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COMPUTER MODELING OF ADSORPTION ON THE IMPREGNATED AL$_2$O$_3$, SIO$_2$ BY MONTE-CARLO METHOD

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Multisorption of heavy metals from aqueous solutions is very important in hydrometallurgy, industrial waste disposal, and water purification. The aim of this study is Monte Carlo simulation of the adsorption process of the Cd^{2+}, Pb^{2+}, Zn^{2+} ions on the SiO_2, Al_2O_3 sorbents impregnated with organic ligands (dithizone, PAN, benzothiazole). The impregnated alumina has a multisorption capacity, and silicon oxide impregnated by dithizone exhibits high selectivity to cadmium ions. The calculated data on the adsorption energy good correlate with the experimental data on multisorption activity of impregnated sorbents.

Keywords: sorption, molecular modeling, ligand, SiO_2, Al_2O_3

КОМПЬЮТЕРНОЕ МОДЕЛИРОВАНИЕ АДСОРБЦИИ НА ПРОПИТАННЫХ Al$_2$O$_3$, SiO$_2$ МЕТОДОМ МОНТЕ-КАРЛО

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Мультисорбция тяжелых металлов из водных растворов имеет важное значение в гидрометаллургии, утилизации промышленных отходов и очистке воды. Цель данного исследования – моделирование методом Монте-Карло процесса адсорбции ионов Cd^{2+}, Pb^{2+}, Zn^{2+} на импрегнированных с помощью органических лигандов SiO_2, Al_2O_3 (дитизон, ПАН, бензотиазол). Импрегнированный оксид алюминия обладает мультисорбционной способностью, а оксид кремния, импрегнированный дитизоном, проявляет высокую селективность по отношению к ионам кадмия. Расчетные данные по энергии адсорбции достаточно хорошо коррелируют с экспериментальными данными по мультисорбционной активности импрегнированных сорбентов.

Ключевые слова: сорбция, молекулярное моделирование, лиганд, SiO_2, Al_2O_3

MONTE-KARLO USULIDA IMPREGNIRLANGAN Al$_2$O$_3$, SiO$_2$ LARDA ADSORPSIYA JARAYONINI KOMPYUTERDA MODELLASHTIRISH

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Og'ir metallarni suvli eritmalardan multisorbsiyalash gidrometallurgiya, sanoat chiqindilarini utilizatsiya qilish va suvni tozalashda katta ahamiyatga ega. Ushbu tadqiqotning maqsadi organik ligandlar (ditizon, PAN, benzotiazol) bilan impregnirlangan SiO2, Al2O3 ga Cd2+, Pb2+, Zn2+ ionlarini adsorbsiyalash jarayonini Monte-Karlo usulida modellashtirish. Impregnirlangan aluminiy oksidi multisorbsiya qobiliyatiga ega bo'lsa, ditizon bilan impregnirlangan kremniy oksidi esa kadmiy ionlariga nisbatan yuqori selektivlikni namoyon etdi. Adsorbsion energiya bo'yicha hisoblangan ma'lumotlar impregnirlangan sorbentlarning multisorbsion faolligi bo'yicha eksperimental ma'lumotlarga juda mos keladi.

Kalit so'zlar: sorbsiya, molekulyar modellashtirish, ligand, SiO_2, Al_2O_3

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Introduction

The heavy metals belong to a group of substances that are difficult to degrade in nature at high level of accumulation in the human body [1]. The heavy metal contaminations of soils and water are frequently determined in mining industry; in addition, mine effluents and wastes are also sources of hazardous pollution that contain heavy metals in the highest concentrations [2]. Some regions of the active mining have been detected as a serious threat to human life due to high concentrations of heavy metals. It is known that adsorption and extraction technologies are widely used for water treatment and hydrometallurgy applications [3]. One of the modern prominent technology is solid-state extraction with application of organic solvent impregnated resin (SIR) [4]. Previously, we have enhanced sorption properties of different inorganic sorbents prepared from industrial wastes of Uzbekistan – phosphogypsum, steel -making slug, spent catalysts, polymer sorbents, minerals and etc [5-7].

The aim of this study is enhanced sorption activity of alumina oxide and silica based on molecular modeling in the multisorption process from water solution using solid-phase extraction with the novel impregnated sorbents. These sorbent based on organic ligands - 2-mercaptobenzothiazole (MBT), 1-(2-Pyridylazo)-2-naphthol (PAN), diphenylthiocarbazone (dithizone) (DTZ).

2-Mercaptobenzothiazole (MBT) is valuable precursor for synthesis of the MBT functionalized porous materials which can be used as an adsorbent for the removal of heavy metal from aqueous solution. Also it can be used as a reference compound and starting material for the organic synthesis and preparation of metal complexes [8-9].

1-(2-Pyridylazo)-2-naphthol (PAN), an orange colored dye, is commonly used as an acid-base indicator. It can form chelates with metal ions, which makes it a valuable indicator in complexometric titrations and many other analytical techniques. The PAN is also a spectrophotometric reagent, which can extract metal chelates into an organic solvent [10].

Dithizone (DTZ) is a sulfur-containing organic ligand that easily forms complexes with many metals such as lead and mercury [11].

Research methods

The Monte Carlo (MC) simulation was performed by the Adsorption Locator module in the BIOVIA Materials Studio 2017 package (https:// www. 3ds. com). The mineral surface models (Al_2O_3 (0 1 -1), (0 0 1), SiO_2 (0 1 0), (1 0 -1)) were built from the crystal structure of alumina and silica based on cif files (http:// www.crystallography.net/cod/), respectively. The crystal cell and the organic ligands molecules were optimized using the Universal forcefield, and the QEq charge method was applied. The optimization process was done by the Forcite module (Materials Studio 2017 package) with the ultra-fine convergence tolerance quality. The adsorption of organic ligands molecules on the alumina and silica surfaces was carried out using MC simulation by using the Adsorption Locator module with the Metropolis MC method to obtain the lowest-energy conformers between the adsorbate molecules/ions and adsorbent surface. This module calculates adsorption energy (Ead), kcal/mol and differential adsorption energy related to different types of adsorbate (Ligand: dEad/dNi, Metal: dEad/dNi, Water: dEad/dNi) (Table 1-2). The surfaces were cleaved from the optimized crystal cell using build tool with 35 Å-thick vacuum slab above the modeled active surfaces. The model example is shown in Figure 1-2. The van der Waals forces and electrostatic interactions were used by the atom-based and Ewald methods, respectively.

The organic ligands were impregnated by procedure described earlier [12]. The multisorption experiments were carried out by a batch method using aqueous solution of cadmium, zinc and lead nitrates (98%, Merck). The sorption test conditions: solid:solution (m/V) ratio = 3.33 g/L (m = mass of sorbent, g; V = volume of solution, L) under magnetic stirring (150 rpm); initial concentration of metal ions in aqueous solution = 5 mM; temperature = 25 °C; and duration = 0-3000 min. Aliquots were analyzed by ICP-OES (iCapPro, Thermo Fisher Scientific). The measured pH of the suspension was about 4-5 (FiveEasy F20, Mettler Toledo).

The sorbed amount of metal, Qe (mmol/g), was calculated by Eq. 1:

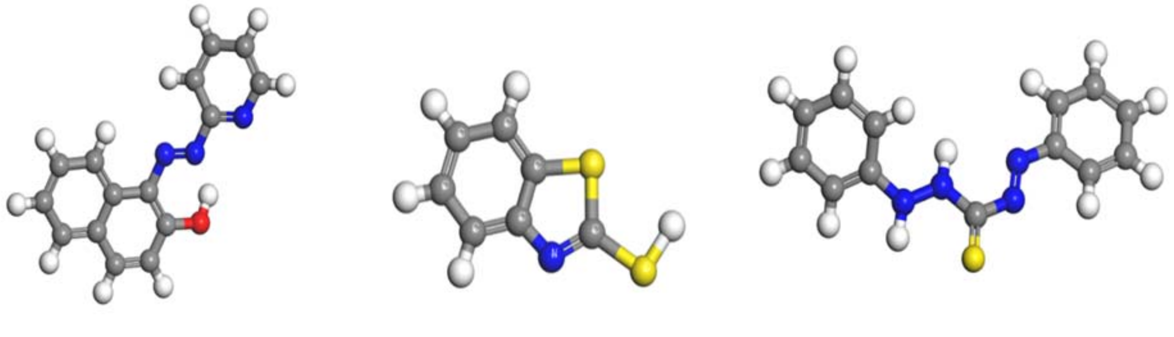
$$Q_e = \frac{C_0 - C_e}{m} V$$

where C_0 is the initial concentrations, mmol/L; and C_e is the final concentrations, mmol/L; V is the volume of sample, L; m is the mass of sorbent, g.

Results and Discussion

The Figure 1 shows the structures of impregnating organic ligands molecules; the Table 1 listed calculated adsorption energies.

The DTZ, MBT and PAN can form stable complexes with Cd^{2+}, Ni^{2+}, Zn^{2+} [31-33] due to SH and –NH – functional groups [34-38]. The tautomeric equilibrium between the thion (Ph–NH–NH]CS–N]N–Ph) and the thiol forms (Ph–NH–N]C(SH)–N]N–Ph) of the DTZ ligand, as well as, the keto and enol forms



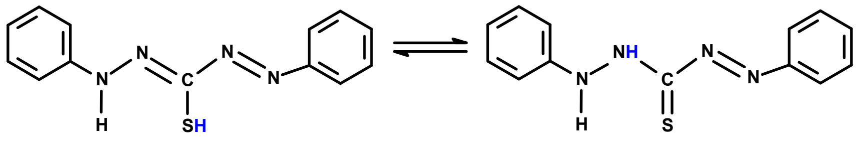
a b c

Figure 1. Structures of organic ligands: a) 1-(2-Pyridylazo)-2-naphthol (PAN), b) 2-mercaptobenzothiazole (MBT), c) Diphenylthiocarbazone (ditizone) (DTZ).
Atoms: *red* - oxygen, *yellow* - sulphur, *blue* - nitrogen, *grey* - carbon, and *white* - hydrogen.

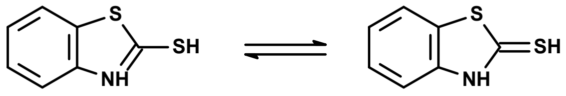
Table 1

Energetic parameters of adsorption on impregnated ligands

Adsorbent	Total energy, kcal/mol	Adsorption energy, E_{ad} kcal/mol	Rigid adsorption energy, kcal/mol	Deformation energy, kcal/mol	Ligand : dE_{ad}/dN_i	Water : dE_{ad}/dN_i
DTZ						
Al_2O_3 (0 0 1)	-79.16	-111.66	-112.64	0.97	-67.44	-5.35
SiO_2 (1 0 -1)	-27.27	-92.27	-92.66	0.38	-36.69	-3.29
SiO_2 (0 1 0)	-24.06	-89.06	-90.00	0.93	-36.59	-2.56
PAN						
Al_2O_3 (0 1 -1)	-82,51	-173,46	-175,17	1,708	-68,67	-5,64
Al_2O_3 (0 0 1)	-68,49	-113,97	-115,11	1,14	-69,77	-5,12
SiO_2 (0 1 0)	3,09	-87,85	-88,08	0,22	-35,18	-3,88
SiO_2 (1 0 -1)	3,21	-87,73	-88,77	1,036	-35,09	-2,40
MBT						
Al_2O_3 (0 0 1)	-62,99	-84,58	-84,73	0,147	-46,574	-4,80
SiO_2 (1 0 -1)	-25,35	-46,94	-46,98	0,0366	-20,79	-3,29

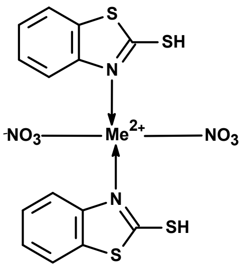


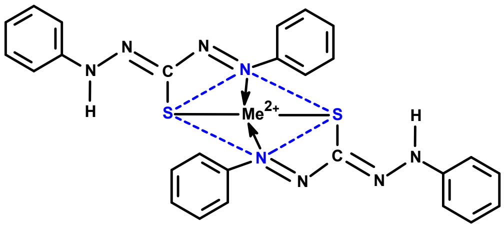
thiol ***thion***

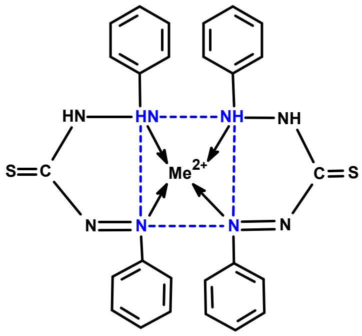


keto ***enol***

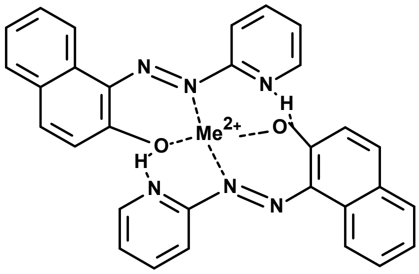
of the MBT ligand depend on pH. The keto form of the MBT is more stable in wide range of pH [13]. The DTZ thiol form is dominant at lower pH while the thion form is dominant at higher pH [14], however, DTZ can exist in both tautomeric forms at neutral pH. It is known that the metal complexes of the DTZ and MBT at neutral pH can stabilize different tautomeric form of ligands:







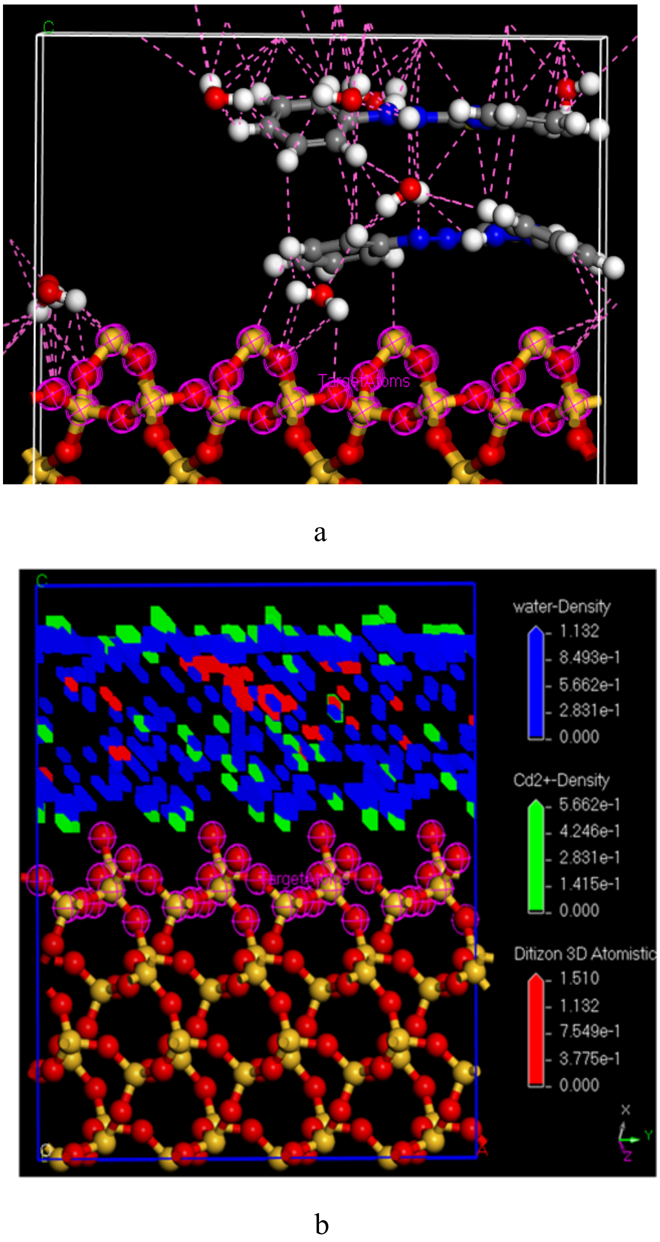
The PAN can form metal complexes with heavy metal and rare earth metal ions via different ionic forms. This reagent is slightly soluble in acidic solutions and soluble in alkaline solutions (pK_{a1}=2.9 and pK_{a2}=11.6) [15].



The molecular modeling of the DTZ, MBT tautomeric and ionic forms of the DTZ, MBT and PAN using BIOVIA Accelrys Material Studio software. The adsorption affinities and preferential sites of the DTZ, MBT and PAN molecules on experimentally observed planes of the XRD were computationally studied using molecular dynamics simulations and visually illustrated in Figure 2.

According to calculation results, the keto and thiol tautomeric forms are more stable and located at the surface using close contacts and hydrogen bonds between the NH-, SH-groups and adsorbed water molecules. Thus, the metal ions can interact with the N_{endo}–atom of the MBT immobilized ligand forming metal complex, as well as, the DTZ immobilized ligand can form metal complex via N and S atoms [14], predominantly. Figure 2a shows the most stable molecule configurations over the predominant adsorption surface planes and formation of the smooth distributed monolayer consisted of the DTZ, water molecules and metal ions on the surface of SiO_2-DTZ sample. Similarly, MBT and PAN molecules form less sterically ordered layer which is lead to possibility more close direct contacts between the surface and metal ions during sorption from water solution. The formation of the hydrogen bond network can stabilize the adsorbed metal complex molecules as a layer on the silica and alumina surfaces (Fig. 2).

The adsorption energies (E_{ad}) of the most stable configuration of the organic ligand molecules and the metal ions in the presence of a number of water molecules (n=1-9) over the mineral surfaces were exothermic due to strong mineral–adsorbate interaction (Table 1).



a

b

Figure 2. Molecular modeling of adsorption of the DTZ molecules on the silica surface.: (a) Snapshot interaction. Atoms: *red* - oxygen, *orange* - silicon, *blue* - nitrogen, *grey* - carbon, *yellow* - sulphur and *white* – hydrogen; (b) Distribution of field density of adsorption on the silica surface. Isosurface: *blue* – water, *green* – Cd^{2+} ions, *red* – dithizone.

According data of Table 2, simultaneous adsorption of the organic ligand tautomer molecules (DTZ, MBT or PAN), the Zn^{2+}, Pb^{2+}, Cd^{2+} ions and water molecules on the alumina and silica mineral surfaces is stronger (more exotermic) compared to that for adsorption on the silica surface. According adsorption energy and the differential adsorption (dE_{ad}/dN_i) values, the strongest adsorption of the Cd^{2+} ions were observed.

The Figure. 3 shows experimental data on sorption uptake (%) for a number of sorbents impregnated by the DTZ, MBT or PAN. All the samples showed multisorption

Table 2

Molecular modeling data (BIOVIA, Adsorption Locator module) of multisorption from water solution

Adsorbent	Total energy, kcal/mol	Adsorption energy, kcal/mol E_{ad}	Rigid adsorption energy, kcal/mol	Deformation energy, kcal/mol	Ligand: dE_{ad}/dN_i	Metal : dE_{ad}/dN_i	Water : dE_{ad}/dN_i	Metal
DTZ								
Al_2O_3 (0 0 1)	-122,71	-155,21	-156,05	0,84	-73,28	-43,19	-4,75	Zn^{2+}
	-159,32	-191,83	-192,61	0,78	-69,82	-81,03	-5,19	Cd^{2+}
	-129,98	-162,48	-163,54	1,06	-76,35	-53,42	-4,89	Pb^{2+}
SiO_2 (1 0 -1)	-104,9	-137,42	-138,31	0,88	-32,406	-80,95	-2,7	Zn^{2+}
	-125,8	-158,32	-158,89	0,56	-32,738	-100,5	-3,238	Cd^{2+}
	-109,49	-141,99	-142,44	0,44	-33,32	-85,67	-2,31	Pb^{2+}
PAN								
Al_2O_3 (0 0 1)	-107,29	-152,77	-154,06	1,29	-71,56	-44,03	-4,13	Zn^{2+}
	-144,01	-189,48	-190,68	1,19	-70,44	-81,21	-5,08	Cd^{2+}
	-114,83	-160,30	-161,16	0,85	-72,05	-52,53	-4,95	Pb^{2+}
SiO_2 (1 0 -1)	-91,77	-137,25	-137,98	0,72	-30,50	-81,04	-3,07	Zn^{2+}
	-111,59	-157,06	-157,84	0,78	-33,54	-100,43	-2,83	Cd^{2+}
	-96,09	-141,569	-142,216	0,646	-31,45	-85,04	-2,97	Pb^{2+}
MBT								
Al_2O_3 (0 0 1)	-106,46	-128,05	-128,17	0,11	-45,42	-43,06	-5,05	Zn^{2+}
	-143,05	-164,65	-164,81	0,158	-42,27	-81,60	-5,13	Cd^{2+}
	-113,83	-135,42	-135,59	0,16	-45,55	-52,87	-4,32	Pb^{2+}
SiO_2 (1 0 -1)	-106,23	-127,83	-127,87	0,047	-19,91	-80,98	-3,308	Zn^{2+}
	-125,22	-146,82	-146,92	0,10	-21,08	-99,90	-3,23	Cd^{2+}
	-110,18	-131,77	-131,83	0,052	-21,87	-85,02	-3,045	Pb^{2+}

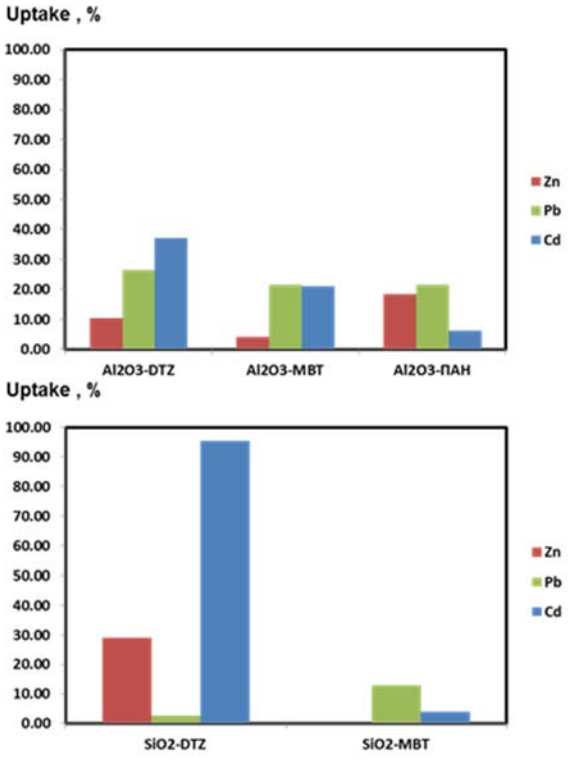


Figure 3. Experimental data on sorption uptake.

capacity (up to 30%) but the SiO_2-DTZ sample exhibited high level of selectivity for Cd^{2+} ions (95% uptake).

To compare experimental and molecular modeling results, the experimental values of sorption capacity and the calculated adsorption energy are plotted on Figure 4. The good correlation observed for all samples except sorption of Zn^{2+}, Pb^{2+} on silica sorbents and Cd^{2+} ions on alumina impregnated by the DTZ as predicted by computer calculation.

Conclusion

In summary, molecular modeling of the multisorption process from water solution (Cd^{2+}, Ni^{2+}, Zn^{2+}) on the alumina and silica impregnated by 2-mercaptobenzothiazole, 1-(2-Pyridylazo)-2-naphthol, diphenylthiocarbazone (dithizone) correlated with experimental results. The adsorption energies were exothermic due to strong mineral–adsorbate interaction. SiO_2-DTZ sample exhibited high level of selectivity to Cd2+ ions. The good correlation observed for all

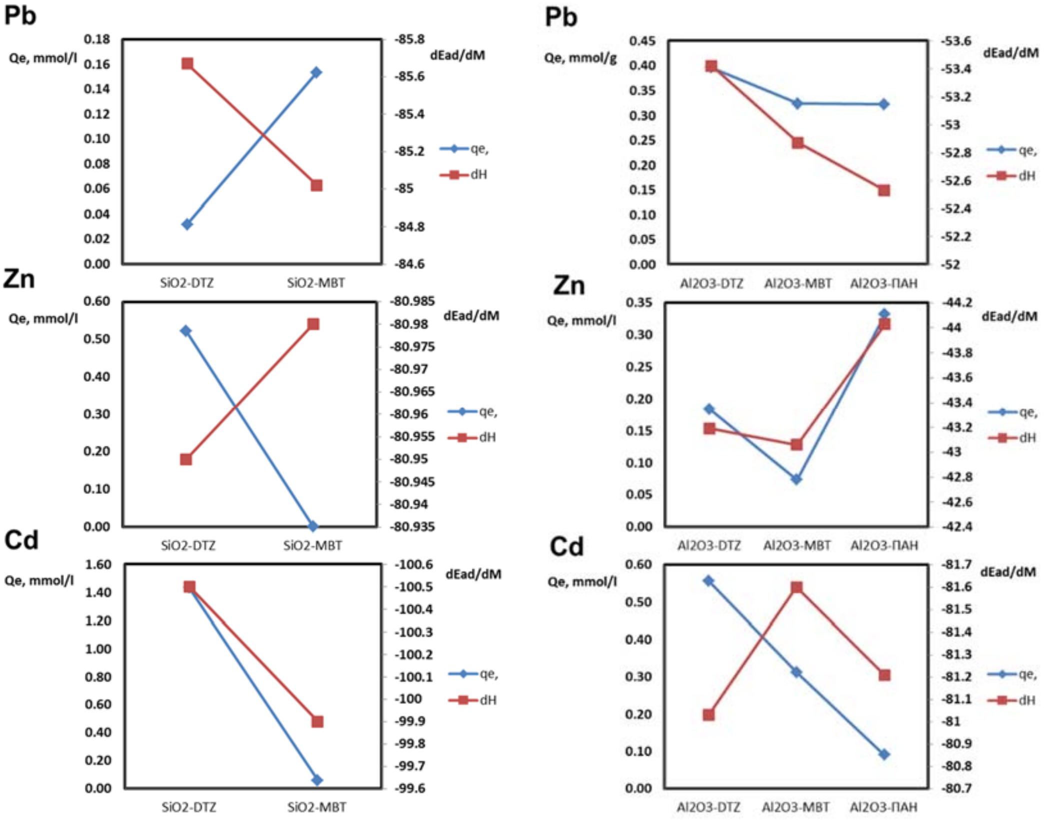


Figure 4. Sorption capacity and adsorption energy for multisorption.

samples except sorption of Zn^{2+}, Pb^{2+} on silica sorbents and Cd^{2+} ions on alumina impregnated by the DTZ as predicted by the dynamic calculation.

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