Industrial Wastes as Potentional Sorbents of Heavy Metals

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Abstract

Industrial wastes can be used as sorbents of heavy metals. Nowadays, the wastes materials are studied as sorbents and the sorption capacities and other properties are comparable or better than in the case of natural or specially prepared sorbents. Blast furnace slag, steel making slag, laboratory and industrial pyrolysis product from tires and coke dust were selected as potential sorbents of heavy metals. The characterization of materials was performed by infrared spectroscopy and kinetic models of sorption were determined. Laboratory and industrial pyrolyzed tires and coke dust contain mainly pure carbon without other functional groups on the contrary to brown coal containing hydroxyl and carboxyl functional groups, which affected sorption properties. Slags contain mainly silicates. The sorption capacities of waste materials were compared with brown coal as example of natural sorbents. The sorption experiments were carried out by batch technique in aqueous medium at ambient condition. The metal ions Cu(II) and Pb(II) were selected as adsorbates. Sorption of metal ions was studied in the concentration range 2–40 mmol · l⁻¹. The sorption capacities show that blast furnace slag, laboratory and industrial pyrolysis product from tires and coke dust exhibit the comparable values of removal amounts. The brown coal exhibits better results than other carbonaceous materials. Steel making slag's sorption capacities are 0.65 mmol · g⁻¹ for Cu(II) and 0.32 mmol · g⁻¹ for Pb(II). The steel making slag is the best sorbent from the studied wastes for both cations. The sorption properties and mechanism can be predicted from the obtained sorption data.

Keywords: sorption, wastes, metal cations, carbonaceous materials, slag

Introduction

The wastes and their processing represent a major environmental issue of whole earth. The production of wastes cannot be stopped, but it can be limited or the wastes processing can be more effective.

Using wastes as sorbents of pollutants is very interesting research direction. The organic wastes can be pyrolysed under different conditions for utilization as energy source (Ahmad et al.,2014) or for creating of effective sorbents (Triego et al.,2016) with high sorption capacities, high stability in the environment, high specific surface area, etc. Used tires are one of the biggest environmental issues. It is very difficult to reprocess them. Interesting carbonaceous materials can be prepared from the tires by pyrolysis process (Mui et al., 2004). These materials have been studied as sorbents of inorganic and organic pollutants in aqueous medium (Troca-Torrado et al., 2011; Gupta et al., 2011; Calisir et al., 2009). Another carbonaceous resources eg. coal (Simate et al., 2016; Januš et al., 2005), coke dust (Burmistrz et al., 2014) peat and others (Hanzlík et al., 2004) can be used for purifying of drinking and waste water.

Slags from the metallurgical process represent another type of wastes. Slags are multicomponent by-product of production of pig iron or steel. Slags are commonly applied in the construction industry (Das et al., 2007). Properties of slags depend on their chemical composition, type and managing of the production process and the type of cooling process. The sorption properties of slags have been studied for inorganic (Bláhová et al., 2015; Dimitrova, 1996; Dimitrova and Mehanjiev, 2000; Xue et al., 2009) and organic (Genz and Oguz, 2010) pollutants.

Utilization of wastes as sorbents of heavy metals solves two global problems – namely recycling of wastes and removal of heavy metals from the environment. The aim of this work was to compare sorption capacities of wastes and natural sorbents. The sorption experiments were performed on the wastes: steel making slag, blast furnace slag, laboratory and industrial pyrolysed tires and coke dust and for comparison brown coal. The materials were studied as sorbents of Cu(II) and Pb(II).

Materials and methods

Blast furnace slag (BFS) and steel making slag (SMS) were provided by ArcelorMittal Ostrava a.s.. The laboratory (LPT) and industrial (IPT) pyrolysed tires, brown coal (BC) and coke dust (CD) were provided by AGH University of Science and Technology of Cracow. All materials were used for experiments with-
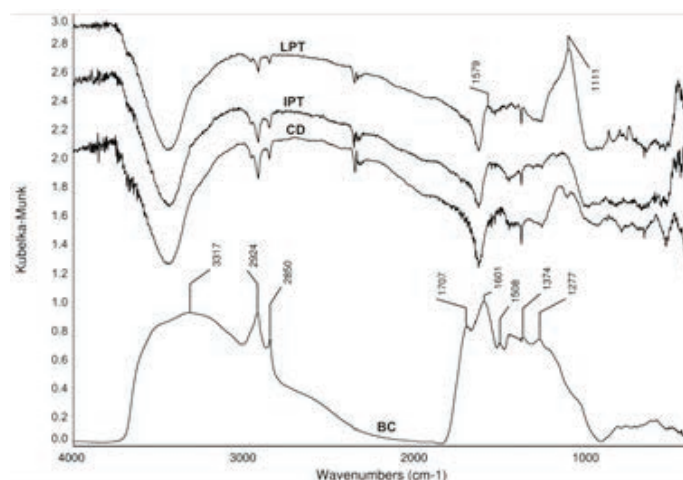
Fig. 1. Infrared spectra of the used carbonaceous materials

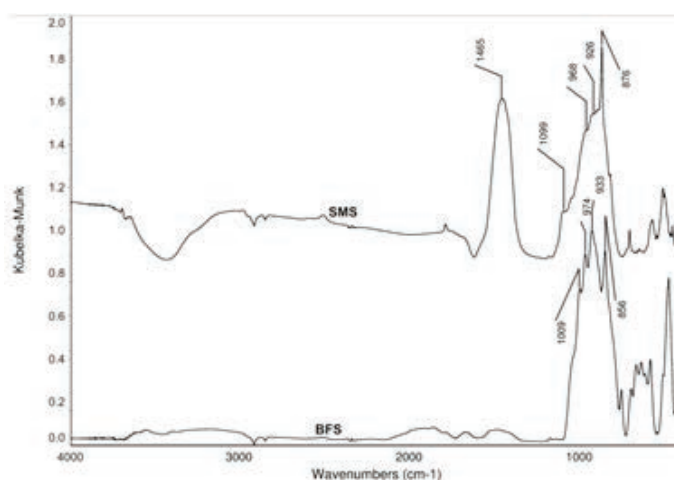Rys.1. Spektrum w podczerwieni badanych materiałów węglowych

Fig. 2. Infrared spectra of the used slags

Rys. 2. Spektrum w podczerwieni badanych żużli

out any treating or drying. All used chemicals were of analytical grade. $Cu(NO_3)_2 \cdot 3H_2O$ and $Pb(NO_3)_2$ (Lach-Ner, s.r.o. Czech Rep.) were used for preparation of the metals cations solutions. The standards for atomic absorption spectroscopy (Cu, Pb – Sigma-Aldrich) were used for AAS analysis of the metals.

All studied materials were characterized by infrared spectroscopy. The infrared spectra were measured on FTIR Nicolet 6700 (Thermo Scientific, USA) by diffuse reflectance method (DRIFT). The infrared spectra where recorded in the spectral range 4000–400 cm^1 (128 scans, 4 cm^{-1} resolution, with Happ-Genzel apodization). The baseline correction was carried out and spectra were normalized.

All sorption experiments were performed by batch technique. The adsorbent dose and volume of solution were in the ratio 1 g : 25 ml for both studied cations. The contact time influence on the removal of metals

cations (concentration of metals cations 10 mmol · l^{-1}) was investigated for contact times 1, 2, 4, 8 and 24 hours. The experimental data from these experiments were used for description of kinetics of metals sorption. The pseudo-first and pseudo-second order kinetics were considered. The contact time (24 hours) was chosen for further experiments based on the kinetics measurements. Sorption experiments were investigated in the concentration range 2–20 mmol · l^{-1} for four carbonaceous materials. The sorption experiments on the blast furnace slag were investigated in the concentration range 2–20 mmol · l^{-1} for Cu(II) and 2–40 mmol · l^{-1} for Pb(II). The sorption experiments on the steel making slag were investigated in the concentration range 2–40 mmol · l^{-1} for Cu(II) and 2–60 mmol · l^{-1} for Pb(II). The concentration range was extended for both slags due to unsaturation of the sorption capacities for both cations. The concentrations of metals cations in

Tab. 1. Parameters of kinetic models

Tab. 1. Parametry modelu kinetycznego

Sample	Metal cation	pseudo-first order				pseudo-second order			
		R^2	k [min^{-1}]	mesasured Qe [mmol·g^{-1}]	calculated Qe [mmol·g^{-1}]	R^2	k [g mg^{-1} min^{-1}]	mesasured Qe [mmol·g^{-1}]	calculated Qe [mmol·g^{-1}]
LPT	Cu(II)	0.9518	0.08	0.114	0.000	0.7648	0.17	0.114	0.232
IPT		0.5491	0.14	0.075	0.033	0.9957	9.12	0.075	0.078
BC		0.9575	0.08	0.186	0.174	0.9052	0.18	0.186	0.304
CD		0.7501	0.11	0.106	0.033	0.9978	10.26	0.106	0.109
BFS		0.9703	0.16	0.167	0.094	0.9984	4.14	0.167	0.175
SMS		0.9914	0.29	0.254	0.214	0.9988	1.99	0.254	0.274
LPT	Pb(II)	0.9785	0.11	0.110	0.094	0.9671	16.12	0.110	0.136
IPT		0.9201	0.16	0.115	0.046	0.9988	8.36	0.115	0.120
BC		0.9845	0.14	0.220	0.219	0.9691	3.34	0.220	0.299
CD		0.8959	0.12	0.125	0.034	0.9990	7.82	0.125	0.128
BFS		0.9990	20.20	0.153	0.224	0.9995	6.44	0.153	0.155
SMS		0.9921	0.45	0.230	0.125	0.9997	4.24	0.230	0.236

all solutions were measured by atomic absorption spectroscopy (AA 240FS Varian, USA).

Results and discussion
Characterization of studied materials

Characterization of studied materials was carried out by infrared spectroscopy. Spectra of the carbonaceous materials are depicted on the Fig. 1. It is evident that materials LPT, IPT and CD contain only small amounts of functional groups. These materials contain aromatic systems, which can be stated from the band around 1579 cm^{-1} and they contain small amounts of oxygen bearing groups, which can be concluded from several bands around 1100 cm^{-1} (C-O stretch vibration). Brown coal (BC) contains variety of functional groups. Band of O-H stretch vibration (3317 cm^{-1}) with several shoulders indicate content of hydroxyl groups. Bands at 2924 and 2850 cm^{-1} belong to the stretch vibrations of C-H bond in the saturated hydrocarbons. Band at 1707 cm^{-1} indicates content of the carbonyl groups (probably mainly carboxylic acids). Content of the aromatic conjugated systems in the BC is indicated by the bands around 1601 and 1508 cm^{-1}. Bands around 1430 and 1374 cm^{-1} belong to the deformation vibrations of C-H bonds in saturated aliphatic hydrocarbons. The stretch vibrations of C-O bonds (various types) occur in the range 1277–1000 cm^{-1}. Structure of these materials probably will affect the sorption process. Mainly physisorption can be expected by the LPT, IPT and CD due to lack of functional groups. Content of the functional groups – hydroxyl and carboxyl – and π-electron systems of the aromatic parts of structure of BC can positively affect the sorption process and the chemisorption probably occurs, too.

Fig. 2 shows spectra of the used slags. It can be stated from the spectrum of BFS that this material consists mainly of silicate minerals, which indicate several bands and shoulders in the range 1100–800 cm^{-1} (Si-O stretch vibrations). SMS contains less of the silicate minerals according to BFS, which can be stated from the absorbances of the Si-O bands. Strong bands at 1465 and 876 cm^{-1} belong probably to carbonates contained in the material. The physisorption on the surface of silicates or ion exchange reactions can be considered as the sorption mechanism. Some of the contained minerals are subject to hydrolysis which leads to the increase of solution pH value. Hydrolysis can cause precipitation or co-precipitation of the studied cations, too.

Sorption of copper and lead cations

Firstly, the kinetic study was realized and the obtained data are showed in the Table 1. Based on these data it was decided that the sorption kinetics for all samples of sorbents is controlled according to the pseudo-second order kinetic model. The coefficients of determination for the pseudo-second order kinetics reached higher values than in the case of the pseudo-first order. The second decisive factor was comparison of measured and calculated values of the equilibrium removal amounts. The measured removal amounts are values obtained for a 24-hours contact time. The measured and calculated removal amounts fit better for the pseudo-second order kinetics for almost all samples. The measured and calculated removal amounts
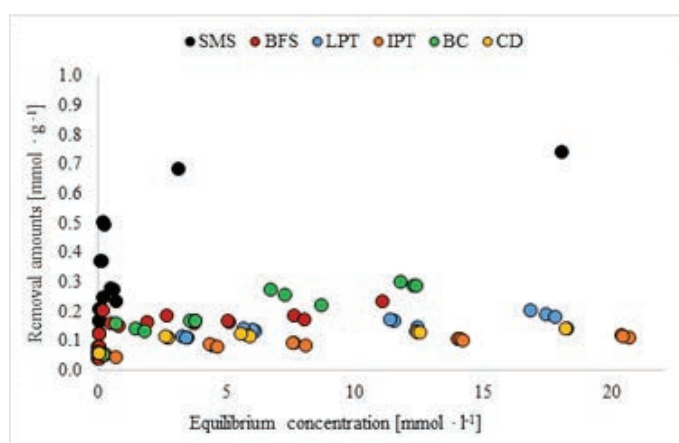
Fig. 3. Sorption isotherms of Cu(II) cations

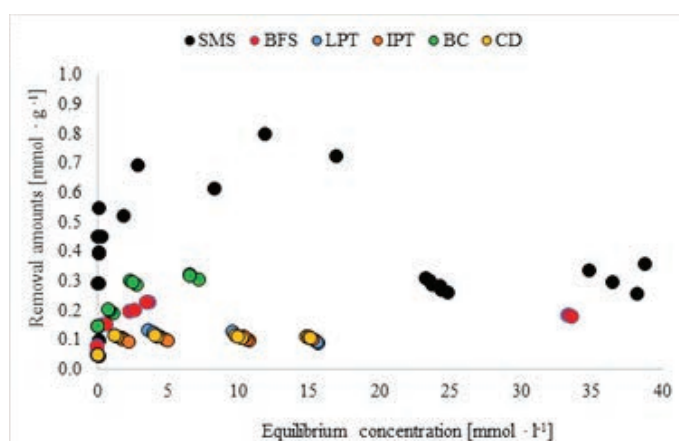Rys. 3. Izotermy sorpcji kationu Cu(II)

Fig. 4. Sorption isotherms of Pb(II) cations

Rys. 4. Izotermy sorpcji kationu Pb(II)

do not fit for LPT and BC, but it can be caused by no achieved equilibrium state.

The contact time of 24 hours was chosen for all further experiments to ensure the achievement of the sorption equilibrium for IPT, CD, BFS and SMS. The samples LPT and BC did not achieve equilibrium after 24 hours, but the chosen time was a boundary for all experiments (the economical aspect). As can be seen on the Fig 3, the removal amounts of Cu by carbonaceous materials and BFS achieved the similar values. The BC exhibits the highest removal amount among the carbonaceous materials. It is probably caused by its structural properties (see infrared characterization of this material). The removal amount of SMS achieved for Cu(II) 0.65 mmol · g^{-1}, which makes the SMS the best sorbent for Cu(II).

The sorption properties of all materials for removing of the Pb(II) cations were investigated, too. The sorption isotherms for the Pb removal are depicted on the Fig 4. The carbonaceous materials LPT, IPT and CD achieved the low values of removal amounts.

The mechanism of the Pb(II) removing on these materials is probably adsorption on the surface. However, the lead cation is bigger than the copper cation therefore the values of the removal amounts for Pb(II) are lower than for Cu(II). It can be seen in the Fig 4. that BC and BFS achieved the similar values of the removal amounts of Pb(II). The steel making slag achieves very high removal amount of Pb(II) at the initial concentration 15 mmol · l^{-1}. Then the removal amount sharply decreased on the level of BFS and BC. Probably the mechanism of the Pb(II) removing has been changed for the concentrations higher than 15 mmol · l^{-1} The SMS is still the best sorbents for removal Pb(II) with the maximal removal amount 0.32 mmol · g^{-1}.

Conclusion

The sorption of Cu(II) and Pb(II) was studied on various waste materials and the results from the experiments were compared with results of brown coal and coke dust. Structure of the used sorbents was char-

acterized by the infrared spectroscopy. The materials LPT, IPT, and CD consisted mainly of carbon without other functional groups. Material BC contains variety of functional groups mainly hydroxyls and carboxyls which affect the sorption process. The used slags are constituted mainly by silicates, SMS contains lower amount of silicates than BFS. The sorption experiments of Cu(II) and Pb(II) were performed on all materials. It was found out that the pseudo-second order kinetics fits for all materials and for both cations. The contact time 24 hours for all materials was chosen for further sorption experiments. The carbonaceous materials (laboratory pyrolysed tires, industrial pyrolysed tires and coke dust) removed the metals cations from the solution probably by physisorption process. The functional groups in the structure of BC improves its sorption properties. The mechanism of the metals cations removal by slags is probably co-precipitation or incorporation in the structure. The best sorbent among the studied materials for both studied cations is steel making slag with removal amounts 0.65 mmol $\cdot$ g^{-1} for Cu(II) and 0.32 mmol $\cdot$ g^{-1} for Pb(II).

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Odpady przemysłowe jako potencjalne sorbenty metali ciężkich

Odpady przemysłowe mogą być stosowane jako sorbenty metali ciężkich. Obecnie materiały odpadowe są badane jako sorbenty, a pojemność sorpcyjna i inne właściwości są porównywalne lub lepsze niż w przypadku naturalnych lub specjalnie przygotowanych sorbentów. Żużel wielkopiecowy, żużel stalowniczy, produkt pirolizy z opon uzyskany w warunkach laboratoryjnych i przemysłowych oraz pył koksowy zostały wybrane jako potencjalne sorbenty metali ciężkich. Charakterystykę materiałów zbadano metodą spektroskopii w podczerwieni i wyznaczono kinetyczne modele sorpcji. Laboratoryjne i przemysłowe karbonizaty z opon i pyły kokosowe zawierają głównie czysty węgiel bez innych grup funkcyjnych w przeciwieństwie do węgla brunatnego zawierającego grupy funkcyjne hydroksylowe i karboksylowe, które wpływają na właściwości sorpcyjne. Żużle zawierają głównie krzemiany. Pojemność sorpcyjną materiałów odpadowych porównano z węglem brunatnym jako przykładem naturalnych sorbentów. Eksperymenty sorpcyjne przeprowadzono metodą okresową w środowisku wodnym w warunkach otoczenia. Jony metali Cu (II) i Pb (II) wybrano jako adsorbaty. Sorpcję jonów metali badano w zakresie stężeń 2-40 mmol /g. Pojemność sorpcyjna wskazuje, że żużel wielkopiecowy, produkt pirolizy laboratoryjnej i przemysłowej opon i pyłu koksowego wykazuje porównywalne wartości wielkości sorpcji. Węgiel brunatny wykazuje lepsze wyniki niż inne materiały węglowe. Zdolność sorpcyjna żużla z produkcji stali wynosi 0,65 mmol /g dla Cu (II) i 0,32 mmol /g dla Pb (II). Żużel stalowniczy jest najlepszym sorbentem z badanych odpadów dla obu kationów. Właściwości sorpcyjne i mechanizm można przewidzieć na podstawie uzyskanych izoterm sorpcji.

Słowa kluczowe: sorpcja, odpady, kationy metali, materiały węglowe, żużel