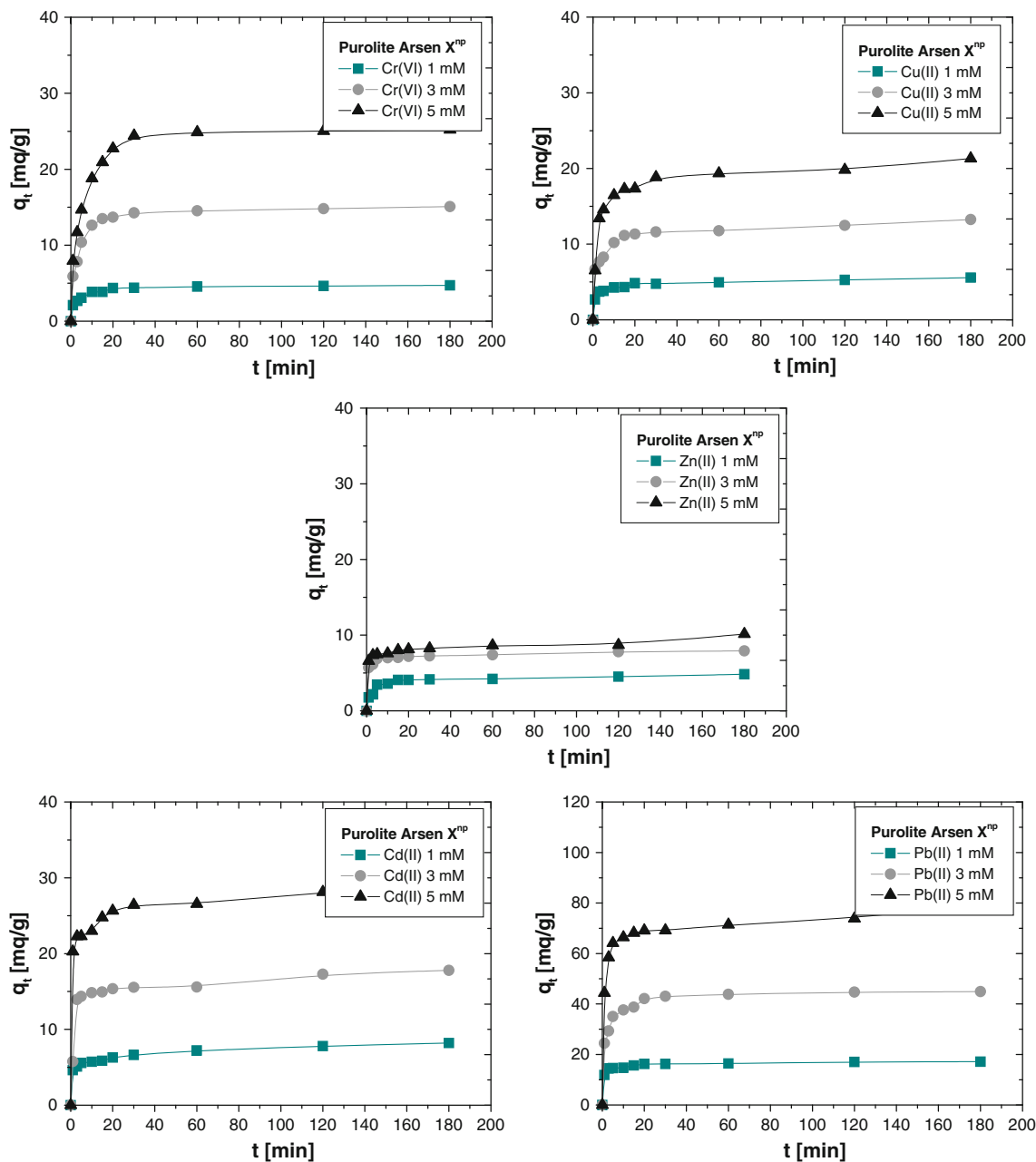
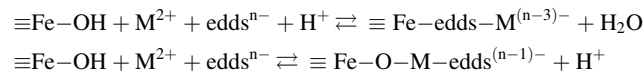


Fig. 3 Effect of the phase contact time on the adsorption of Cr(VI), Cu(II), Zn(II), Cd(II), and Pb(II) at different initial concentrations on Purolite Arsen X^{np}

and Pb(II), however, for Cd(II) an increase of the removal efficiency was observed. In the case of Lewatit FO36, much better adsorption in the presence of EDSS was found for Cu(II), Zn(II), and Cd(II), while it had no effect on Cr(VI) adsorption. As for Pb(II) ions, their removal from waste waters decreases. The increase in the metal adsorption is probably related to the formation of stable negatively charged M(II)-EDDS complexes of the type $M[(\text{Hedds})]^{3-}$ or $[M(\text{edds})]^{2-}$. These complexes increase the adsorption capacity of the surface due to the involvement of positively charged sorption sites into the

adsorption process. Their adsorption on the hybrid sorbents surface can occur via the metal–surface interaction and through the organic ligand [20, 30].



where M^{2+} is the metal cation and edds^{4-} is the ligand.

Moreover, especially for Lewatit FO36 with weakly basic functional groups, the anion exchange process should be considered, and this mechanism is probably responsible

Table 1 Kinetic parameters for Cr(II), Cu(II), Zn(II), Cd(II), and Pb(II) ion sorption on Purolite Arsen X^{np} and Lewatit FO36 at initial concentration 1 mmol L⁻¹

System	Cr(VI)	Cu(II)	Zn(II)	Cd(II)	Pb(II)
Purolite Arsen X ^{np}					
PF-order					
q_{exp}	5.19	5.05	8.35	6.42	16.47
q_1	2.62	2.24	2.98	3.16	3.63
k_1	0.094	0.051	0.020	0.024	0.065
R^2	0.9284	0.9109	0.9510	0.9115	0.9049
PS-order					
q_2	4.80	5.03	8.31	6.44	16.61
k_2	0.078	0.129	0.211	0.163	0.081
h	1.806	3.275	14.556	6.775	22.422
R^2	0.9922	0.9907	0.9910	0.9968	0.9976
Lewatit FO36					
PF-order					
q_{exp}	5.80	2.87	3.05	2.72	18.65
q_1	4.12	4.37	4.46	1.50	12.11
k_1	0.141	0.009	0.008	0.069	0.127
R^2	0.9985	0.9791	0.9562	0.7931	0.9571
PS-order					
q_2	5.88	3.10	3.06	2.92	18.55
k_2	0.039	0.122	0.144	0.445	0.011
h	1.359	1.170	1.356	3.804	3.900
R^2	0.9982	0.9913	0.9932	0.9957	0.9963

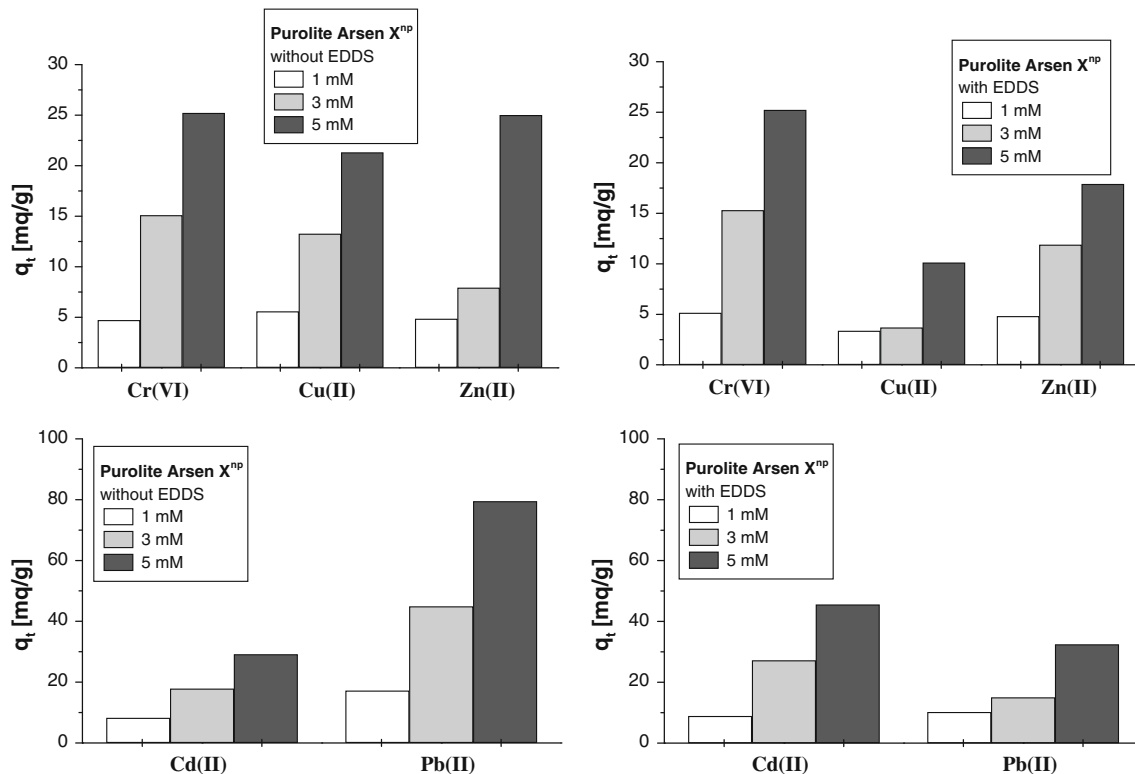


Fig. 4 Comparison of sorption properties of Purolite Arsen X^{np} toward Cr(VI), Cu(II), Zn(II), Cd(II), and Pb(II) ions without and with the addition of EDDS

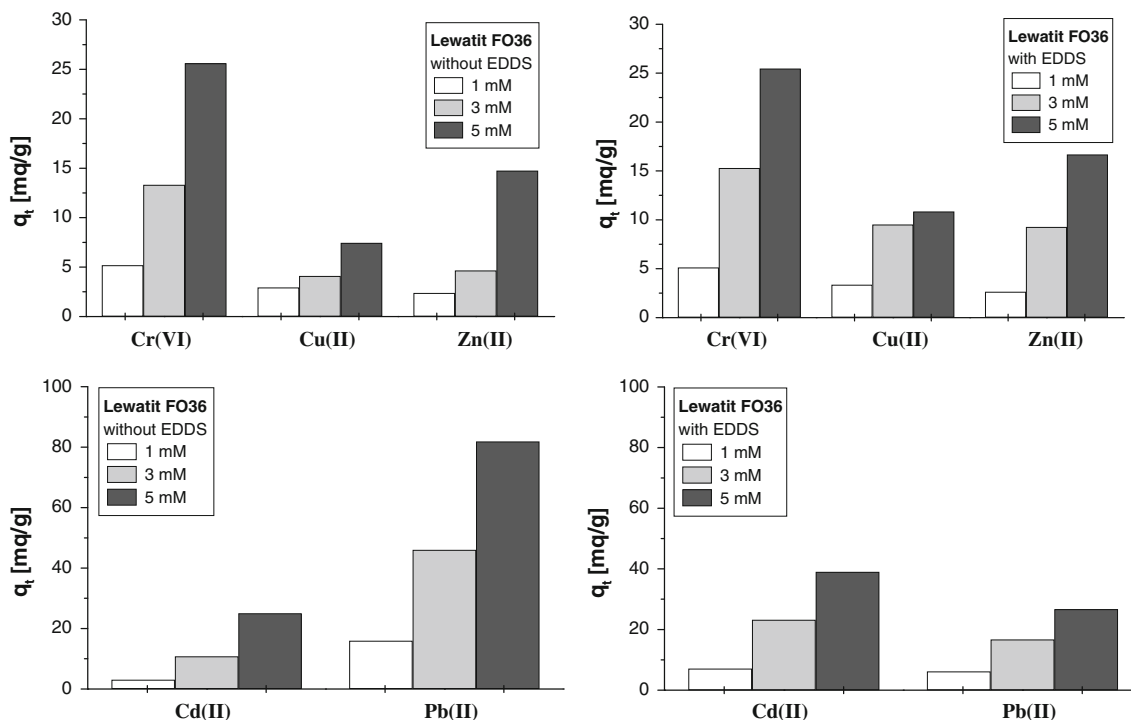


Fig. 5 Comparison of sorption properties of Lewatit FO36 toward Cr(VI), Cu(II), Zn(II), Cd(II), and Pb(II) ions without and with the addition of EDDS

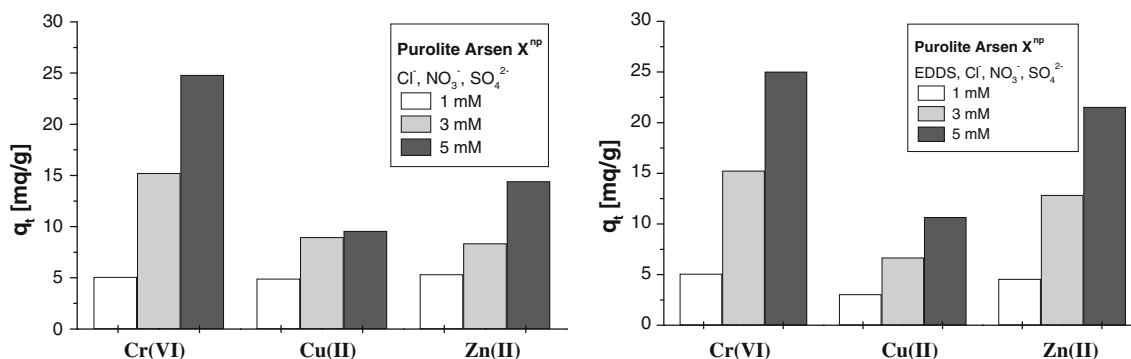
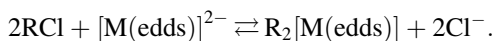


Fig. 6 Comparison of sorption properties of Purolite Arsen X^{np} toward Cr(VI), Cu(II), and Zn(II) ions in the presence of Cl⁻, NO₃⁻, SO₄²⁻ ions, and EDDS, Cl⁻, NO₃⁻, SO₄²⁻ ions

for the enhanced adsorption of the negatively charged complexes:



As was shown by Ali and Dzombak [31], sulfate ligands can dramatically enhance the adsorption of heavy metals on iron oxides by modifying the electrostatic environment at the interface or by forming metal-sulfate ternary surface complexes like ≡Fe–OHCuSO₄. As was mentioned earlier, Qiu et al. [11] also found that the Cu(II) adsorption on a hybrid sorbent based on the PS–SO₃⁻ matrix is strongly inhibited by the presence of the SO₄²⁻

ligand. Therefore, the effects of accompanying ions such as Cl⁻, NO₃⁻, and SO₄²⁻ were studied. From the obtained results, it should be noted that the effects of accompanying ions are negligible; however, the addition of the complexing agent EDDS to the system in the presence of Cl⁻, NO₃⁻, and SO₄²⁻ ions improves the sorption process parameters for both hybrid sorbents. This is mainly noticeable in the case of Zn(II), where the addition of EDDS significantly improves the sorption capacity from 14.43 to 21.50 mg g⁻¹ for Purolite ArsenX^{np} as well as from 14.43 to 21.50 mg g⁻¹ for Lewatit FO36 (initial concentration 3 mmol L⁻¹). In the case of Cr(VI), this

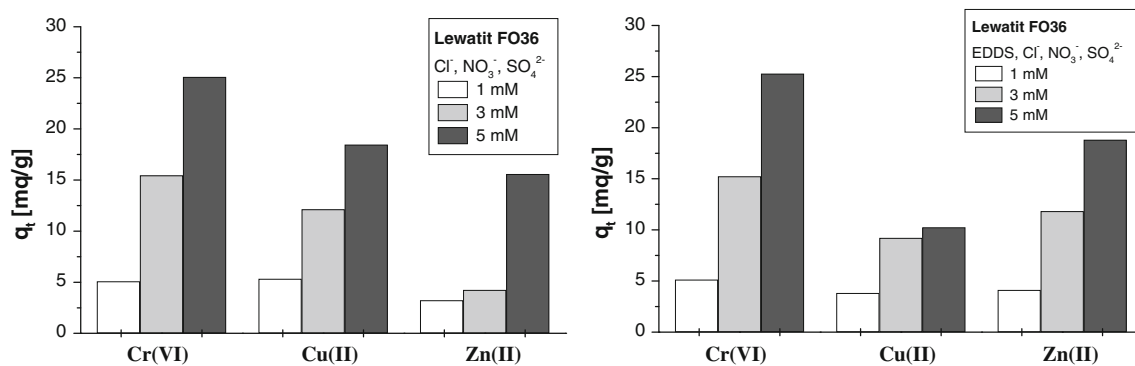


Fig. 7 Comparison of sorption properties of Lewatit FO36 toward Cr(VI), Cu(II), and Zn(II) ions in the presence of Cl^- , NO_3^- , SO_4^{2-} ions, and EDDS, Cl^- , NO_3^- , SO_4^{2-} ions

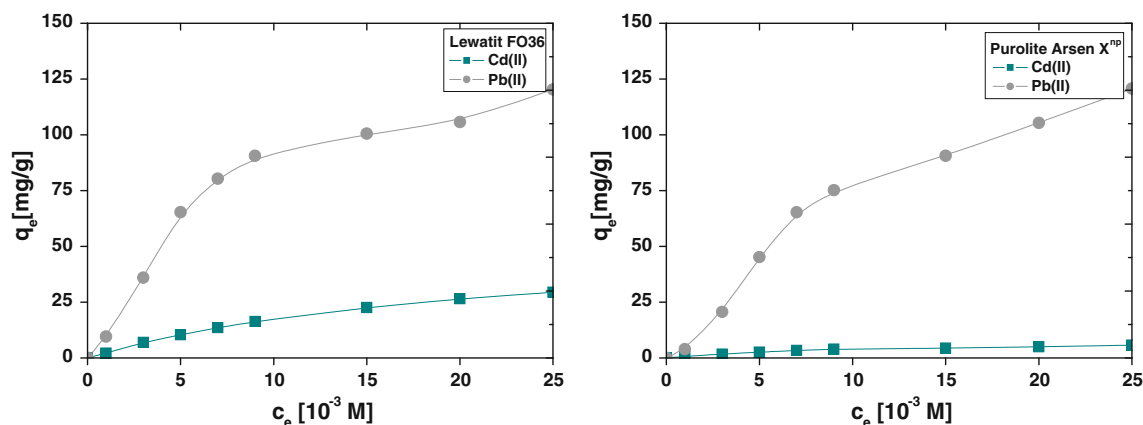


Fig. 8 The Langmuir sorption isotherms of Cd(II) and Pb(II) on Lewatit FO36 and Purolite Arsen X^{np} (1.0×10^{-3} – 2.5×10^{-2} M, shaking time 24 h, shaking speed 180 rpm, temperature 295 K)

increase is negligible, and in the case Cu(II) ions the sorption capacity decreases from 18.46 to 9.22 mg g^{-1} in the same conditions (Figs. 6, 7).

In addition, it is found that the sorption capacity of the sorbents slightly increased when the temperature of heavy metal solutions increased from 20 to 60 °C. The sorption of the above complexes could be described by the Langmuir isotherm with high correlation coefficients ranging from 0.9986 to 1.000, whereas for the Freundlich isotherm they range from 0.8345 to 0.9871. The values of the separation factor, R_L , indicate the nature of the adsorption process with: $R_L > 1$ unfavorable; $R_L = 1$ linear; $0 < R_L < 1$ favorable; and $R_L = 0$ irreversible. In the present study, these values indicate that the adsorption process is favorable for both the Purolite ArsenX^{np} and Lewatit FO36 samples. The maximum capacities of adsorption of Cr(VI), Cu(II), Zn(II), Cd(II), and Pb(II) on Purolite Arsen X^{np} are equal to 25.55, 21.47, 10.11, 28.99, and 81.85 mg g^{-1} , respectively, and they increase with the increasing temperature. Meanwhile, the Langmuir equilibrium constants (K_L) (L g^{-1}) for Purolite Arsen X^{np} decrease as follows: Cr(VI): 0.240–0.017;

Table 2 The Langmuir and Freundlich parameters for adsorption of Cd(II) and Pb(II) on Lewatit FO36 and Purolite Arsen X^{np} (1.0×10^{-3} – 2.5×10^{-2} M, shaking time 24 h, shaking speed 180 rpm, temperature 295 K)

System	Langmuir model				Freundlich model		
	q_0	K_L	R_L	R^2	K_F	n	R^2
Lewatit FO36							
Cd(II)	50.00	0.001	0.385	0.8346	6.29	1.48	0.9655
Pb(II)	138.89	0.004	0.043	0.9882	9.89	3.02	0.9266
Purolite Arsen X ^{np}							
Cd(II)	11.15	0.001	0.373	0.7918	9.82	0.53	0.9028
Pb(II)	147.06	0.005	0.035	0.9827	15.77	3.57	0.8953

Cu(II): 0.185–0.014; Zn(II): 0.122–0.0087; Cd(II): 0.221–0.013; and Pb(II): 0.324–0.025. The Langmuir sorption isotherms of Cd(II) and Pb(II) on Lewatit FO36 and Purolite Arsen X^{np} are presented in Fig. 8. Moreover, the Langmuir and Freundlich parameters of sorption isotherms of Cd(II) and Pb(II) on hybrid sorbents are presented in Table 2. The comparison between the determined sorption

Table 3 Comparison of adsorption capacities for heavy metal ions onto different sorbents containing hydrous iron oxides

Sorbents	Conditions	Adsorption capacity for experimental conditions	Ref.
HIO hydrous iron oxide in chloride–sulfate 1:1 system in the presence of phosphate, acetate, and oxalate ions	$m = 1 \text{ mg}$ $C_{\text{Cu(II)}} = 10 \text{ mg L}^{-1}$ $C_{\text{Zn(II)}} = 10 \text{ mg L}^{-1}$ $V = 50 \text{ mL}$ $\text{pH} = 5.5$	$\text{Cu(II)} > 90 \%$ $\text{Zn(II)} > 90 \%$	[21]
Nano-Fe ₃ O ₄ –SiO ₂ –TETA magnetic nano-iron oxide–nano-silicon oxide–triethylenetetramine	$m = 5 \text{ mg}$ $V = 50 \text{ mL}$ $C_{\text{Cu(II)}} = 127 \text{ mg L}^{-1}$ $C_{\text{Pb(II)}} = 414 \text{ mg L}^{-1}$ $\text{pH} = 1\text{--}7$	$\text{Pb(II)} 269 \text{ mg g}^{-1}$ in $\text{pH} 7.0$ $\text{Cu(II)} 76 \text{ mg g}^{-1}$ in $\text{pH} 7.0$.	[33]
SCMN shellac-coated magnetic nanoparticle adsorbent	$m = 0.5 \text{ mL}$ $V = 50 \text{ mL}$ $C_{\text{Cd(II)}} = 50 \text{ mg L}^{-1}$ $\text{pH} = 8$	$\text{Cd(II)} 20.6612 \text{ mg g}^{-1}$	[34]
INS iron-oxide nano-particles-immobilized sand	$m = 0.5 \text{ g}$ $V = 100 \text{ mL}$ $C_{\text{Cu(II)}} = 20 \text{ mg L}^{-1}$ $C_{\text{Cd(II)}} = 20 \text{ mg L}^{-1}$ $C_{\text{Pb(II)}} = 20 \text{ mg L}^{-1}$ $\text{pH} = 1\text{--}10$	$\text{Cu(II)} 1.26 \text{ mg g}^{-1}$ $\text{Cd(II)} 0.52 \text{ mg g}^{-1}$ $\text{Pb(II)} 2.08 \text{ mg g}^{-1}$	[32]
INR iron nanorods	$m = 50 \text{ mg}$ $V = 50 \text{ mL}$ $C_{\text{Fe(II)}} = 10 \text{ mg L}^{-1}$ $C_{\text{Pb(II)}} = 10 \text{ mg L}^{-1}$ $C_{\text{Zn(II)}} = 10 \text{ mg L}^{-1}$ $C_{\text{Ni(II)}} = 10 \text{ mg L}^{-1}$ $C_{\text{Cd(II)}} = 10 \text{ mg L}^{-1}$ $C_{\text{Cu(II)}} = 10 \text{ mg L}^{-1}$ $\text{pH} = 1\text{--}8$	$\text{Fe(II)} 43.11 \text{ mg g}^{-1}$ $\text{Pb(II)} 38.04 \text{ mg g}^{-1}$ $\text{Zn(II)} 36.12 \text{ mg g}^{-1}$ $\text{Ni(II)} 32.13 \text{ mg g}^{-1}$ $\text{Cd(II)} 29.76 \text{ mg g}^{-1}$ $\text{Cu(II)} 25.62 \text{ mg g}^{-1}$	[35]
HFO–PS [−] and HFOPS ⁰ , respectively) hydrous ferric oxide (HFO) nanoparticles—polystyrene beads (negatively charged and covalently bonded with neutral chloromethyl) in the presence of SO ₄ ^{2−} and NO ₃ [−] ions	$m = 5 \text{ mg}$ $V = 50 \text{ mL}$ $C_{\text{Cu(II)}} = 10 \text{ mg L}^{-1}$ $\text{pH} = 5.5$	$\text{Cu(II)} 215.7 \text{ mg g}^{-1}$ (for 100 mg L^{-1} of Ca(II)), 184.2 mg g^{-1} (for 200 mg L^{-1} of Ca(II)) 165.2 mg/g (for 300 mg L^{-1} of Ca(II))	[9]
MNPs-NH ₂ amino-functionalized magnetic nano-adsorbent	$m = 5 \text{ mg}$ $V = 50 \text{ mL}$ $C_{\text{Pb(II)}} = 5 \text{ mg L}^{-1}$ $C_{\text{Pb(II)}} = 15 \text{ mg L}^{-1}$ $C_{\text{Pb(II)}} = 25 \text{ mg L}^{-1}$ $\text{pH} = 5.0$	$\text{Pb(II)} 8.82 \text{ mg g}^{-1}$ (for $\text{Pb(II)} C_0 5 \text{ mg L}^{-1}$) $\text{Pb(II)} 22.78 \text{ mg g}^{-1}$ (for $\text{Pb(II)} C_0 15 \text{ mg L}^{-1}$) Pb(II) 41.10 mg g^{-1} (for $\text{Pb(II)} C_0 25 \text{ mg L}^{-1}$)	[36]
Magnetic maghemite (γ -Fe ₂ O ₃) nanotubes	$m = 50 \text{ mg}$ $V = 100 \text{ mL}$ $C_{\text{Cu(II)}} = 100 \text{ mg L}^{-1}$ $C_{\text{Zn(II)}} = 100 \text{ mg L}^{-1}$ $C_{\text{Pb(II)}} = 100 \text{ mg L}^{-1}$ $\text{pH} = 6.0$	$\text{Cu(II)} 37.31 \text{ mg g}^{-1}$ $\text{Zn(II)} 31.25 \text{ mg g}^{-1}$ $\text{Pb(II)} 24.87 \text{ mg g}^{-1}$	[37]

Table 3 continued

Sorbents	Conditions	Adsorption capacity for experimental conditions	Ref.
Fe–Al–NF Iron oxide–alumina mixed nanocomposite fiber	$m = 50 \text{ mg}$ $V = 20 \text{ mL}$ $C_{\text{Cu(II)}} = 5 \text{ mg L}^{-1}$ $C_{\text{Ni(II)}} = 5 \text{ mg L}^{-1}$ $C_{\text{Pb(II)}} = 5 \text{ mg L}^{-1}$ $C_{\text{Hg(II)}} = 5 \text{ mg L}^{-1}$ $\text{pH} = 6.0$	Cu(II) 10.2 mg g^{-1} Ni(II) 13.5 mg g^{-1} Pb(II) 21.1 mg g^{-1} Hg(II) 19.4 mg g^{-1}	[38]
Purolite Arsen X ^{np} Lewatit FO36 without EDDS and accompanying ions	$m = 2 \text{ g}$ $V = 200 \text{ mL}$ $C_{\text{Cu(II)}} = 63 \text{ mg L}^{-1}$ $C_{\text{Zn(II)}} = 65 \text{ mg L}^{-1}$ $C_{\text{Cr(VI)}} = 52 \text{ mg L}^{-1}$ $C_{\text{Pb(II)}} = 207 \text{ mg L}^{-1}$ $C_{\text{Cd(II)}} = 112 \text{ mg L}^{-1}$ $\text{pH} > 4.5$	For Purolite Arsen X ^{np} $C_{\text{Cu(II)}} = 5.57 \text{ mg g}^{-1}$ $C_{\text{Zn(II)}} = 4.84 \text{ mg g}^{-1}$ $C_{\text{Cr(VI)}} = 4.77 \text{ mg g}^{-1}$ $C_{\text{Pb(II)}} = 17.14 \text{ mg g}^{-1}$ $C_{\text{Cd(II)}} = 8.20 \text{ mg g}^{-1}$ for Lewatit FO36 $C_{\text{Cu(II)}} = 2.94 \text{ mg g}^{-1}$ $C_{\text{Zn(II)}} = 2.37 \text{ mg g}^{-1}$ $C_{\text{Cr(VI)}} = 5.19 \text{ mg g}^{-1}$ $C_{\text{Pb(II)}} = 15.93 \text{ mg g}^{-1}$ $C_{\text{Cd(II)}} = 3.02 \text{ mg g}^{-1}$	Present study

capacities of Purolite ArsenX^{np} and Lewatit FO36 toward heavy metal ions is presented in Table 3.

It can be observed that the adsorption capacity of both ion exchangers is equal and also higher than that of some other sorption materials reported in the literature. For example, Lee et al. [32] found that sorption capacity of the iron oxide nanoparticles immobilized sand for Cd(II) 1.26 mg g^{-1} and for Pb(II) 2.08 mg g^{-1} , respectively. For the used ion exchangers Lewatit FO36 and Purolite Arsen X^{np}, these values are equal to 15.93, 3.02, 17.14, and 8.20 mg g^{-1} , respectively. However, it should be mentioned that in the case of applicability of EDDS, the mechanism of sorption is quite different and connected with the presence of anionic complexes (ion exchange). In the literature data, there is no information concerning the applicability of ethylenediaminedisuccinic acid as a complexing agent for heavy metal ion removal on HIX based on the hydrous iron oxides. EDDS was only used for heavy metal ion removal in the anionic complexes on anion exchangers, as shown in [39–41]. The preliminary results for heavy metal ion removal on Lewatit FO36 were also presented in our previous article [42]. Such biodegradable chelating agents as EDDS are commonly used to enhance the heavy metal extraction from the contaminated soils.

EDDS causes a much lower potential metal leaching than EDTA, and it is less toxic to soil microorganisms [43].

As was previously mentioned, the sorption of anionic complexes of Cu(II), Zn(II), Cd(II), and Pb(II) with EDDS is connected with the ion exchange process. This mechanism was confirmed by the ATR/FT-IR analysis. The exemplary results for Purolite Arsen X^{np} and Lewatit FO36 are presented in Fig. 9. In the recorded spectra, the stretching vibrations at 3290 and 3170 cm^{-1} are connected with the presence of hydroxyl and amine groups (Lewatit FO36). Other characteristic bands appear at the wavelengths 1636 cm^{-1} and 1478 cm^{-1} . These are related to the presence of the NH deformation vibration and that of symmetric and asymmetric $\nu_{\text{as}}\text{COO}^-$ and $\nu_{\text{s}}\text{COO}^-$. In addition, the bands at 1031 and 1086 cm^{-1} are connected with the stretching vibrations of CO group. Changing the pH of the solution causes a slight shift of various bands, \emptyset most noticeably in the case with Purolite Arsenic X^{np}.

The AFM images illustrate the changes in the surface of the HIX Purolite Arsen X^{np} used in the studies before and after sorption (Fig. 10). No significant changes in the surface morphology were observed before and after the sorption. Based on the observations, it was found that

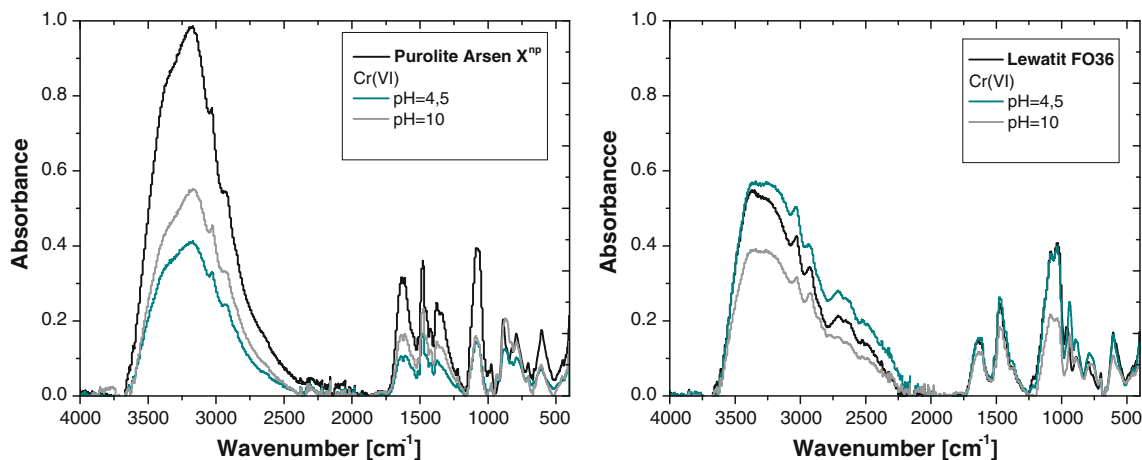


Fig. 9 FT-IR images of the HIX Purolite Arsen X^{np} and Lewatit FO36 before and after the adsorption process

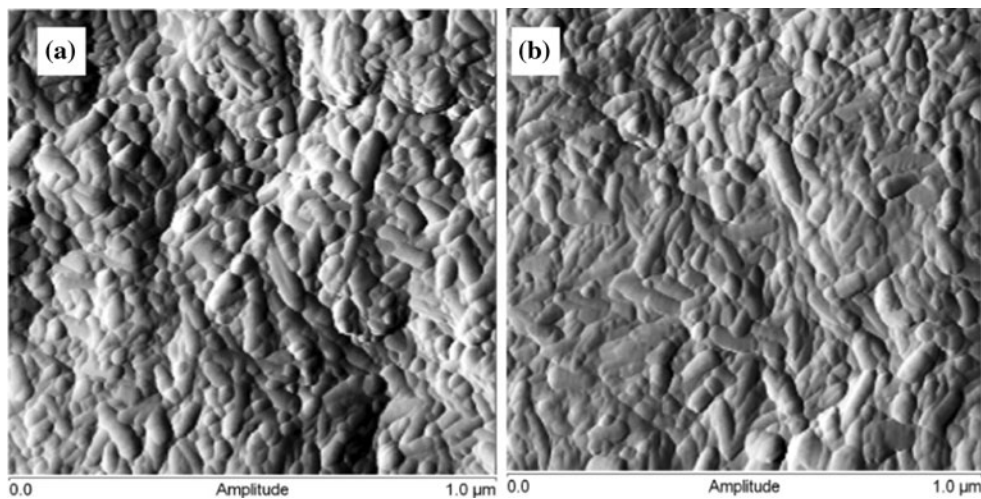
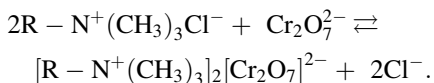


Fig. 10 AFM scans of Purolite Arsen X^{np} before (a) and after (b) sorption of Cr(VI)

Cr(VI) ions present in the solution penetrate inside the ion exchanger pores according to the reaction:



Desorption of hybrid sorbents proceeds easily on alkalization of the adsorbent surface. In an alkaline environment, the dominant form on the surface of iron oxides are $\equiv Fe-O^-$ groups, and they adsorb anions in solution. Some ions may, however, remain inside the polymer by reducing the effective sorption capacity by 10–20 %. It has been shown in subsequent regeneration cycles that this effect gets smaller. Regeneration is carried out with a mixture of NaOH and NaCl or NaOH (4–10 %). Depending on conditions and sorption properties of the hybrid material, in the regeneration process, 90–98 % ions are removed. In order

to increase the efficiency of regeneration, this process is sometimes carried out at elevated temperatures.

Conclusions

Based on the results obtained, both Purolite Arsen X^{np} and Lewatit FO36 may find use in removing heavy metal ions such as Cu(II), Zn(II), Cd(II), and Pb(II) in the presence of EDDS. The interactions of metal ions with the hybrid sorbents are complex, probably simultaneously dominated by adsorption and ion exchange. The pH dependence of ion exchange may suggest that the metal ions are adsorbed according to an ion exchange mechanism. The effect of sulfate ligands on metal adsorption to hybrid sorbents is largely dependent on the surface properties of these materials.

On the basis of the studies, it can be stated that the effectiveness of sorption for Cr(VI), Cu(II), Zn(II), Cd(II), as well as Pb(II) ions depends on the conditions under which the process is carried out. The main parameters affecting sorption are initial concentration of the solution, pH, and phase contact time. Temperature has only a slight influence. With respect to effectiveness of the removal of Cr(VI), Cu(II), Zn(II), Cd(II), and Pb(II), the hybrid sorbents can be arranged as Purolite Arsen X^{np} > Lewatit FO36. It should also be emphasized that the best results are obtained for Cr(VI) ions. Therefore, they can be applied in systems of drinking and industrial water purification.

Open Access This article is distributed under the terms of the Creative Commons Attribution License which permits any use, distribution, and reproduction in any medium, provided the original author(s) and the source are credited.

References

1. Barceloux DG (1999) Chromium. *J Toxicol Clin Toxicol* 37: 173–194
2. Clifford DA, Ghurye GL (2002) Metal-oxide adsorption, ion exchange and coagulation-microfiltration for arsenic removal from water. In: Frankenberger WT (ed) *Environmental chemistry of arsenic*. Marcel Dekker, New York, pp 217–245
3. Clifford DA, Ghurye GL, Tripp AR (1999) Development of an anion exchange process for arsenic removal from water. In: Chappell WR, Abernathy CO, Calderon RL (eds) *Arsenic exposure and health effects*. Elsevier Science, Oxford, pp 379–387
4. Cumbal L, Greenleaf J, Leun D, SenGupta AK (2003) Polymer supported inorganic nanoparticles: characterization and environmental applications. *React Funct Polym* 54:167–180
5. Cumbal L, SenGupta AK (2005) Arsenic removal using polymer supported hydrated iron(III) oxide nanoparticles: role of Donnan membrane effect. *Environ Sci Technol* 39:6508–6515
6. Elangovan R, Philip L, Chandraraj K (2008) Biosorption of hexavalent and trivalent chromium by palm flower (*Borassus aethiopicum*). *Chem Eng J* 141:99–111
7. US EPA (2000) Arsenic removal from drinking water by ion exchange and activated alumina plants. Prepared by Battelle under contract 68-C7-0008 for EPA ORD
8. Mohan D, Pittman ChU Jr (2007) Arsenic removal from water/wastewater using adsorbents: a critical review. *J Hazard Mater* 142:1–53
9. Hua M, Zhang S, Pan B, Zhang W, Lv L, Zhang Q (2012) Heavy metal removal from water/wastewater by nanosized metal oxides: a review. *J Hazard Mater* 211–212:317–331
10. Kołodziejńska D (2011) Organic–inorganic composite materials as sorbents and ion-exchangers used in environmental protection. In: Inamuddin (ed) *Advanced organic–inorganic composites: materials, devices and allied applications*. Nova Science Publishers, New York, pp 69–130
11. Qiu H, Zhang S, Pan B, Zhang W, Lv L (2012) Effect of sulfate on Cu(II) sorption to polymer-supported nano-iron oxides: behavior and XPS study. *J Colloid Interface Sci* 366:37–43
12. Sarkar S, Blaney LM, Gupta A, Ghosh D, SenGupta AK (2008) Arsenic removal from groundwater and its safe containment in a rural environment: validation of a sustainable approach. *Environ Sci Technol* 49:4268–4273
13. Brochure of Purolite International Ltd. 2011
14. Lanxess (2007) Engineering information, arsenic separation from ground water using Lewatit FO 36 ion exchange/iron oxide hybrids system, Leverkusen
15. Langmuir I (1916) The constitution and fundamental properties of solids and liquids. *J Am Chem Soc* 38:2221–2295
16. Freundlich HFM (1906) Über die adsorption in Lösungen. *Z Phys Chem* 57:385–470
17. Lagergren S (1898) Zur Theorie der sogenannten Adsorption gelöster Stoffe. *Kungliga Svenska Vetenskapsakademiens Handlingar* 24:1–39
18. Blanchard G, Maunay M, Martin G (1984) Removal of heavy metals from waters by means of natural zeolites. *Water Res* 18:1501–1507
19. Ho YS, McKay G (1998) Sorption of dye from aqueous solution by peat. *Chem Eng J* 70:115–124
20. Juang R, Wu W (2002) Adsorption of sulphate and copper(II) on goethite in relation to the changes of zeta potentials. *J Colloid Interface Sci* 249:22–29
21. Boukhalfa Ch (2010) Sulfate removal from aqueous solutions by hydrous iron oxide in the presence of heavy metals and competitive anions. *Macroscopic and spectroscopic analyses*. *Desalination* 250:428–432
22. Chardichai P, Ritchie GSP (1992) The effect of pH on zinc adsorption by a lateritic soil in the presence of citrate and oxalate. *J Soil Sci* 43:713–728
23. Christophi ChA, Axe L (2000) Competition of Cd, Cu, and Pb adsorption on goethite. *J Environ Eng* 126:66–74
24. Jaworska JS, Schowaneck D, Feitzel TCJ (1999) Environmental risk assessment for trisodium [S,S]-ethylene diaminedisuccinate, a biodegradable chelator used in detergent applications. *Chemosphere* 38:3597–3625
25. Loonen H, Lindgren F, Hansen B, Karcher W, Niemelä J, Hiromatsu K, Takatsuki M, Peijnenburg W, Rorije E, Struijs J (1999) Prediction of biodegradability from chemical structure: modeling of ready biodegradation test data. *Environ Toxicol Chem* 18:1763–1768
26. Tandy S, Ammann A, Schulin R, Nowack B (2006) Biodegradation and speciation of residual S,S-ethylenediaminedisuccinic acid (EDDS) in soil solution left after soil washing. *Environ Pollut* 142:191–199
27. Elliot HA, Huang CP (1981) Adsorption characteristics of some Cu(II) complexes on aluminosilicates. *Water Res* 15:849–855
28. Kołodziejńska D (2011) Application of strongly basic anion exchangers for removal of heavy metals in the presence of green chelating agent. *Chem Eng J* 168:994–1007
29. McBride MB (1989) Reactions controlling heavy metal solubility in soils. *Adv Soil Sci* 10:1–56
30. Perelomov LV, Pinskiy DL, Violante A (2011) Effect of organic acids on the adsorption of copper, lead, and zinc by goethite. *Eur Soil Sci* 44:22–28
31. Ali MA, Dzombak DA (1996) Interactions of copper, organic acids, and sulfate in goethite suspensions. *Geochim Cosmochim Acta* 60:5045–5053
32. Lee SM, Laldawngliana C, Tiwari D (2012) Iron oxide nanoparticles-immobilized-sand material in the treatment of Cu(II), Cd(II) and Pb(II) contaminated waste waters. *Chem Eng J* 195–196:103–111
33. Mahmoud ME, Abdelwahab MS, Fathallah EM (2013) Design of novel nano-sorbents based on nano-magnetic iron oxide-bound-nano-silicon oxide-immobilized-triethylenetetramine for implementation in water treatment of heavy metals. *Chem Eng J* 223:318–327
34. Gong J, Chen L, Zeng G, Long F, Deng J, Niu Q, He X (2012) Shellac-coated iron oxide nanoparticles for removal of cadmium(II) ions from aqueous solution. *J Environ Sci* 24: 1165–1173

35. Karami H (2013) Heavy metal removal from water by magnetite nanorods. *Chem Eng J* 219:209–216
36. Tan Y, Chen M, Hao Y (2012) High efficient removal of Pb(II) by amino-functionalized Fe₃O₄ magnetic nano-particles. *Chem Eng J* 191:104–111
37. Roy A, Bhattacharya J (2012) Removal of Cu(II), Zn(II) and Pb(II) from water using microwave-assisted synthesized magnetite nanotubes. *Chem Eng J* 211–212:493–500
38. Mahapatra A, Mishra BG, Hota G (2013) Electrospun Fe₂O₃–Al₂O₃ nanocomposite fibers as efficient adsorbent for removal of heavy metal ions from aqueous solution. *J Hazard Mater* 258–259:116–123
39. Kołodzyńska D (2010) Biodegradable complexing agents as an alternative to chelators in sorption of heavy metal ions. *Desalination Water Treat Sci Eng* 16:146–155
40. Kołodzyńska D (2011) Green complexing agent EDDS in removal of heavy metal ions on strongly basic anion exchangers. *Desalination* 280:44–57
41. Kołodzyńska D (2011) The chelating agents of a new generation as an alternative to conventional chelators for heavy metal ions removal from different waste waters. In: RY Ning (ed) *Expanding issues in desalination*. InTech Publishers, ISBN 978-953-307-326-2, pp 339–371
42. Kowalczyk M, Hubicki Z, Kołodzyńska D (2013) Modern hybrid sorbents: new ways of heavy metal removal from waters. *Chem Eng Process* 70:55–65
43. Grčman H, Vodnik D, Velikonja-Bolta Š, Leštan D (2003) Ethylenediaminedissuccinate as a new chelate for environmentally safe enhanced lead phytoextraction. *J Environ Qual* 32:500–506