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(54) Title: MAGNETIC ADSORBENT OF IONS FROM AN AQUEOUS ENVIRONMENT BASED ON LADLE FURNACE SLAG

(57) Abstract: The invention relates to a magnetic adsorbent based on slag from an iron or steel metallurgical production process, in particular based on ladle furnace slag, for adsorbing ions from an aqueous environment, wherein said magnetic adsorbent comprises Ca in an amount expressed in the form of CaO containing at least 50 wt. % CaO, Al in an amount expressed in the form of Al_2O_3 containing at least 7.5 wt. % Al_2O_3, Si in an amount expressed in the form of SiO_2 containing at least 5 wt. % SiO_2, Mg in an amount expressed in the form of MgO containing at least 2 wt. % MgO, and at least one magnetically active iron oxide selected from the group consisting of Fe_2O_3 and Fe_3O_4 and in an amount expressed in the form of Fe containing at least 2.5 wt. % Fe. The invention further relates to a method of producing said magnetic adsorbent and to use thereof for adsorbing Be^{2+}, Sr^{2+} and/or Ce^{4+} ions from an aqueous environment.

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Description

Title of Invention: Magnetic adsorbent of ions from an aqueous environment based on ladle furnace slag

Technical Field

[0001] The present invention relates to a magnetic adsorbent based on ladle furnace slag for adsorbing ions from aqueous environment, a method of production and use of said magnetic adsorbent.

Background Art

[0002] The presence of metal ions in the environment can be related to various anthropogenic activities such as wastewater discharges or accidental spills from storage tanks.

[0003] Various physicochemical methods of sedimentation using gravity, centrifugation, chemical emulsification, pH adjustment, thermal treatment, chemical removal by oxidizing agents, or biological methods at lower concentrations have been investigated for the removal of non-biodegradable ions of elements from surface and industrial waters.

[0004] Adsorption may be considered as probably the most appropriate, rapid and effective removal, especially in the case of accidents and accidental releases of ion-containing liquids into the environment. By selecting a suitable adsorbent, the cost of pollutant removal can be minimised, using a variety of differently modified materials that exhibit high adsorption efficiency and do not pollute the environment. In addition, in the case of magnetic treatment of the adsorbent, the adsorbent and the pollutants can be easily separated using a magnetic field.

[0005] Adsorbent production can be a cost and time consuming process, hence the emerging need for more affordable adsorbents with high adsorption capacity in the prior art.

[0006] One option includes waste materials, whether of biological, inorganic or organic origin. So far, magnetically modified adsorbents based on biological waste and clay minerals have been published and experimentally verified, e. g. in Tokarčíková et al., 2020 (Easy and low-cost preparation method of magnetic montmorillonite/Fe_xO_y composite: initial study for future applications); Ghaemi et al., 2011 (Characterizations of strontium(II) and barium(II) adsorption from aqueous solutions using dolomite powder); Gu et al., 2018 (Clay mineral adsorbents for heavy metal removal from wastewater: a review); Ye et al., 2008 (Comparison of strontium and calcium adsorption onto composite magnetic particles derived from Fe_3O_4 and bis(trimethoxysilylpropyl)amine); Feng et al., 2010 (Adsorption of Cd(II) and Zn(II) from aqueous solutions using magnetic hydroxyapatite nanoparticles as adsorbents);

and Chen et al., 2012 (Removal of radionuclide Sr^{2+} ions from aqueous solution using synthesized magnetic chitosan beads).

Summary of Invention

[0007] It is an object of the present invention to provide a simple-to-produce, magnetically modified adsorbent, obtainable from waste materials, in particular from ladle furnace or blast furnace slags from iron or steel metallurgical processes.

[0008] The above-mentioned object is achieved by a magnetic adsorbent based on slag from an iron or steel metallurgical production process, in particular based on ladle furnace slag or blast furnace slag, for adsorbing ions from an aqueous environment, wherein said magnetic adsorbent comprises Ca in an amount expressed in the form of CaO containing at least 50 wt. % CaO, Al in an amount expressed in the form of Al_2O_3 containing at least 7.5 wt. % Al_2O_3, Si in an amount expressed in the form of SiO_2 containing at least 5 wt. % SiO_2, Mg in an amount expressed in the form of MgO containing at least 2 wt. % MgO, and at least one magnetically active iron oxide selected from the group consisting of Fe_2O_3 and Fe_3O_4 and in an amount expressed in the form of Fe containing at least 2.5 wt. % Fe. The carrier or support of the adsorbent are therefore structures combining Ca, Al, Si and Mg in the form of oxides, hydrates, silicates, aluminates, aluminosilicates, etc. The magnetically active iron oxide may be Fe_2O_3 or Fe_3O_4 or a combination of Fe_2O_3 and Fe_3O_4 with virtually identical magnetic properties.

[0009] For optimum magnetic properties, the magnetic adsorbent may comprise at least one magnetically active iron oxide selected from the group consisting of Fe_2O_3 and Fe_3O_4 and in an amount expressed in the form of Fe containing at least 10.0 wt. % Fe (such as 10.0 wt. %; 10.1 wt. %; 10.2 wt. %; 10.3 wt. %; 10.4 wt. %; 10.5 wt. % or 10.6 wt. %), which ensures good separability of the adsorbent by a magnet.

[0010] In order to maintain optimum adsorption capacity properties, the magnetic adsorbent may comprise at least one magnetically active iron oxide selected from the group consisting of Fe_2O_3 and Fe_3O_4 and in an amount expressed in the form of Fe containing up to 12.0 wt. % Fe (such as 11.0 wt. %; 11.1 wt. %; 11.2 wt. %; 11.3 wt. %; 11.4 wt. %; 11.5 wt. %; 11.6 wt. %; 11.7 wt. %; 11.8 wt. %; 11.9 wt. % or 12.0 wt. %), which ensures that the active adsorption sites on the adsorbent support are not blocked with magnetically active iron oxide(s).

[0011] In particular, the magnetically active iron oxide may be Fe_2O_3 in the form of γ-hematite and/or Fe_3O_4 in the form of magnetite. The magnetic adsorbent may comprise other impurities derived from the feedstock, in particular any of Ti in an amount expressed in the form of TiO_2, Cr in an amount expressed in the form of Cr_2O_3, K in an amount expressed in the form of K_2O, Na in an amount expressed in the form of Na_2O, Mn in an amount expressed in the form of MnO, and FeO, which is not magnetic.

[0012] Preferably, the magnetic sorbent has a particle size of up to 40 μm.

[0013] The above-mentioned object is further achieved by a method of producing said magnetic adsorbent, said method comprising the following steps:

[0014] a. providing slag from a metallurgical process for the production of iron or steel, in particular ladle furnace slag;

[0015] b. preparing at least one magnetically active iron oxide selected from the group consisting of $Fe_2O_3$and Fe_3O_4 and having a particle size of up to 10 μm;

[0016] c. magnetic treatment of said slag by mixing it with at least one magnetically active iron oxide (preferably in aqueous suspension) selected from the group consisting of Fe_2O_3 and Fe_3O_4.

[0017] In step b., said magnetically active iron oxide is prepared from a general inorganic iron salt, in particular from $FeSO_4$, $FeCl_2$ or $FeCl_3$ or hydrates thereof or a combination thereof, by an alkaline precipitation step with an aqueous hydroxide solution (e. g. NaOH or KOH) to form an iron hydroxide (generally a mixed hydroxide, or hydrated ferrous-ferric hydroxide, subject to partial oxidation to ferric hydroxide), which is followed by a step of microwave irradiation of the resulting iron hydroxide (exemplary conditions: 700 W, 2450 MHz, at boiling water temperature for about 10 min.) to form a magnetically active iron oxide selected from the group consisting of $Fe_2O_3$and Fe_3O_4.

[0018] Subsequent processing includes decantation of the remaining ions, step c. of the magnetic treatment, filtration and drying. The purpose of the magnetic treatment is to magnetize the slag while not introducing too much Fe to maintain its adsorption capacity. An exemplary preparation procedure (albeit on a different substrate) can be found on page 6 of the above mentioned publication Tokarčíková et al., which is incorporated herein by reference.

[0019] The above-mentioned object is further achieved by using said magnetic adsorbent for adsorption of Be^{2+}, Sr^{2+} and/or Ce^{4+} ions from an aqueous environment.

[0020] In previous applications, adsorbents were generally removed by filtration and sedimentation, e. g. industrially in filter presses. The present magnetic adsorbent based on ladle furnace slag is able to bind mainly Sr^{2+}, Be^{2+} and/or Ce^{4+} ions from a liquid, especially aqueous environment (e. g. wastewater or its mixture with organic solvents) and it can be removed by a magnetic field without the need of filtration and sedimentation steps. A key advantage of the present magnetic adsorbent is that it comprises magnetic iron oxide particles which are, e. g., by means of van der Waals forces, firmly attached to the adsorbent (i. e. at least one inorganic mineral forming the ladle furnace slag), allowing its removal from the liquid environment by means of a magnetic field applied to a sieve or a container wall.

[0021] The magnetic adsorbent binds Be^{2+}, Sr^{2+} and/or Ce^{4+} ions from an aqueous environment, and if all of them are present in the solution, it binds them with different efficiency according to the capacity, i. e. one completely, the other less and the third the least depending on their mutual concentration in the solution, the pH of the solution and possibly the presence of other ions - cations and anions. In general, cations with smaller radii (in this case in the order of $Be^{2+} < Sr^{2+} < Ce^{4+}$) and cations in higher concentrations are adsorbed at higher rates.

[0022] The waste material used (ladle furnace slag) can be quickly and efficiently modified to produce a magnetic adsorbent with good adsorption properties in terms of removal of ions of elements from an aqueous environment, which magnetic adsorbent can be separated from the liquid by a magnetic field. This offers an efficient use of ladle furnace slag, which is only partially recycled in the metallurgical industry.

Brief Description of Drawings

Fig.1

[0023] [Fig.1] graphically shows a dependence of the amount of Sr^{2+} ions adsorbed by a magnetic adsorbent A on the equilibrium concentration of Sr^{2+} ions in an aqueous solution.

Fig.2

[0024] [Fig.2] graphically shows a dependence of the amount of Be^{2+} ions adsorbed by a magnetic adsorbent A on the equilibrium concentration of Be^{2+} ions in an aqueous solution.

Fig.3

[0025] [Fig.3] graphically shows a dependence of the amount of Sr^{2+} ions adsorbed by a magnetic adsorbent B on the equilibrium concentration of Sr^{2+} ions in an aqueous solution.

Fig.4

[0026] [Fig.4] graphically shows a dependence of the amount of Ce^{4+} ions adsorbed by a magnetic adsorbent B on the equilibrium concentration of Ce^{4+} ions in an aqueous solution.

Fig.5

[0027] [Fig.5] shows the results of EDS analysis of a sample of magnetic adsorbent B with adsorbed Sr^{2+} ions.

Fig.6

[0028] [Fig.6] shows an image of magnetic adsorbent B particles with adsorbed Sr^{2+} ions.

Fig.7

[0029] [Fig.7] shows an image of magnetic adsorbent B particles with adsorbed Sr^{2+} ions, indicating Fe distribution

Fig.8

[0030] [Fig.8] shows an image of magnetic adsorbent B particles with adsorbed Sr^{2+} ions, indicating Sr distribution

Examples

Example 1 - magnetic adsorbent A

[0031] Ladle furnace slag A as input material has the following composition:

Adsorbent	Element content expressed in the form of oxide in % wt.										
	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	Na_2O	MnO	Fe_2O_3
A	3.52	19.1	9.26	<0.001	0.89	0.015	51.0	0.25	0.08	2.68	3.72
Note: the remaining components making up to 100 % of the mixture are losses through heat treatment (e. g. carbonates)											

[0032] The above-mentioned values are the contents of the individual elements expressed in the form of an oxide in wt. %, but in fact they are not only present as oxides but also in other forms (e. g. magnesium(II), calcium(II), magnesium(II)-calcium(II) etc. aluminates, silicates, aluminosilicates etc.).

[0033] After magnetic treatment of the ladle furnace slag A according to the procedure described above in the publication of Tokarčíková et al., the total content of the magnetically active iron oxides expressed in the form of total Fe content increases from 2.60 wt. % (after recalculation from the above value of 3.72 wt. % in the form of Fe_2O_3) to 10.6 wt. %, thus producing a magnetic adsorbent A in bulk form suitable for the separation of ions from an aqueous environment. The magnetic adsorbent A in this case may also comprise Fe_3O_4 in combination with or without the presence of Fe_2O_3.

[0034] 0.1 g of magnetic adsorbent A was weighed into 100 mL sample tubes and 50 mL of a solution with a defined concentration of 1 mg/L to 150 mg/L Sr^{2+} ions was added (Example 1.1). Alternatively, 0.1 g of magnetic adsorbent A was weighed into 100 mL sample tubes, 50 ml of a solution with a defined concentration of 0.1 mg/L or 10 mg/L Be^{2+} ions was added (Example 1.2).

[0035] Adsorption was carried out for 1 hour under continuous shaking in a laboratory shaker by head-end rotation. After this time, the liquid phase was separated from the solid phase containing magnetic adsorbent A by filtration through a PRAGOPOR filter having a pore size of 0.40 μm. All experiments were performed in duplicates.

[0036] The determination of non-adsorbed ions was determined for each sample by atomic emission spectrometry with inductively coupled plasma (AES-ICP). From the measured concentrations, the adsorbed ion amount was calculated according to the equation (1):

[0037] $a = \frac{\Delta m_n}{m_{Ver}}$ (1)

[0038] where:

[0039] a...adsorbed amount per unit mass of adsorbent $[mg/g]$

[0040] m_{Ver}...magnetic adsorbent loading $[g]$

[0041] Δm_n...adsorbed amount, i. e. the difference in absolute ion content before and after adsorption according to the equation (2) $[mg]$:

[0042] $\Delta m_n = m_{before} - m_{after}$ (2)

[0043] The results of the experiments are shown by

- an adsorption isotherm in [Fig.1], which shows that the adsorbed amount is up to approximately 50 mg of Sr^{2+} ions per 1 g of adsorbent (Example 1.1); and
- an adsorption isotherm in [Fig.2], which shows that the adsorbed amount is approximately 6.3 mg of Be^{2+} ions per 1 g of adsorbent (Example 1.2), wherein from the adsorption isotherm it can be concluded that at higher initial concentrations of Be^{2+}, the adsorbed amount will increase and given the expected concentrations of these ions in wastewater, the highest initial concentration of 10 mg/L was chosen.

Example 2 - magnetic adsorbent B

[0044] Ladle furnace slag B as input material has the following composition:

Adsorbent	Element content expressed in the form of oxide in % wt.										
	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	Na_2O	MnO	Fe_2O_3
B	2.35	8.19	5.14	<0.001	0.85	0.05	69.8	0.62	<0.001	4.86	5.10
Note: the remaining components making up to 100 % of the mixture are losses through heat treatment (e. g. carbonates)											

[0045] The above-mentioned values are the contents of the individual elements expressed in the form of an oxide in wt. %, but in fact they are not only present as oxides but also in other forms (e. g. magnesium(II), calcium(II), magnesium(II)-calcium(II) etc. aluminates, silicates, aluminosilicates etc.).

[0046] After magnetic treatment of the ladle furnace slag B according to the procedure described above in the publication of Tokarčíková et al., the total content of the magnetically active iron oxides expressed in the form of total Fe content increases from 3.57 wt. % (after recalculation from the above value of 5.10 wt. % in the form of Fe_2O_3) to 11.0 wt. %, thus producing a magnetic adsorbent B in bulk form suitable for the separation of ions from an aqueous environment. The magnetic adsorbent B in this case may also comprise Fe_3O_4 in combination with or without the presence of Fe_2O_3.

[0047] 0.1 g of magnetic adsorbent B was weighed into 100 mL sample tubes and 50 mL of a solution with a defined concentration of 1 or 1000 mg/L Sr^{2+} ions was added (Example 2.1). Alternatively, 0.1 g of magnetic adsorbent B was weighed into 100 mL sample tubes, and 50 mL of a solution with a defined concentration of 0.1 or 10 mg/L Ce^{4+} ions was added (Example 2.2).

[0048] Adsorption was carried out for 1 hour under continuous shaking in a laboratory shaker by head-end rotation. After this time, the liquid phase was separated from the solid phase containing magnetic adsorbent A by filtration through a PRAGOPOR filter having a pore size of 0.40 μm. All experiments were performed in duplicates.

[0049] The determination of non-adsorbed ions was determined for each sample by atomic emission spectrometry with inductively coupled plasma (AES-ICP). From the measured concentrations, the adsorbed ion amount was calculated according to the equations (1) and (2) from Example 1.

[0050] The results of the experiments are shown by

- an adsorption isotherm in [Fig.3], which shows that the adsorbed amount is up to approximately 35 mg of Sr^{2+} ions per 1 g of adsorbent (Example 2.1); and
- an adsorption isotherm in [Fig.4], which shows that the adsorbed amount is approximately 6.6 mg of Ce^{4+} ions per 1 g of adsorbent (Example 2.2), wherein from the adsorption isotherm it can be concluded that at higher initial concentrations of Ce^{4+}, the adsorbed amount will increase and given the expected concentrations of these ions in wastewater, the highest initial concentration of 10 mg/L was chosen.

[0051] Magnetic adsorbent B after adsorption and drying was subjected to EDS analysis by scanning electron microscopy, which showed the trapping of Sr^{2+} ions on magnetic adsorbent B as documented in Figures 5 to 8.

Industrial Applicability

[0052] The above-mentioned magnetic adsorbent can be used in the field of occupational safety, in accidents in chemical plants, in the transport of chemicals or in accidents in plants using the radioactive isotope Sr (e. g. in radiomedicine).

Claims

[Claim 1] Magnetic adsorbent based on slag from an iron or steel metallurgical production process, in particular based on ladle furnace slag, for adsorbing ions from an aqueous environment, **characterised in that** it comprises Ca in an amount expressed in the form of CaO containing at least 50 wt. % CaO, Al in an amount expressed in the form of Al_2O_3 containing at least 7.5 wt. % Al_2O_3, Si in an amount expressed in the form of SiO_2 containing at least 5 wt. % SiO_2, Mg in an amount expressed in the form of MgO containing at least 2 wt. % MgO, and at least one magnetically active iron oxide selected from the group consisting of Fe_2O_3 and Fe_3O_4 and in an amount expressed in the form of Fe containing at least 2.5 wt. % Fe.

[Claim 2] The magnetic adsorbent according to claim 1, **characterized in that** the magnetically active iron oxide is Fe_2O_3 in the form of γ-hematite and/or Fe_3O_4 in the form of magnetite.

[Claim 3] The magnetic adsorbent according to claim 1 or 2, **characterized in that** it has a particle size of up to 40 μm.

[Claim 4] The magnetic adsorbent according to any one of the preceding claims, **characterized in that** it comprises at least one magnetically active iron oxide selected from the group consisting of Fe_2O_3 and Fe_3O_4 and in an amount expressed in the form of Fe containing at least 10.0 wt. % Fe.

[Claim 5] Magnetic sorbent according to any one of the preceding claims, **characterized in that** it comprises at least one magnetically active iron oxide selected from the group consisting of Fe_2O_3 and Fe_3O_4 and in an amount expressed in the form of Fe containing up to 12.0 wt. % Fe.

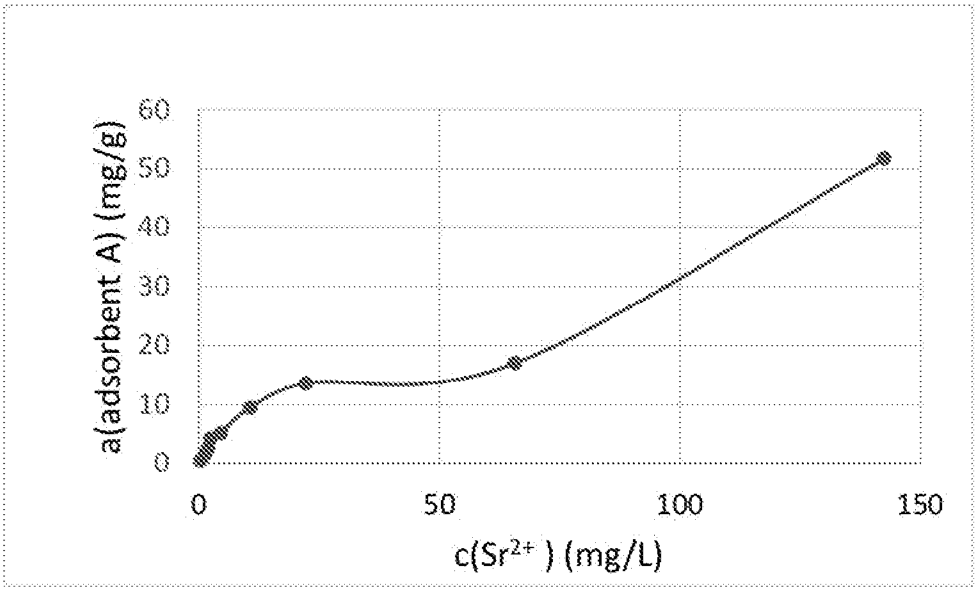
[Claim 6] A method of producing the magnetic adsorbent according to any one of the preceding claims, **characterized in that** it comprises the following steps:

a. providing slag from a metallurgical process for the production of iron or steel, in particular ladle furnace slag;
b. preparing at least one magnetically active iron oxide selected from the group consisting of $Fe_2O_3$and Fe_3O_4 and having a particle size of up to 10 μm; and
c. magnetic treatment of said slag by mixing it with at least one magnetically active iron oxide selected from the group consisting of Fe_2O_3 and Fe_3O_4.

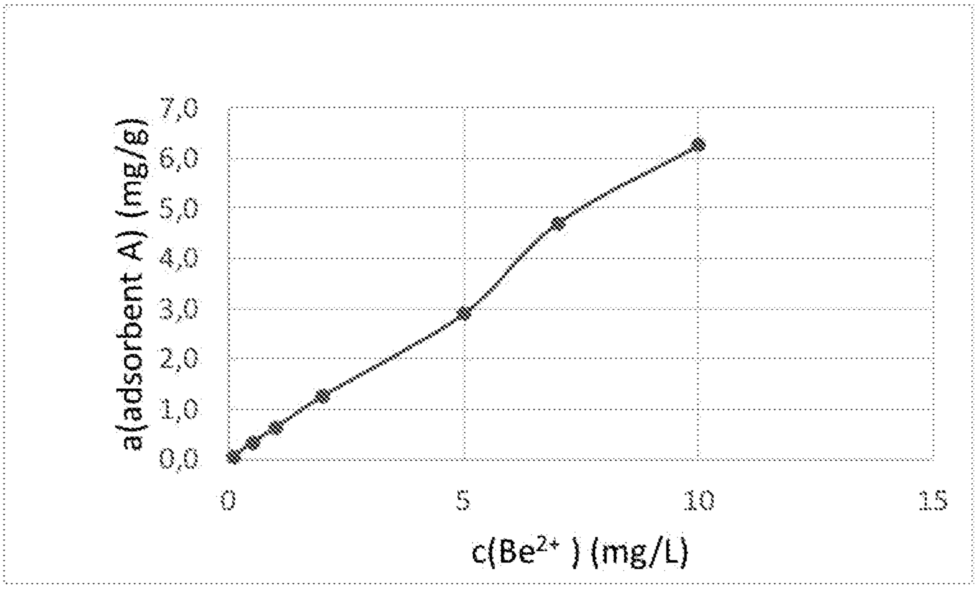
[Claim 7] The method according to claim 6, **characterized in that** in step b., said magnetically active iron oxide is prepared from an inorganic iron salt, in particular from $FeSO_4$, $FeCl_2$ or $FeCl_3$ or hydrates thereof or a combination thereof, by an alkaline precipitation step to form an iron hydroxide, followed by a step of microwave irradiation of the resulting iron hydroxide to form a magnetically active iron oxide selected from the group consisting of $Fe_2O_3$and Fe_3O_4.

[Claim 8] Use of the magnetic adsorbent according to any one of claims 1 to 5 for adsorbing Be^{2+}, Sr^{2+} and/or Ce^{4+} ions from an aqueous environment.

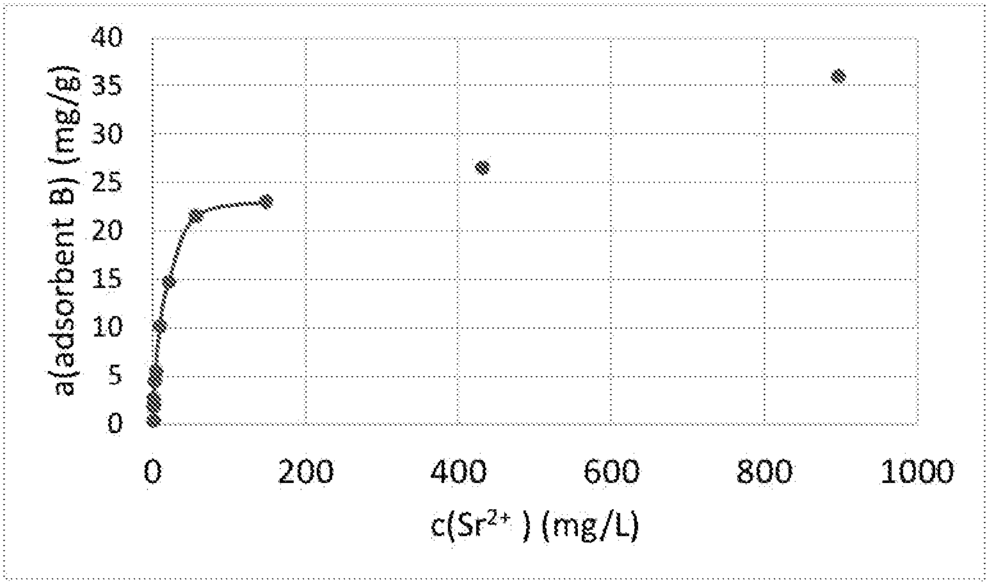
[Fig. 1]



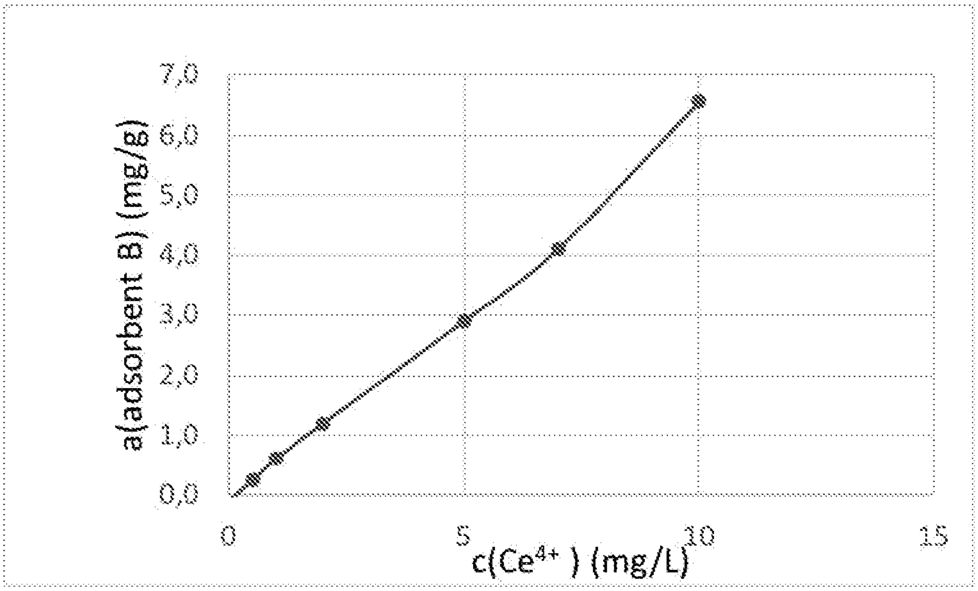
[Fig. 2]



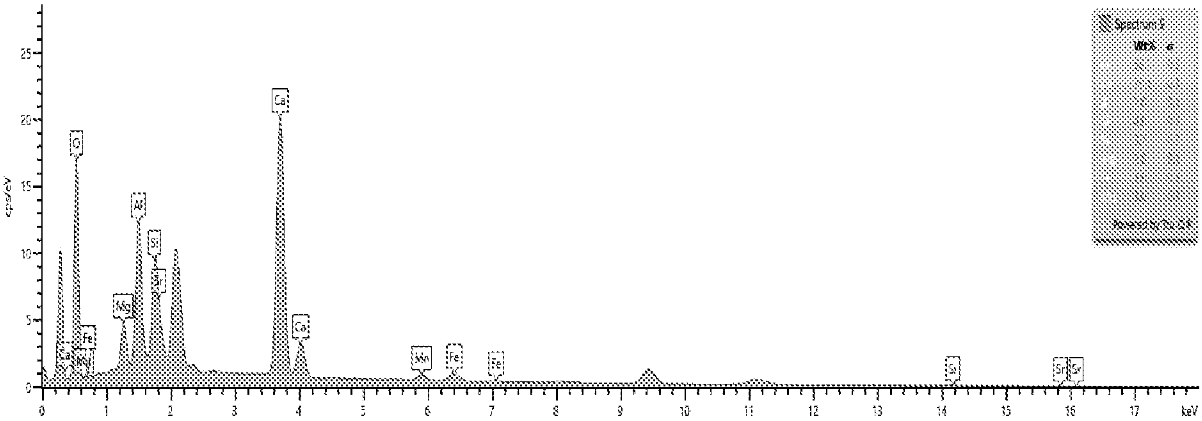
[Fig. 3]



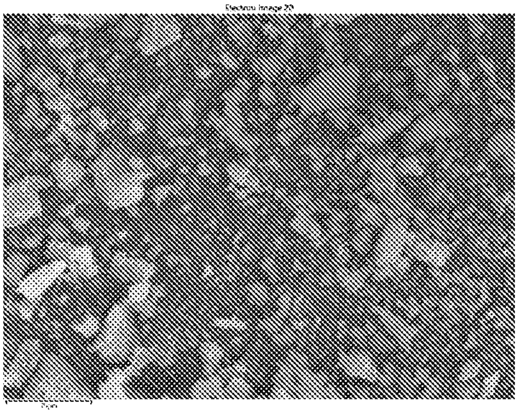
[Fig. 4]



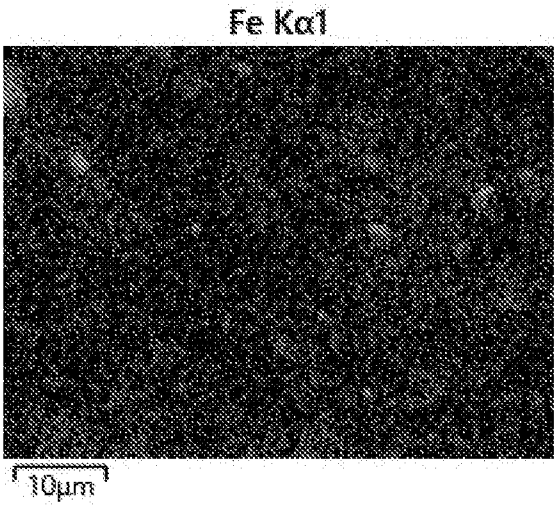
[Fig. 5]



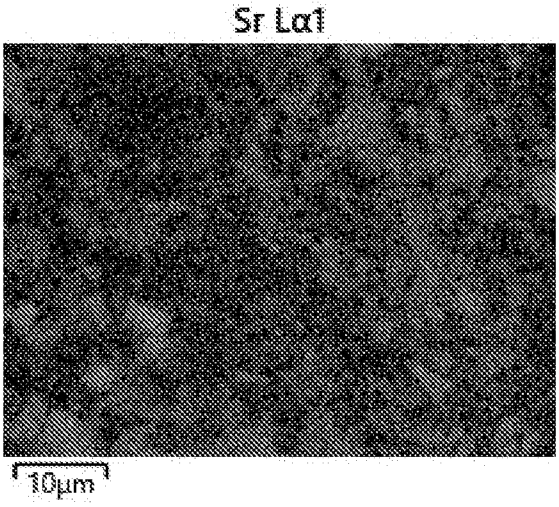
[Fig. 6]



[Fig. 7]



[Fig. 8]



INTERNATIONAL SEARCH REPORT

International application No.

PCT/CZ2022/050090

A. CLASSIFICATION OF SUBJECT MATTER

B 01 J 20/04, C 04 B 5/06, B 01 J 20/30, C 02 F 1/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B 01 J, C 04 B, C 02 F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Database IPO CZ

Electronic database consulted during the international search (name of database and, where practicable, search terms used)

EPOQUE (EPODOC, PATENW), STN (Compendex, Inspec, Inpadoc)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	RADENOVIC A. et al., Characterization of Ladle Furnace Slag from Carbon Steel Production as a Potential Adsorbent, Advances in Materials Science and Engineering, 01.09.2013, 2013, p. 1-6, ISSN 1687-8442, retrieved on 2023-04-25, retrieved from: https://doi.org/10.1155/2013/198240 (p. 2-3)	1 - 8
Y	TOKARČÍKOVÁ et al., Magnetically modified montmorillonite - characterisation, sorption properties and stability, Materials Today: Proceedings, 15.10.2020, p. 48-52, ISSN 2214-7853, retrieved on 2023-04-25, retrieved from: https://doi.org/10.1016/j.matpr.2020.08.721 (p. 1-3)	1 - 8
A	RU 2716445 C1 (FEDERALNOE GOSUDARSTVENNOE BYUDZHETNOE OBRAZOVATELNOE UCHREZHDENIE VYSSHEGO OBRAZOVANIYA PETERBURGSK), 11 March 2020 (2020-03-11), description	1 - 8

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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