

Hybrid sorbents in metal ions removal from water and wastewater

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Introduction

Industrial development results in greater and greater environmental pollution. Highly toxic substances affecting negatively plant and animal organisms as well as human health and life. A large group of them are metals such as lead(II), copper(II), cadmium(II), zinc(II), nickel(II), mercury(II), chromium(VI) and arsenic(III,V). Their main source are waste water originating from metallurgical, textile, tanning, artificial fertilizers, pesticides, dyeing, textile, mechanization, power industries. Of great hazard are also sewages from which there are washed away precipitations i.e. refluxes from dumps and fertilization of soils with mineral fertilizers and sludges. According to the WHO recommendations very harmful for living organisms are cadmium(II), nickel(II), lead(II), mercury(II), as well as arsenic(III,V) and chromium(VI). It is worth noting that some of them like copper(II), zinc(II) or chromium(VI) are indispensable elements for proper functioning of many organisms.

Copper is the element occurring in all kinds of water and its content is largely differentiated. The admissible concentration of copper in ground water is 20 $\mu\text{g}/\text{dm}^3$. Its toxicity in the aqueous medium depends on pH, water, hardness, concentration of dissolved oxygen, presence of chelating agents, presence of humus acids, content of solids suspensions and interactions among other metals. Copper(II) is also a microelement which is a component of many enzymes. It takes part in formation of erythrocytes, is a component of hemocyanine, has a positive effect on the membrane surrounding nerve cell and participates in sending nerve impulses and connective tissue formation.

Waste water from zinc plants and metal treatment plants as well as chemical ones are the source of zinc in surface water. Zinc gets into the environment due to combustion of coal, petroleum and its products. Another source of zinc is secondary raw materials such as remains after galvanizing, power from steel plants or scraps from brass treatment. Another sources of this metal in soil are herbicides and phosphate fertilizers.

The zinc(II) content in water ranges from a few to several hundred $\mu\text{g}/\text{dm}^3$. Despite great susceptibility to migration, zinc gets into underground water in relatively small amounts. Its content in natural soil drinkable water in Poland is about 15 $\mu\text{g}/\text{dm}^3$ and does not exceed 80 $\mu\text{g}/\text{dm}^3$. Toxicity extent of zinc(II) is not large but its depends on the ionic form and changes due to water hardness and pH. Like copper zinc is an element indispensable for proper functioning of living organisms. It takes part in metabolism of proteins and carbohydrates. According to the decree of the Environment Ministry of 27 November 2002 the admissible concentration of zinc on water is 0.5 mg/dm^3 .

However, as follows from the literature data in Polish ground waters the chromium content ranges from 0.02 to 0.07 $\mu\text{g}/\text{dm}^3$. In the production and application of chromium compounds waste solutions and waters are formed containing chromium from 0.5 to 270 mg/dm^3 [1]. Their main sources are galvanizing plants, chromium plating and

etching of various metals. Like zinc(II) chromium(VI) plays a significant role in metabolism of some proteins and fats. It also performs an important function in metabolism of glucose. Its deficiency weakens the insulin action.

Arsenic belongs to semi-metals characterized by the properties intermediate between metals and non-metals. This element and its compounds possess very strong toxicity and ability to cumulate in organisms. Therefore, its presence is undesirable in surface water designed for drinking. Thus there is tendency to decrease as much as possible the level of contamination with this element. It is estimated that the surface water in Poland contain on the average below 40 $\mu\text{g}/\text{dm}^3$ of arsenic. According to the WHO its admissible content in drinkable water is 0.01 mg/dm^3 . Arsenic cumulates in creatine rich tissues such hair, nails and skin. Arsenic compounds similar to chromium compounds exhibit affinity for many enzymes and can inhibit their activity, first of all causing disturbances in Krebs cycle. Serious arsenic poisoning damages alimentary tract, causes chronic anemia, brittleness of hair and nails as well as skin changes, breathing disturbances, changes in the circumferential nerve system, heart and liver.

It should be stressed that even the elements indispensable for proper functioning of living organisms in small or trace amounts are toxic in large concentrations. Therefore finding effective methods for their removal is of significant importance. In technology of water and waste water purification adsorption methods and ion exchange are successfully applied.

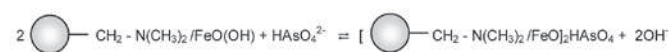
Adsorption capabilities of Cu(II), Zn(II), As(V) and Cr(VI) ions are exhibited among others by oxides and hydroxides of metals (MnO_2 , TiO_2 , SnO_2 , Fe_3O_4 , $\text{Fe}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$), active carbons, synthetic ion exchange resins and more and more commonly used low cost sorbents.

The paper presents the results of studies on sorption of such heavy metal ions such as Cu(II) and Zn(II) in the presence of biodegradable complexing agent – iminodisuccinic acid (IDS) from aqueous solutions as well as As(V) and Cr(VI) on the commercial ion exchangers Lewatit FO36 and Purolite Arsen X^{np} containing inbuilt iron nanooxide molecules of the goethite structure. In the production process iron oxide was distributed in the pores of the above mentioned ion exchangers as a layer of a few nanometers thickness.

Experimental part

Sorbents and reagents

Lewatit FO36 is a weakly basic macroporous anion exchanger based on the polystyrene-divinylbenzene copolymer of 0.35 mm beads containing iron nanooxide. Sorption of oxoanions, such as arsenate(V) on the ion exchanger Lewatit FO36 proceeds due to their reactions with hydroxyl groups on the iron oxide surface according to the reaction:



This ion exchanger is recommended for purification of drinkable water containing arsenic ions. The removal of the above mentioned ions using Lewatit FO36 is 0,01 mg/dm³. It can be also applied for removal of HPO₄²⁻, H₂BO₄²⁻, SCN⁻ ions and others. The SEM scans of Lewatit FO 36 are given in Figure 1. It should be stressed that its advantages is the slight affinity for SO₄²⁻, NO₃⁻ and Cl⁻ ions.

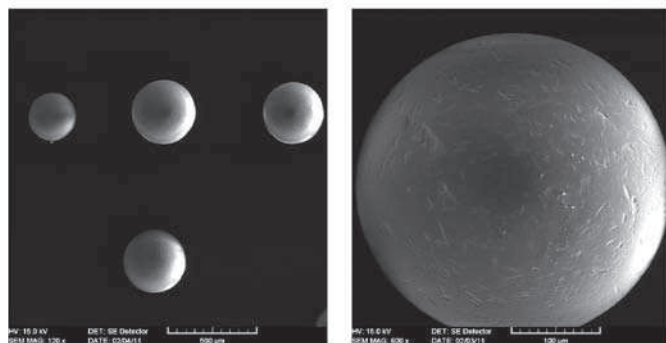
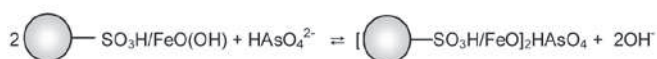


Fig. 1. SEM scans of Lewatit FO36

Purolite Arsen X^{np} is a selective, nanomolecular resin based on a polystyrene-divinylbenzene skeleton designer for removal of arsenic(III and V) ions. It combines a unique structure of hydrated iron nanomolecules spread on the polymer matrix. This ion exchanger is characterised by great strength and selectivity towards the above mentioned ions and the mechanism of their removal can be written according to the reaction:



In the case of Purolite Arsen X^{np} to prepare a hybrid sorbent there was applied a polymer skeleton of large beads sizes (0.3-1.2 mm) and large ion exchange capacity 1.56 meq/dm³. For the sorbent Purolite Arsen X^{np} his capacity is 0.92 meq/dm³ [2]. The determined sorption static capacity for As(V) is in the range 0.5-4.0 g As/dm³ depending on the initial solution concentration of 0.01-0.1 mg/dm³ [3]. This ion exchanger was patented by SenGupta and co-workers in 2007 [4], and then modified and produced on the commercial scale by Purolite International Ltd. At present it is used, among others, in portable systems used for fast determination of metal ions in aqueous solutions, removal of uranium(VI) or phosphates(V) [5,6]. The SEM scans of Purolite Arsen X^{np} are given in Figure 2.

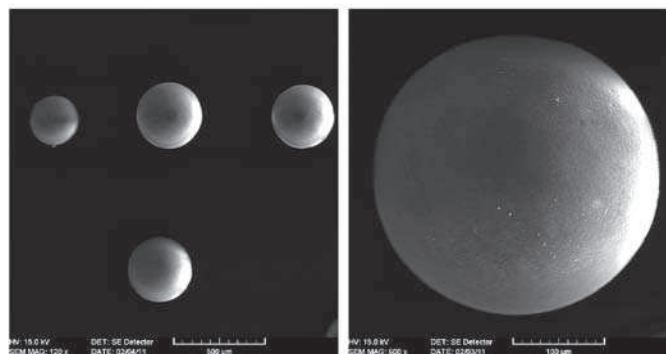


Fig.2. SEM scans of Purolite Arsen Xnp

IDS – iminodisuccinic acid, known of the commercial name Baypure CX 100 (Lanxess), is a mixture of iminodisuccinic acid (>32%), aspartic acid (<7.0%), fumaric acid (<3.5%), hydroxosuccinic acid (<0.9%) and maleic acid (<0.9%). It undergoes biodegradation in 80% within 7 days. It is mainly applied in production of clearing agents, detergents for dishwashers and fluid microelement fertilizers.

Measurement and methods

Sorption of Cu(II) and Zn(II) ions in the presence of IDS as well as As(V) and Cr(VI) was carried out from the solutions of 20 cm³ volume to which 0.2 g the above- mentioned sorbents was added. The ion solutions used in the static method were prepared by dilution of the suitable preliminary solutions CuCl₂·2H₂O, ZnCl₂ as well as Na₂HAsO₄ and K₂Cr₂O₇. In the case of the solutions containing Cu(II) and Zn(II) a suitable amount of the IDS solution was added. The flasks were shaken and after some time their contents were filtered off. The phase contact time 3 h was established from the earlier studies. The isotherms of Cu(II) and Zn(II) adsorption in the presence of IDS, As(V) and Cr(VI) were determined with the solution pH 6,0±0,2. Concentration of Cu(II) and Zn(II) were determined by means of the atomic absorption spectroscopy method (AAS) using spectrometer SpectrAA 240 FZ (Varian), and those of As(V) and Cr(VI) were determined by means of Specord M42 (Carl Zeiss), using the reactions of formation of their coloured complexes with ammonium molybdate and diphenylcarbazide, respectively [6]. The sorption process was carried out with different phase contact times, concentrations and pH. Sorption capacities of the studied sorbents were calculated from the Eq. 1:

$$q_t = \frac{(c_0 - c_t)V}{m} \quad (1)$$

where: c₀ is the initial concentration of the solution mg/dm³, c_t is the concentration of the solution after time t mg/dm³, c_e is the concentration in the equilibrium state mg/dm³, V is the volume of solution dm³, m is the mass of the dry ion exchanger g.

Results and discussion

The reaction of formation of M(II) complexes with IDS can be presented accordingly to the reaction (where: M= Cu, Zn; n=0-3):

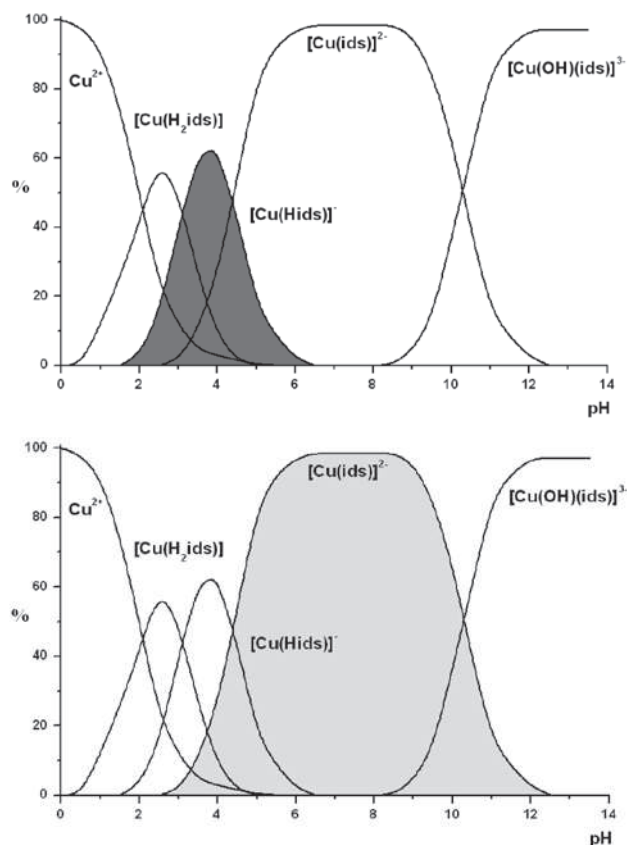
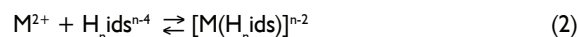


Fig.3. Speciation diagrams of the Cu(II) complexes with IDS

It proved that over 90% of metal ions complexed by IDS in a wide pH range, whereby the complexes obtained for lower pH values are less stable e.g. for Cu(II) the effective complexing range is included in the pH range 3-12, but for Zn(II) 5-11. Based on the speciation distribution of the Cu(II) complexes with IDS it was stated that complexes of the $[M(ids)]^{2-}$ or $[M(Hids)]^{-}$ type should be effectively sorbed (Rys.3a-b). According to Cokes and co-workers [7] the Ca(II)-IDS and Fe(II)-IDS complexes are readily biodegradable. The Mn(II)-IDS and Cu(II)-IDS complexes undergo biodegradation in 55% and 40% after 28 days i.e. under standard conditions they are practically non-biodegradable.

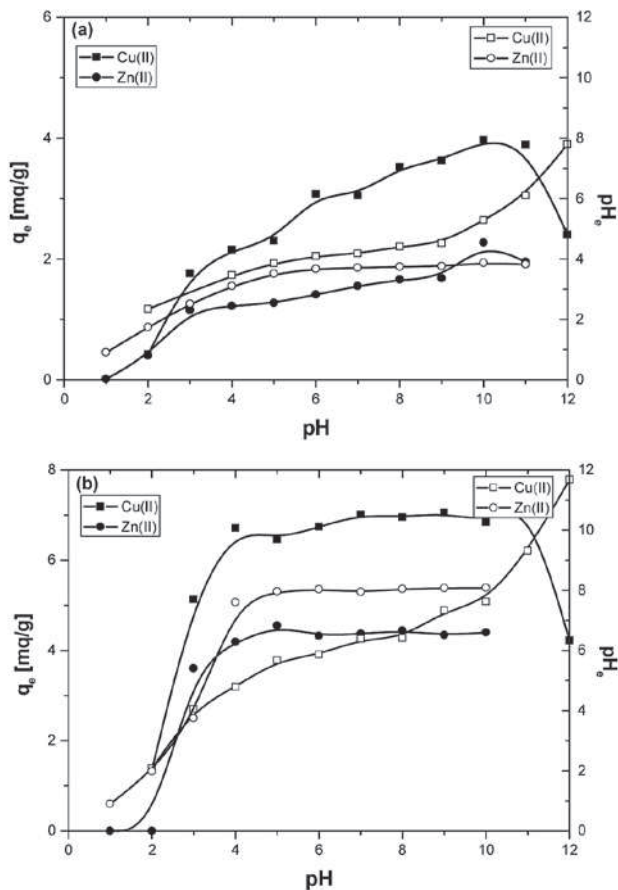
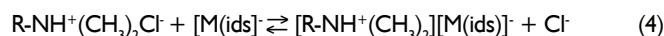
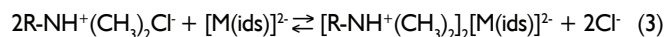


Fig.4a-b. The effect of pH on sorption of the Cu(II) and Zn(II) complexes with IDS in the M(II)-IDS=1:1 system on Lewatit FO 36 (a) and Purolite ArsenXnp (b) (t=3h)

Taking into account the effect of pH on the sorption effectiveness of Cu(II) and Zn(II) complexes with IDS as well as As(V) and Cr(VI) for Lewatit FO36 it was proved that the sorption capacity increases to the pH value 10, for As(V) 6,0, and then slightly decreases. For Purolite Arsen X^{np} the sorption capacity increases for As(V) slightly increases to pH 1-4 and then is almost constant. In the case of the sorption process of Cr(VI) the pH value does not affect the sorption process. The exemplary results for Cu(II) and Zn(II) sorption in the M(II):IDS=1:1 system are shown in Figure 4. Taking into account the pH change values as well as the fact that Lewatit FO36 possesses the polystyrene-divinylbenzene matrix with amine functional groups the following mechanism of the Cu(II) and Zn(II) complexes with IDS can be proposed:



It should be also mentioned that the exchange between the complexes of the $[M(ids)]^{2-}$ type and the OH⁻ groups of the hydrated iron oxide is possible (as in the case of HAsO₄²⁻ ions sorption).

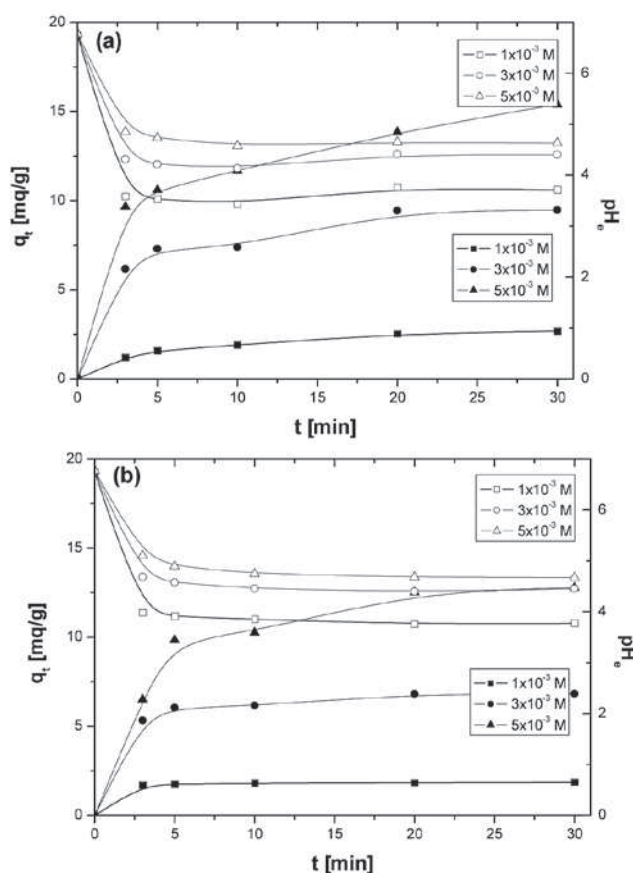


Fig.5a-b. The effect of phase contact time on sorption of the Cu(II) and Zn(II) complexes with IDS in the M(II)-IDS=1:1 system with various initial concentrations of the complexes on Lewatit FO36 (a)-Cu(II); (b)-Zn(II)

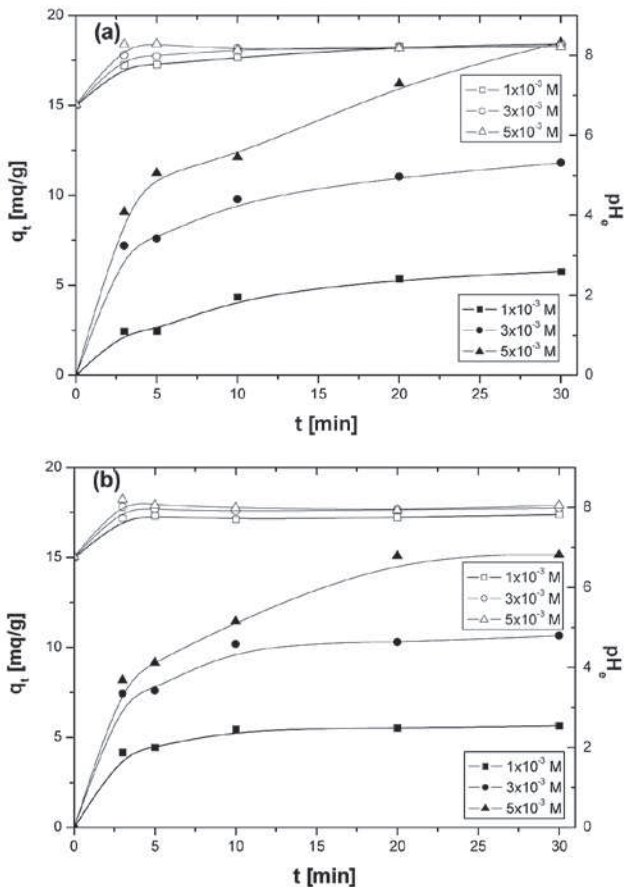


Fig.6a-b. The effect of phase contact time on sorption of the Cu(II) and Zn(II) complexes with IDS in the M(II)-IDS=1:1 system with various initial concentrations of the complexes on Purolite ArsenXnp (a)-Cu(II); (b)-Zn(II)

In the next stage the amounts of retained heavy metal ions in time depending on the initial concentration for the ion exchangers Lewatit FO36 and Purolite Arsen X^{np} were compared. For all studied systems the typical dependence $q_t=f(t)$ was obtained. The exemplary results obtained for Cu(II) and Zn(II) in the presence of IDS are presented in Figures 5a-b and 6a-b. In the initial sorption stage there is observed a fast increase of sorption capacities (q_t) which is connected with a large number of accessible active sites in relation to the number of sorbed complexes. The studied complexes undergo fast sorption on the sorbent surface. With the process progress their number decreases gradually and q_t reaches the constant value. The equilibrium state, which is about 120 min. is established. Comparing the calculated kinetic parameters for the equation of the pseudo first order (PF-order) and pseudo second order (PS-order) with respect to linear dependence $t/q_t=f(t)$ and close to unity values of correlation coefficients (R^2) and good agreement with the experimental data it was proved that the PS-order kinetic model is suitable for description of the sorption process. The obtained data are presented in Table I.

Table I
Kinetic parameters of Cu(II) and Zn(II) sorption in the presence of IDS as well as As(V) and Cr(VI) on the ion exchanger Purolite Arsen X^{np} and Lewatit FO36

System		Cu(II)-IDS=1:1	Zn(II)-IDS=1:1	As(V)	Cr(VI)
Purolite Arsen X ^{np}					
$q_{e,exp}$		6.10	6.26	8.80	5.44
PF-order	q_1	4.94	1.93	2.39	11.68
	k_1	0.092	0.043	0.086	0.128
	R^2	0.9899	0.7604	0.9604	0.9241
PS-order	q_2	7.21	5.88	8.91	5.45
	k_2	0.019	0.135	0.099	3.696
	h	0.988	4.695	7.868	10.890
	R^2	0.9845	0.9993	0.9995	0.9997
Lewatit FO 36					
$q_{e,exp}$		2.73	1.91	6.67	5.42
PF-order	q_1	1.23	4.79	1.29	2.48
	k_1	0.128	0.048	0.074	0.106
	R^2	0.9904	0.9064	0.9585	0.8408
PS-order	q_2	3.15	1.87	6.66	5.45
	k_2	0.059	1.451	0.200	0.649
	h	0.587	5.107	8.873	19.305
	R^2	0.9962	0.9999	0.9998	1.0000

Based on the determined sorption isotherms, it was possible to compare the sorption process for the systems under investigations. The parameters of the adsorption process were estimated based on the linear form of the Langmuir, Freundlich, Temkin and Dubinin-Radushevish isotherms. Suitable equations are presented in paper [8].

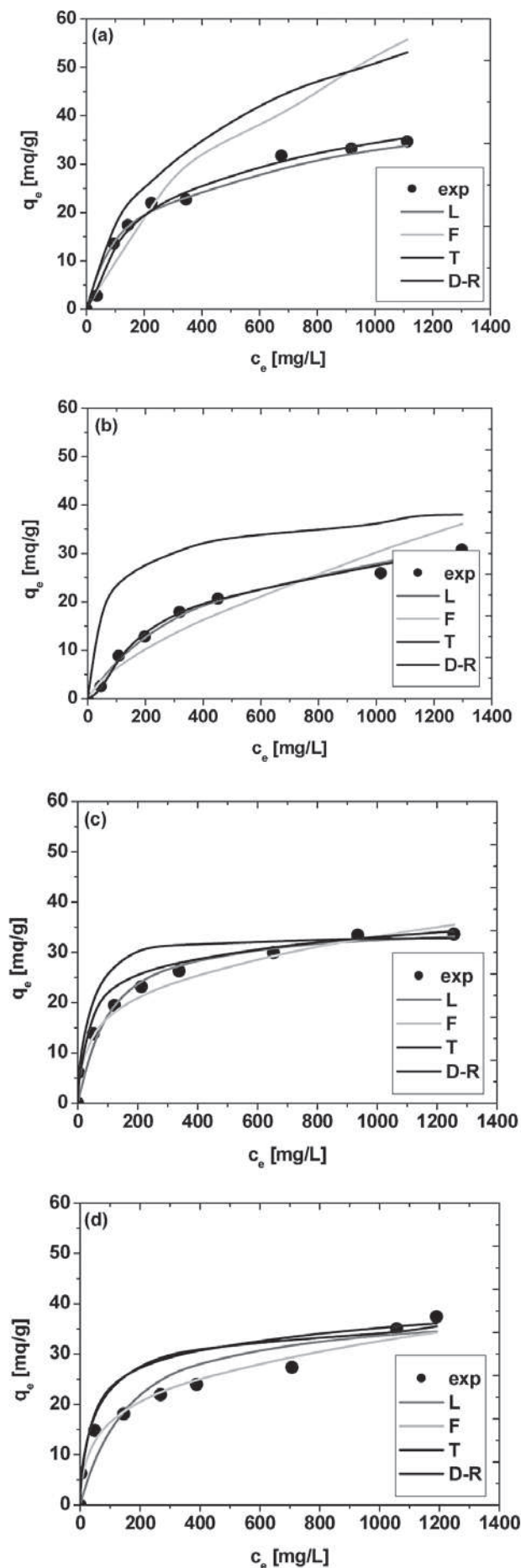


Fig.7a-d. The isotherms of the sorption of the Cu(II) and Zn(II) complexes with IDS and their fit by means of the Langmuir, Freundlich, Temkin and Dubinin-Radushevich: (a) Cu(II)-IDS=1:1 on Lewatit FO36; (b) Zn(II)-IDS=1:1 on Lewatit FO36; (c) Cu(II)-IDS=1:1 on Purolite ArsenXnp; (d) Zn(II)-IDS=1:1 on Purolite ArsenXnp

As follows from the calculated sorption parameters the experimental data obtained for the Cu(II) and Zn(II) complexes with IDS on the ion exchangers Lewatit FO36 and Purolite Arsen X^{np} are described well the Langmuir and Temkin isotherm equations. The other models describe satisfactory the experimental isotherms in the limited concentration range. As predicted the amount of the adsorbed complexes increases gradually with the increasing initial concentration of solutions and then reaches the constant value. In order to determine maximal sorption capacities the concentrations were from 1×10^{-3} M to 25×10^{-3} M for Cu(II) and Zn(II) as well as 1×10^{-3} M to 3×10^{-3} M for As(V) and Cr(VI), respectively. The exemplary results sorption isotherms of the Cu(II) and Zn(II) complexes with IDS and their fit by means of the above mode are presented in Figures 7a-d.

It should be mentioned that in the removal process of anion complexes of metals and also As(V) and Cr(VI) ions there are also applied anion exchangers, particularly those of quaternary ammonium and amine functional groups [9-11]. They exhibit great affinity for sulfate(VI) and nitrate(V) (according to the affinity $\text{SO}_4^{2-} > \text{NO}_3^-$) and removal of As(V) or Cr(VI) from the solutions containing these ions is not fully effective. However, hybrid ion exchangers used in the paper can be recommended for their removal in the presence of sulfate(VI) ions which is decisive for their unique properties.

Conclusions

The paper presents the studies of application of hybrid ion exchangers based on iron oxides in the process of removing copper(II), zinc(II), arsenic(V) and chromium(VI) ions from water and waste water containing complexing agent IDS. The studies were carried out using the ion exchangers Lewatit FO36 and Purolite Arsen X^{np}. Owing to good total capacity and suitable physicochemical properties these ion exchangers can be recommended in these processes. As follows from the studies sorption effectiveness of the above mentioned ions is closely dependent on the conditions such phase contact time and pH value.

Considering the effectiveness of ions removal the above-mentioned hybrid ion exchangers can be put in the following order: **Cu(II)-IDS=1:1** Lewatit FO36 > Purolite Arsen X^{np}; **Zn(II)-IDS=1:1** Purolite Arsen X^{np} > Lewatit FO36. However, in the case of As(V) and Cr(VI) ions these were obtained the following series: **As(V)** Purolite Arsen X^{np} > Lewatit FO36 and **Cr(VI)** Purolite Arsen X^{np} = Lewatit FO36.

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