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Environmental Management

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Title: **EVALUATION OF THE ADSORPTION POTENTIAL OF ECO-FRIENDLY ACTIVATED CARBON PREPARED FROM CHERRY KERNELS FOR THE REMOVAL OF Pb²⁺, Cd²⁺ AND Ni²⁺ FROM AQUEOUS WASTES**

Authors: **Sabolč Pap^a, Jelena Radonić^a, Snežana Trifunović^b, Dragan Adamović^a, Ivana Mihajlović^a, Mirjana Vojinović Miloradov^a, Maja Turk Sekulić^{a*}**

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Type of contribution: original scientific paper.

Dear Editors and Reviewers of the *Journal of Environmental Management*,

Thank you very much for the possibility of considering our manuscript for publication in your prestigious journal.

The Author warrants that the manuscript submitted to the *JOURNAL OF ENVIRONMENTAL MANAGEMENT*, for review is original, has been written by the stated authors and has not been published elsewhere; is currently not being considered for publication by any other journal and will not be submitted for such a review while under review by the *JOURNAL OF ENVIRONMENTAL MANAGEMENT*; the manuscript contains no libellous or other unlawful statements and does not contain any materials that violate any personal or proprietary rights of any other person or entity.

Considerable efforts have been devoted to development and improvement of green technologies, based on environmentally acceptable standards, in all areas of process manufacturing. Consequently, there is a growing requirements for alternative, efficient and economically viable techniques for the remediation of wastewaters before their discharge into the environment. Activated carbon obtained from different waste biological materials has proved to be an adsorption medium that, due to its chemically active and highly porous surface, separates from aqueous solutions a wide range of pollutants in a very efficient and cost-effective way. This study is engaged with selection, synthesis, characterization and efficiency evaluation of a novel adsorbent material for removing inorganic ions from aqueous wastes. The main source of biomass for the production of activated carbons were lignocellulosic raw materials (sweet and sour cherry kernels), as industrial waste byproducts and components of organic solid waste.

New, low-cost, sustainable and locally available materials/techniques, which remove pollutants from the effluents of different industries are of great importance, as to the present day, Serbia has a low level of implemented wastewater treatments. Most of industrial wastewaters are directly discharged, endangering various water bodies. This study will be invaluable for the future activities regarding different wastewater treatment and water protection together with generated waste management in the country, almost certainly as your reflection. That is why we hope that you will take this manuscript into consideration for publication in your journal. It will be invaluable for our future activities in case of personal and professional development. Despite the

extremely poor financial situation in our country with a very little and limited investment in science we are trying to get the maximum and to follow the global trends in the field of science.

We hope that you will take this manuscript into consideration for publication in your journal, even though we have noticed that majority of the authors in your journal are from your part of the world. We are convinced that that does not limit us.

With respect,
Authors

We suggest these reviewers:

- Ø Stuart Gibb
- Ø Jasna Huremović
- Ø Tatjana Solević

Corresponding author: PhD Maja Turk Sekulic, Associate Professor, University of Novi Sad, Faculty of Technical Sciences, Department of Environmental Engineering and Occupational Safety and Health, Trg Dositeja Obradovica 6, Novi Sad, Serbia, Phone: +381 21 4852498, Fax: +381 21 6350696, e-mail: majaturk@uns.ac.rs

REVISION COVER LETTER WITH DETAILED RESPONSE TO THE EDITORS COMMENTS

Title: Evaluation of the adsorption potential of eco-friendly activated carbon prepared from cherry kernels for the removal of Pb^{2+} , Cd^{2+} and Ni^{2+} from aqueous wastes

Journal of Environmental Management

Dear Editor,

Thank you very much for Your suggestions concerning the improvements of our manuscript. We have studied the suggestions very carefully and made corrections in accordance with Your recommendations. For Your guidance, a list of changes and our comments for both points are appended below.

Please find also the revised manuscript entitled “**Evaluation of the adsorption potential of eco-friendly activated carbon prepared from cherry kernels for the removal of Pb^{2+} , Cd^{2+} and Ni^{2+} from aqueous wastes**” that we would like to be considered for publication in Journal of Environmental Management.

We do hope that You and the Reviewers find this manuscript acceptable for publication in Journal of Environmental Management.

Answers to editor - JEMA-D-16-01215R2

Editor comments

Detailed comments

C1: Table 1: Confusing. Please prepare the table clearly with identifiable row and columns.

A1: The required simplifications have been done in Table 1, in the revised manuscript. One part of the previous Table 1 has been shifted to the Supplementary material as a new table (Table S1). We hope that this separation will significantly improve presentation of obtained results, in the manuscript.

C2: Fig 5: For graphical representations, abscissa and ordinate should be labeled as: Title (unit). Abscissa and ordinate should have tic marks. Print size used should not be smaller than 10 point. All print should be legible after 1/4th reduction. Please review the figures and revise accordingly.

A2: We accepted the editor’s comments and corresponding corrections are done in the revised manuscript. Even if abscissa should be labeled as: Title (unit), at our diagram (Fig 5) abscissa presents different metal ion systems without any units. From our point of view, this is basically the same situation with tick marks, because we don’t need them to provide reference for points on a scale. If You still think the decision is wrong, we will change it, with a pleasure, but please be so kind and give us some advice.

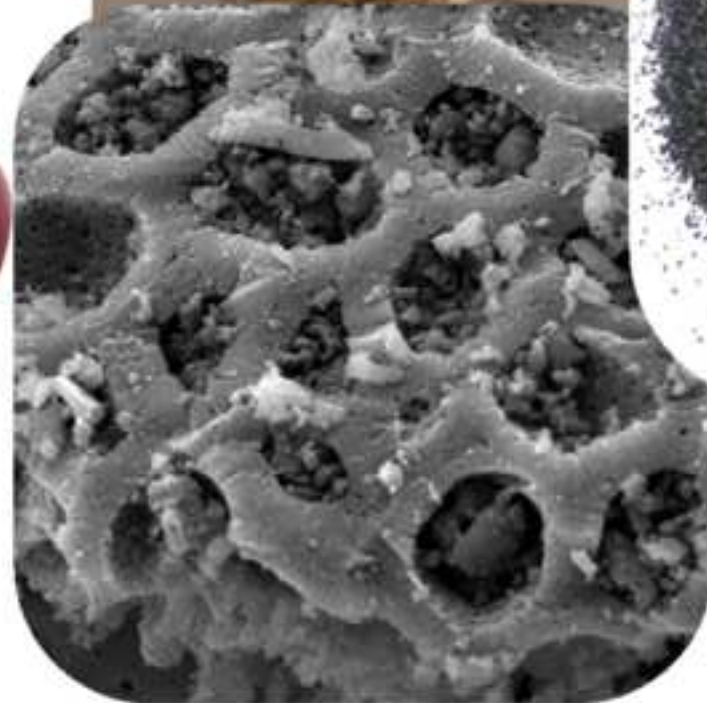
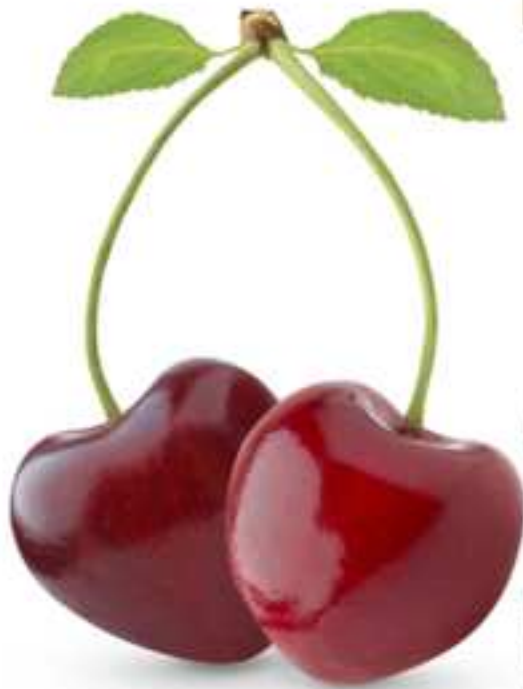
Dear Editor,

We sincerely thank You for the excellent suggestions that we have received. We did our best to improve the quality and significance of the manuscript. All the changes made based on the suggestions of the Reviewers and Editor are marked in red. We deeply hope that the revised manuscript will meet the requirements of Journal of Environmental Management and will be considered for publication in your eminent Journal.

Best regards

Maja Turk Sekulic

Corresponding author



Journal of Environmental Management

Highlights

- ✓ Pb^{2+} , Cd^{2+} and Ni^{2+} removal on cherry kernels activated carbon were studied.
- ✓ Low-cost activation develops large pore volume with $657.1 \text{ m}^2 \text{ g}^{-1}$ surface area.
- ✓ The sorption capacity with 171.4 mg g^{-1} mainly depends on the surface chemistry.
- ✓ The produced adsorbent could be applied into wastewater treatment.
- ✓ Our approach was simple and inexpensive.

Evaluation of the adsorption potential of eco-friendly activated carbon prepared from cherry kernels for the removal of Pb^{2+} , Cd^{2+} and Ni^{2+} from aqueous wastes

Sabolč Pap^a, Jelena Radonić^a, Snežana Trifunović^b, Dragan Adamović^a, Ivana Mihajlović^a, Mirjana Vojinović Miloradov^a, Maja Turk Sekulić^{a,*}

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Abstract

Development, characterization and evaluation of the efficiency of cost-effective medium for the removal of Pb^{2+} , Cd^{2+} and Ni^{2+} from aqueous systems, as a novel, eco-friendly solution for wastewater remediation were done. The precursors for low-cost adsorbent were lignocellulosic raw materials (sweet/sour cherry kernels), as industrial byproducts and components of organic solid waste. Activated carbon synthesis was carried out by thermochemical conversion (H_3PO_4 , 500 °C) in the complete absence of inert atmosphere. Characterization of the activated carbon was performed by elemental analysis, FTIR, SEM, EDX and BET. BET surface area corresponds to 657.1 $m^2 g^{-1}$. The evaluation also included the influence of pH, contact time, solute concentration and adsorbent dose on the separation efficiency in the batch operational mode. The equilibrium and kinetic studies of adsorption were done. The maximum adsorption capacity of the activated carbon for Cd^{2+} ions was calculated from the Langmuir isotherm and found to be 198.7 $mg g^{-1}$. Adsorption of Pb^{2+} and Ni^{2+} were better suitable to Freundlich model with the maximum adsorption capacity of 180.3 $mg g^{-1}$ and 76.27 $mg g^{-1}$, respectively. The results indicate that the pseudo-second-order model best describes adsorption kinetic data. Based on desorption study results, activated carbon was successfully regenerated with HNO_3 for 3 cycles. In order to provide the results for basic cost-effective analysis, competing ion-effects in a real sample have been evaluated.

Keywords: Adsorption, Heavy metals, Industrial wastes, Sweet and sour cherry kernels, Aqueous wastes

1. Introduction

The presence of heavy metals in the aquatic environments is being recognized as a priority problem at industrial waste sites. Metal ions are introduced in the freshwater from a variety of industrial and human activities involving the mining, processing,

1 leaching from uncontrolled landfill sites or use of metals and substances that contain
2 metal pollutants (Zuo et al., 2009; Tabaraki and Nateghi, 2014). Due to the metal ions
3 cannot be degraded into any less harmful components in the biotic and abiotic
4 matrices, metal ion pollution causes significant production of toxic oxygen radicals, a
5 toxicity mechanism now known to be of considerable environmental damage (Walker
6 et al., 2003). The main threats to human health from heavy metals are associated with
7 exposure to lead, cadmium, nickel, mercury and arsenic. These metals have been
8 extensively studied and global bodies such as the World Health Organization (WHO)
9 regularly review their effects on human health.
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12 Lead poisoning in humans causes serious damage to the nervous system, kidney,
13 liver, reproductive system and reduction in hemoglobin formation, mental retardation,
14 infertility and abnormalities in pregnant women (Goel et al., 2005; Martins et al.,
15 2006; Tunali et al., 2006). Therefore, the permissible level for lead in drinking water
16 is 0.05 mg L^{-1} and 0.01 mg L^{-1} according to the US Environmental Protect Agency
17 (EPA) and the World Health Organization (WHO), respectively. Cadmium and nickel
18 are among the most toxic heavy metals in the environmental matrixes (Khairy et al.
19 2014). Chronic accumulation of cadmium in human bodies causes the damage in
20 kidney, liver, cardiovascular and skeletal systems, while high dosage uptake causes
21 Itai-Itai disease or even death (Kumar and Chawla, 2014). Exposure to nickel over
22 permissible value causes various diseases, such as renal edema, lung cancer,
23 pulmonary fibrosis, skin dermatitis, and gastrointestinal discomfort (Celekli and
24 Bozkurt, 2011). Due to its harmful effect to human health, the permissible
25 concentration of WHO and EPA guidelines in drinking water is strictly restricted to
26 below 0.003 and 0.005 mg L^{-1} for cadmium and 0.01 mg L^{-1} for nickel, respectively.
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29 The widely utilized technologies for heavy metal-contaminated wastewater effluents
30 are usually activated carbon adsorption, ion exchange, precipitation, membrane
31 filtration, reverse osmosis, solidification/stabilization etc. Filtration with the different
32 adsorbents is probably the most used, but there are a few limiting factors in the
33 maintenance of the system. Thus, great attention is given to the characterization and
34 understanding of the sorption properties of alternative low-cost materials (Akunwa et
35 al., 2014). A number of studies have been reported for heavy metal ions removal by
36 using different biomass waste materials, such as agriculture residues (Chuah et al.,
37 2005), date stones (Bakouri et al., 2009), olive stone (Kula et al., 2008), hard shell of
38 fruit stones (Mouni et al., 2011; Abbas et al., 2014; Soleimani and Kaghazchi, 2008;
39 Tseng, 2007; Olivares et al., 2006a; Olivares et al., 2006b; Angin, 2014) grapefruit
40 peel (Torab-Mostaedi et al., 2013), rice bran (Zafar et al., 2015), eggshell and
41 powdered marble (Elabbas et al., 2016), white pine sawdust (Salazar-Rabago and
42 Leyva-Ramos, 2016), etc. Lignocellulosic biomass derived from fruit by-products has
43 proven to be a promising type of raw material for producing cost-effective activated
44 carbons, in particular due to its local availability and removal efficiency at a low price
45 (Nor et al., 2013).
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48 The objective of this study was selection, synthesis, characterization and efficiency
49 evaluation of a novel adsorbent material for removing inorganic ions from aqueous
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1 wastes. The main source of biomass for the production of activated carbons were
2 lignocellulosic raw materials (sweet and sour cherry kernels), as industrial waste
3 byproducts and components of organic solid waste. Adsorbent synthesis was
4 performed by thermochemical conversion. In order to minimize the operational costs,
5 as one of the main challenges of most research studies, the process of activated carbon
6 synthesis was carried out in the complete absence of nitrogen inert atmosphere. A
7 detailed characterization of the obtained activated carbon was performed through
8 various instrumental analyses, comprising of elemental analysis, FTIR, SEM, EDX
9 and BET. The effects of different process parameters such as pH of solution,
10 adsorbent dosage, contact time and solute concentration on the efficiency of the Pb^{2+} ,
11 Cd^{2+} and Ni^{2+} separation from the aqueous system in the batch operational mode were
12 investigated. Data analysis revealed stable as well as unreliable domain in the
13 adsorber performance, thus allowing further optimization of the operating conditions
14 in terms of the technological and economic efficacy. Once the evaluation of the key
15 characteristics and optimal process conditions was finalized, equilibrium and kinetic
16 study of the adsorption in the batch operational system mode was conducted. The
17 application of obtained new adsorption material was also evaluate in term of
18 regeneration possibility. In order to provide the comprehensive evaluation of the
19 obtained adsorption process competing ion-effects study, separation from the real
20 samples and basic cost-effective analysis were done.

28 **2. Materials and methods**

30 *2.1. Preparation and analysis of Pb^{2+} , Cd^{2+} and Ni^{2+} ions solutions*

31 In designed experiments, all the reagents were of analytical grade. Stock solutions
32 (1000 mg L⁻¹) were prepared in deionized water using $Pb(NO_3)_2$, $3CdSO_4 \cdot 8H_2O$ and
33 $Ni(NO_3)_2 \cdot 6H_2O$, and adding few drops of 0.1 mol L⁻¹ HNO_3 to prevent the
34 precipitation of metal ions. Other concentrations prepared from stock solution by
35 dilution varied between 5 and 500 mg L⁻¹ and the pH of the working solution was
36 adjusted to desired values using 0.1 mol L⁻¹ NH_4OH or 0.1 mol L⁻¹ HCl (Sadeek et al.,
37 2015). Fresh dilutions were used for each study. The final Pb^{2+} , Cd^{2+} and Ni^{2+}
38 concentrations were determined by using an atomic absorption spectrophotometer
39 (Thermo Scientific S Series) with an air-acetylene flame. The instrument was
40 calibrated within the linear range of analysis. The correlation coefficients for all
41 methods were 0.99 or greater. The instrument calibration was periodically checked by
42 using standard solution for every 10 readings.

49 *2.2. Untreated lignocellulosic biomass*

50 Sour cherry/sweet cherry kernels were obtained from fruit plantation located in Novi
51 Becej, province of Vojvodina (Serbia). The kernels were milled with a mechanical
52 mill and < 3.0 mm fraction was chosen for the thermochemical conversion (Fig. S1. in
53 supplementary materials). Aproximately 140,000 tons of sweet and sour cherry are
54 produced in Serbia every year. The average fruit weights from 2.6-3.0 g, while kernel
55 weight is about 15 % of the total weight of the fruit, which indicates that 21,000 tons
56 of organic solid waste are produced annually as fruit industry byproduct.

2.3. Preparation of activated carbon

In this study, sour cherry/sweet cherry kernels (in the ratio 1:1) were used as a precursor for preparation of activated carbon. The kernels were washed with distilled water, crushed in a mechanical mill and dried for 2 h at 105 °C. Phosphoric acid, as a chemical reagent added during the activation process, helped in producing more specific surface. Fifty grams of the fruit kernels were impregnated with 50 wt.% H₃PO₄ at 22 °C at ratio of 2.66:1 (weight). After 24 h of impregnation, suspension was filtered to remove the residual acid. Subsequently impregnated samples were air dried at room temperature for 2 h, what made the samples ready for the carbonization experiments. During the first phase samples were heated at a rate of 10 °C/min to 180 °C and held at this temperature for 45 min. In the second phase, kernels were heated at a rate of 10 °C/min to 500 °C and held for the next 60 min in the complete absence of inert atmosphere at constant temperature. After cooling, the activated carbon was repeatedly washed with deionized water until the filtrate pH reaches over 4. Prepared activated carbon after H₃PO₄ treatment (Fig. S1. in supplementary materials) will be indicated as CScPA (Cherry and Sweet Cherry Phosphoric Acid) and activated carbon after H₂SO₄ treatment will be indicated as CScSA (Cherry and Sweet Cherry Sulfuric Acid).

2.4. Morphological, physical and chemical characterization of the activated carbon

Upon completion of the lignocellulosic raw materials thermochemical conversion, complete morphological, physical and chemical characterization of the resulting activated carbon was performed. Elemental analysis (percentage content of carbon, hydrogen, nitrogen and sulphur in row kernels and CScPA) were performed by Vario EL III C, H, N, S / O Elemental Analyzer (Elementar, Germany). The oxygen contents were calculated by difference.

The yield of activated carbon, which is an indication of activation process mass efficiency, is the amount of activated carbon produced at the end of the activation step. Yield is usually defined as final weight of activated carbon produced after activation, washing, and drying, divided by initial weight of raw material. The following relationship is used for calculating the yield of activated carbon:

$$\text{Yield}(\%) = \frac{w_0 - w_c}{w_0} \times 100 \quad (1)$$

Where: w_0 is the mass of material before carbonization, w_c is the mass of material after carbonization.

The ASTM D6851-02 determined contact pH with activated carbon. Suspension pH of the activated carbon in water (pH_{sus}) relates with the overall acidity of the adsorbent. 0.2 g of CScPA was suspended into 30 ml of deionized water and equilibrated for 72 h. The solution was occasionally mixed, the pH was measured using a pH meter WTW SenTix® 41 (WTW, Germany) and the reading was recorded. The pH at the point zero charge (pH_{pzc}) was also determined. pH_{pzc} of a activated carbon is important because it indicates the net surface charge. To determine the pH_{pzc}, 0.1 g of CScPA was taken to nine 50 mL plastic bottles containing 30 mL

1 of 0.1 mol L⁻¹ KNO₃ with adjusted pH values from 2 to 10. The plastic vials were
2 sealed and placed in a mechanical stirrer Heidolph Unimax 1010 (Heidolph,
3 Germany) for 24 hours. The content of the flasks was filtered and pH was measured.
4 Determination of moisture content was performed using ASTM D2867-04. Total ash
5 content of the activated carbon was determined by the ASTM D2866-94 method. The
6 density of the sample was determined using graduated cylinder volume of 10 mL. All
7 of the obtained results are given in Table 1.
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10 The microstructures of the CScPA were determined by scanning electron microscope
11 (SEM) JSM 6460LV instrument (JEOL, USA) equipped with an EDX attachment.
12 Scanning electron micrographs were recorded without sample coating, with ×2,000
13 and ×5,000 magnification.
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16 CScPA specific surface area (S_{BET}) determination was done by measurement of N₂
17 adsorption, applying Brunauer–Emmett–Teller technique (BET) and Autosorb iQ
18 instrument (Quantachrome, USA). Cumulative pore volume for mesoporous was
19 calculated using Barret–Joyner–Halenda method. The Dubinin–Radushkevich test
20 was applied to get micropore volume.
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23 A detailed Fourier Transform Infrared spectra (FTIR) study of prepared activated
24 carbon was carried out to identify qualitative characteristics of carbon material and
25 the different functional groups responsible for the adsorption. FTIR spectra of CScPA
26 were recorded with a FTIR/NIR spectrophotometer Nexus 670 (Thermo Nicolet,
27 USA), at wavenumbers from 400 to 4,000 cm⁻¹.
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30 2.5. Variation of operational parameters 31

32 The effect of different process parameters on metal ions adsorption onto CScPA was
33 investigated. The influence of pH was studied by using a 50 mL solution of 100 mg L⁻¹
34 metal ions contacted with 0.1 g (2.0 g L⁻¹) of CScPA for a pH range from 2.0 to 9.0
35 at room temperature (22 °C±2 °C). Flasks were agitated on a shaker for 30 min. At
36 pH 7, the formation of soluble hydroxylated complexes (lead hydroxide, nickel
37 hydroxide and cadmium hydroxide) and precipitation of metal ions were occurred;
38 consequently, the decrease of the adsorbate concentration at pH > 6 could not be
39 attributed only to the process of adsorption.
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43 Batch adsorption tests were done at various time intervals (5, 10, 15, 20, 30, 40, 50
44 and 60 min) with an initial concentration of 100 mg L⁻¹ of metal ions solution at
45 optimum pH (6.0) and room temperature (22 ± 1 °C). The CScPA dose was 0.1 g (2.0
46 g L⁻¹) in 50 mL of solution.
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49 The effect of activated carbon concentration was studied by using CScPA ranging
50 from 0.01 g to 0.5 g (0.2 – 10.0 g L⁻¹) at a 50 mL solution of 100 mg L⁻¹ of metal ions
51 at pH 6.0, for a contact time of 30 min at room temperature (22 ± 1 °C).
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54 In addition, for the assessment of the effect of metal ions concentration on adsorption
55 efficiency, 50 mL of metal solutions ranging from 5 to 500 mg L⁻¹ were contacted
56 with 0.1 g (2.0 g L⁻¹) of CScPA at pH values of 6.0, for a contact time of 30 min at
57 room temperature (22 ± 1 °C).
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2.6. Batch adsorption studies

1 Isotherm batch adsorption experiments were performed by shaking the flasks at 140
2 rmp for a fixed time period using a mechanical stirrer Heidolph Unimax 1010
3 (Heidolph, Germany) to ensure that the equilibrium was reached. The mixtures were
4 then filtered through Macherey-Nagel MN640n filter paper and the residual levels of
5 Pb^{2+} , Cd^{2+} and Ni^{2+} in the filtrates were quantified. Following a methodical process,
6 the adsorption uptake capacity of metal ions in batch system was studied. The data
7 obtained were used to calculate the equilibrium metal ion adsorptive quantity
8 applying the following expression:
9

$$10 \quad q_e = \frac{(C_0 - C_e) \times V}{m} \quad (2)$$

11 Where q_e is the amount of heavy metal ion adsorbed onto the activated carbon, ($mg\ g^{-1}$);
12 V is the volume of solution treated, (L), C_0 is the initial concentration of metal ion,
13 ($mg\ L^{-1}$); C_e is the equilibrium metal ion concentration ($mg\ L^{-1}$); m is the biomass (g).
14

15 Removal percent of metal ions ($Re\ \%$) was calculated using the following expression:
16

$$17 \quad R_e(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (3)$$

2.7. Desorption experiment

18 Desorption study of metal ions from the CScPA was done by using $0.1\ mol\ L^{-1}\ HNO_3$.
19 At first, $3\ g\ L^{-1}$ activated carbon was added in 100 mL of heavy metal mixture
20 solution (Pb^{2+} , Cd^{2+} and Ni^{2+} were of the same concentrations of $100\ mg\ L^{-1}$). After
21 30 min of shaking at pH 6, solution was filtered and activated carbon rinsed with
22 distilled water. In next step, metal ion loaded CScPA was stirred at 140 rpm for 30
23 min at room temperature ($22 \pm 1\ ^\circ C$) in 50 ml $0.1\ mol\ L^{-1}\ HNO_3$ solution. Suspension
24 was filtered, rinsed, dried at $70\ ^\circ C$ and reused. Sorption – desorption cycles were
25 repeated three times. Experiments were carried out in a batch system. Desorption
26 efficiency was calculated using the following equation:
27

$$28 \quad d_E = \frac{q_d}{q_a} \times 100 \quad (4)$$

29 Where d_E is desorption efficiency (%); q_d is amount of metal ions desorbed ($mg\ g^{-1}$);
30 q_a is adsorption capacity of metal ions adsorbed on the activated carbon, ($mg\ g^{-1}$).
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3. Results and discussion

3.1. Characterization of the prepared activated carbon

32 Carbonizing temperature and activating agent had the most influence over the
33 activated carbon's adsorption quality during the performed activating process. Two
34 chemicals have been selected as potential activating agents: H_3PO_4 and H_2SO_4 . To
35 ensure the complete transformation of organic compounds into graphene structures,
36 carbonizing temperatures of $400\ ^\circ C$ and $500\ ^\circ C$ were used. The results of the
37 production yield of activated carbons obtained at various activation temperatures and
38 with different chemical agents are shown in Table S1. After the preliminary study, the
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1 use of H₂SO₄ has been excluded because of the lower production yield, unfavorable
2 porous structures and a smaller removal efficiency of obtained carbons. Concurrently,
3 H₃PO₄ has shown significant development of porosity and active sites with a specific
4 character, acceptable material's loss, low energy costs, as well as easy recovery of the
5 activating agents, as in the several reported studies (Illingworth et al., 2012; Zuo et
6 al., 2009; Zuo et al., 2012). It should be emphasized that these activation results were
7 achieved in the complete absence of inert atmosphere, which essentially favors the
8 development in the carbon's porosity. As can be seen from Table S1, with an
9 increasing in activation temperatures from 400 to 500 °C, the production yield of
10 activated carbons decreased from 84.0 to 72.8 % for CScPA and from 37.4 to 34.4 %
11 for CScSA. However, preliminary experimental findings indicate that activation
12 temperature of 500 °C was highly effective in enhancing the activated carbon
13 adsorption capacity, which served as the fundamental basis for selecting the operating
14 conditions for the further course of study.

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20 Based on the amount of generated waste materials and the yield of preparation
21 process, approximate annual production of activated carbon was calculated. It was
22 found that 17000 t year⁻¹ of activated carbon can be produced in Serbia from these
23 type of waste materials.

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Elemental analyses of the raw material and activated carbon produced from sweet and
sour cherry kernels are given in Table 1. As can be seen, the sweet and sour cherry
kernels have relatively low carbon content (49.28 wt.%), but high oxygen content
(41.86 wt.%). The elemental compositions of the raw kernels can be attributed to the
lignin and cellulose contents. With the thermochemical conversion, the carbon content
significantly increased from 49.28 to 60.38 wt.%; however, the hydrogen content
decreased from 7.39 to 2.13 wt.%, and oxygen content also showed a similar trend,
slightly decreased from 41.86 to 36.42 wt.%. The high oxygen content and low
hydrogen content for CScPA is result of carbonization in the complete absence of an
inert atmosphere.

40 **Table 1**

41 **Chemical and physical characteristics of the CScPA and raw material**

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pH_{pzc} of CScPA was found to be 3.14. It can be explained that the surface charge is
negatively charged above pH_{pzc}. This implies, as the pH of the matrix increases
beyond the pH_{pzc}, that the number of positively charged sites decreases and favors the
binding of Pb²⁺, Cd²⁺ and Ni²⁺ due to electrostatic attraction.

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CScPA has a relatively large bulk density. Bulk density is important for activated
carbon when the carbons are used in column mode. The low ash and moisture content
presented in Table 1 exhibited that the CScPA could be applied as an adsorbent. Ash
in an activated carbon is an impurity and an undesirable product. It is important to
note that the ash content of CScPA was only 4.26 %, which is most probably
attributed to the low ash content of the cherry and sour cherry kernels hard shell.

3.1.1. SEM analysis

The scanning electron microscopy (SEM) equipped with EDX was used to analyze the components and morphology of activated carbon surface. Fig. S2 (a)–(c) (supplementary materials) shows the SEM images of the adsorbent samples before and after metal adsorption and EDX spectrum after adsorption, respectively. The figures show that the activated carbon had an irregular and porous surface indicating relatively high surface areas. The BET surface area of the activated carbon supports this results. The macro- and meso pores were clearly observed on the surface of the CScPA, facilitating the easy diffusion of a large number of pollutants into the pore structure and the adsorption of Pb^{2+} , Cd^{2+} and Ni^{2+} onto the surface of the adsorbent. After adsorption, considerable changes in surface morphology of activated carbon were apparent and the surfaces of adsorbent seemed rougher. Through EDX analysis of the carbon sample after saturation, peaks of metal ions were observed along with all the other components identified in activated carbon. This is due to both the chemical composition of the precursor and the activating agent (H_3PO_4) that promotes depolymerization, dehydration, and redistribution of constituent biopolymers, inducing important changes in the pyrolytic decomposition of the lignocellulosic material. Presence of metal ions on cell surface after adsorption, as seen from EDX image, proved the adsorption of these metal ions by the CScPA.

3.1.2. Surface and porous characteristics

The textural properties of the activated carbon are shown in Table S2 (supplementary materials). The S_{BET} of prepared activated carbon was $657.1 \text{ m}^2 \text{ g}^{-1}$. Even if thermochemical activation of cherry kernels reported in previous studies (Gergova et al., 1994; Lussier et al., 1994) reached developed S_{BET} above $1,000 \text{ m}^2 \text{ g}^{-1}$, our primary goal was to develop low-cost and easy to produce activated carbon. With this aim, in the manufacture of separation media, the emphasis was put on the optimization of all process parameters: rational use of the impregnating agent (through the impregnation ratio), process energy efficiency (through the activation temperature), minimal use of chemicals (carbonization without the protection of an inert gas), production yield maximization (mass activation process efficiency) and a high degree of activated carbon separation efficiency.

Obtained activated carbon has relatively wide range of pores with larger micropores (average width $< 2 \text{ nm}$) than mesopores (average width from 2-50 nm) volume (Table S2). The maximum pore diameter of activated carbon was 32.50 nm. The presence of $46.739 \text{ m}^2 \text{ g}^{-1}$ mesopores surface in combination with micropores is expected to play a significant role in the adsorption of different large molecules of pollutants (Angin, 2004).

3.1.3. FTIR analysis

The chemical structure of the activated carbon is of fundamental importance in understanding the nature of adsorption and mechanism of metal binding process on natural adsorbents. The adsorption efficiency of carbon materials depends on porosity, as well as on the number and chemical reactivity of surface functional groups.

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Obtained results of Fourier transform infrared spectra study of CScPA is given in Fig. S3. The FTIR spectrum display a number of absorption peaks indicating the complex nature of the activated carbon and presence of many functional groups that may be involved in the adsorption process.

The FTIR spectra of CScPA show a broad band at $3,737.91\text{ cm}^{-1}$ due to N–H stretching vibration and a peak at 484.91 cm^{-1} due to O–H bending vibration. Peaks between the regions $3,700.00$ and $3,200.00\text{ cm}^{-1}$ represent the overlapping peaks of stretching vibrations of O–H and N–H groups. The distinct absorption peaks at $2,922.59\text{ cm}^{-1}$ and $2,852.11\text{ cm}^{-1}$ could be assigned to -CH stretching vibrations of -CH₂ and -CH₃ functional groups. The peak at $1,749.23\text{ cm}^{-1}$ is assigned to carbonyl groups stretching from aldehyde and ketones of lignin. The adsorption peak at $1,565.63\text{ cm}^{-1}$ could be characterized by primary and secondary amide bands. The appearance of bands between $1,436.28$ and $1,374.69\text{ cm}^{-1}$ could be the deformation stretching of CH, -CH₃ and -CH₂ functional groups. The sharp band within $1,163.33 - 983.94\text{ cm}^{-1}$ is attributed to the C–O groups, which are confirms the lignin structure of the CScPA (Momčilović et al., 2011; Chakravarty et al., 2010; Mishra et al., 2014).

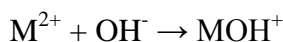
3.2. Effect of solution pH on adsorption

The pH value is one of the most important parameter that determines the removal efficiency of heavy metals from the different aqueous waste solutions. In adsorption, it controls surface charge of the adsorbent, precipitation, ionization and speciation of adsorbate, strongly influencing the uptake of metal ions. In order to evaluate the effect of pH on adsorption of Pb²⁺, Cd²⁺ and Ni²⁺ ions, the batch equilibrium adsorption studies at different pH values were performed. The pH of the samples was kept constant applying a 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NH₄OH as needed, performing the experiments in the range of pH from 2–9. The experiments were performed under the following conditions: metal concentration 100 mg L^{-1} , activated carbon dose 2.0 g L^{-1} , reaction temperature $22 \pm 1\text{ }^{\circ}\text{C}$ and contact time 30 min. Results of the study showed that the amount of Pb²⁺, Cd²⁺ and Ni²⁺ removal increases with the increase in pH, especially at pH values greater than 5 (Fig. 1).

Fig 1. Effect of pH on the adsorption of Pb²⁺, Cd²⁺ and Ni²⁺

The uptake was quite weak at lower pH. In such environment, the surface area of adsorbent was more protonated and access of positive metal ions was disabled as a result of repulsive force. In addition to this, competitive adsorption appeared between H⁺ and metal cations towards the negative active sites on the adsorbent surface. Increasing the pH increased negative charge of the adsorbent surface and a significant enhancement in adsorption was recorded. According to the Pourbaix diagrams for the metal-H₂O system at 22°C, Pb²⁺, Cd²⁺ and Ni²⁺ ions transform in M(OH)⁺ or precipitate as M(OH)₂ at pH values higher then 7, and the decrease in the

1 concentration of adsorbate cannot be attributed only to the process of adsorption
2 (Kovacevic et al., 2000; Sadeek et al., 2015). At pH 6.5, a decrease in adsorption of
3 Cd^{2+} ions was observed due to the formation of soluble hydroxylated complexes and
4 their competition with the active sites (Torab-Mostaedi et al., 2013). Therefore, the
5 optimum pH was found to be 6 with the amounts of adsorbed metal ions of 47.34,
6 45.25 and 21.82 mg g^{-1} for Pb^{2+} , Cd^{2+} and Ni^{2+} , respectively. All further experiments
7 were conducted at this pH value.
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12 3.3. Effect of activated carbon dosage

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14 Adsorption efficiency is strongly affected by the adsorbent dosage, due to the
15 availability of the surface area and exchangeable sites. The results of the experiments
16 with varying activated carbon concentrations are presented in Fig. 2. The values of
17 operational parameters during the experiments were: metal concentration 100 mg L^{-1} ,
18 contact time 30 min, reaction temperature $22 \pm 1 \text{ }^\circ\text{C}$ and pH 6. With increase in the
19 activated carbon mass, from 0.01 g to 0.5 g ($0.2 - 10 \text{ g L}^{-1}$), the amount of adsorbed
20 Pb^{2+} , Cd^{2+} and Ni^{2+} decreases from 144.05 to 9.52 mg g^{-1} , 214.30 to 9.87 mg g^{-1} and
21 73.25 to 7.03 mg g^{-1} , respectively. After dosage of 2.0 g L^{-1} , the removal efficiency
22 was not increased extraordinarily. With the aim of maximizing the separation process
23 efficiency, while retaining minimal operating costs, as the optimal solution for
24 economical wastewater treatment plant applications in the subsequent batch studies,
25 the activated carbon dose of 2.0 g L^{-1} was adopted.
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36 **Fig 2.** Effect of adsorbent concentration on the adsorption of Pb^{2+} , Cd^{2+} and Ni^{2+}
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40 3.4. Effect of contact time

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42 The effects of contact time on the adsorption of Pb^{2+} , Cd^{2+} and Ni^{2+} ions on the
43 CScPA are presented in Fig. 3. The results were obtained at the following
44 experimental conditions: metal concentration 100 mg L^{-1} , activated carbon dose 2.0 g
45 L^{-1} , reaction temperature $22 \pm 1 \text{ }^\circ\text{C}$ and pH = 6. The figure reveals that increasing in
46 contact time increased the uptake of metal ions into two different phases; an initial
47 very fast step where >90% of adsorbed ions were bound within the first 15 min and
48 the second phase where equilibrium is attained within 30 min. It is easy to spot that
49 Pb^{2+} , Cd^{2+} and Ni^{2+} adsorption on the CScPA is very quick. Based on the obtained
50 results, 30 min was chosen as the optimum equilibrium time throughout the rest of the
51 batch experiments in further study.
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58 **Fig 3.** Effect of contact time on the adsorption of Pb^{2+} , Cd^{2+} and Ni^{2+}
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3.5. Effect of initial adsorbate concentration

Adsorption of Pb^{2+} , Cd^{2+} and Ni^{2+} ions onto CScPA was investigated at various initial ion concentrations of 5 - 500 mg L^{-1} at pH 6, activated carbon dose 2.0 g L^{-1} , reaction temperature 22 ± 1 °C and contact time 30 min (Fig. 4). With increasing in the initial metal ion concentration, the amount of Pb^{2+} , Cd^{2+} and Ni^{2+} adsorbed increases, but the efficiency of the process after 100 mg L^{-1} is decreased from 94.48 to 68.56 %, 90.61 to 67.30 % and 43.99 to 30.51 %, respectively. This increase is result of the increase in the driving force i.e. concentration gradient with increasing the initial concentration in order to overcome the all mass transfer resistance of metal ions between the liquid and solid phases. However, the decrease in process efficiency may be attributed to the lack of sufficient sorption sites on the surface area to accommodate much more metal ion available in the solution. Obtained data suggests that the separation of Pb^{2+} , Cd^{2+} and Ni^{2+} is significantly concentration dependent, so purification yield can be improved by diluting the wastewaters.

Fig 4. Effect of initial concentrations of Pb^{2+} , Cd^{2+} and Ni^{2+} (range from 5 to 500 mg L^{-1}) onto adsorption process

3.6. Kinetic studies

Kinetic adsorption models are used to analyze experimental results in order to determine the adsorption mechanism and identify the process limiting step. In this context, the limiting stage defines the process speed and may arise from a chemical reaction, diffusion or mass transport through the phase interface. Three types of well-known kinetic models were used to explain the mechanism of the adsorption processes: pseudo-first order, pseudo-second order model and intraparticle diffusion model. The linear form of the adsorption kinetic models can be expressed as:

Pseudo-first order model:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (5)$$

Pseudo-second order model:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

Intraparticle diffusion model:

$$q_t = K_i t^{1/2} + C \quad (7)$$

where q_e and q_t are the sorption capacity (mg g^{-1}) of the metal ions at equilibrium and at a contact time t , respectively; K_1 , the equilibrium rate constant for pseudo-first order adsorption (l min^{-1}); K_2 , the equilibrium rate constant for pseudo-second order

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adsorption ($\text{mg g}^{-1} \text{ min}^{-1}$); K_i , the intraparticle diffusion rate constant ($\text{mg g}^{-1} \text{ min}^{-1/2}$)
and C , a constant (mg g^{-1}). Plot of $\log(q_e - q_t)$ versus t gives a straight line for first
order adsorption kinetics which allows computation of the rate constant K_1 (Fig. S4).
The equilibrium adsorption capacity q_e , and the second order constants K_2 can be
determined experimentally from the slope and intercept of plot t/q_t versus t (Fig. S5).
The values of constants from intraparticle diffusion model, K_i and C , were calculated
from the slope of the plot q_t versus $t^{1/2}$ (Fig. S6).

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All kinetic data and corresponding R^2 values for the adsorption of Pb^{2+} , Cd^{2+} and Ni^{2+}
ions onto CScPA are summarized in Table 2. Comparison of the R^2 values for applied
models suggests that the pseudo-second order kinetic model fits best since its highest
values. The pseudo-first order model considers the rate of adsorption sites occupation
to be proportional to the number of unoccupied sites. For this model, the correlation
coefficient is always less than 0.982, indicating a weaker correlation. As well, the
calculated theoretical values of $q_{e, cal}$ are not in good agreement with the experimental
ones ($q_{e, exp}$). This may be owing to the limitations of the boundary layer. R^2 values for
the intraparticle diffusion model are between 0.690 and 0.958, showing that this
model is not suitable for modeling the adsorption of Pb^{2+} , Cd^{2+} and Ni^{2+} ions onto
CScPA.

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Table 2

Kinetic parameters for the adsorption Pb^{2+} , Cd^{2+} and Ni^{2+} onto CScPA

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The plot given in Fig. S6 presents multi-linearity correlations, which indicates the
occurrence of two or even more steps during the process (Kannan and Sundaram,
2001). However, correlation coefficients are higher than 0.980 for CScPA and the
theoretical values of $q_{e, cal}$ calculated from pseudo-second order kinetics are very close
to the experimental values of $q_{e, exp}$, for all metal ions. These results indicate that the
adsorption kinetics of Pb^{2+} , Cd^{2+} and Ni^{2+} ions onto prepared activated carbon could
be well explained and best approximated by the pseudo-second order kinetic model.
Based on this observation, it could be concluded that chemical reaction might be the
rate-limiting step that controls the adsorption Pb^{2+} , Cd^{2+} and Ni^{2+} ions onto CScPA.

46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 3.7. Adsorption isotherms

The equilibrium adsorption isotherms are one of the most important data to
understand the mechanism of the adsorption systems. They represent the equilibrium
distribution of metal ions between the solid and liquid phases, defining the correlation
with the amount of adsorption and liquid phase concentration. Three types of well-
known adsorption isotherms equations were tested to fit the experimental data:
Langmuir, Freundlich and Temkin isotherms. The Langmuir isotherm is based on the
assumption that the adsorption take place only at specific localized sites on the
surface and the saturation coverage corresponds to complete occupancy of these sites,
each site can accommodate only one molecule and the surface is energetically

1 homogeneous. The linear form of the adsorption isotherm equation can be expressed
2 as:

$$3 \frac{C_e}{q_e} = \frac{1}{q_{max}b} + \frac{C_e}{q_{max}} \quad (8)$$

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6 Where q_e is the equilibrium amount of solute adsorbed per unit weight of activated
7 carbon (mg g^{-1}); C_e , the equilibrium concentration of solute in the bulk solution (mg
8 L^{-1}); q_{max} , maximal monolayer adsorption capacity under the experimental conditions
9 (mg g^{-1}); b , the constant related to the free energy of adsorption. The adsorption
10 isotherm for heterogeneous surface is fully described by the Freundlich adsorption
11 isotherm, whose main assumption is that the metal ions can be applied for multilayer
12 sorption. The linear form of the adsorption isotherm equation can be expressed as:

$$13 \log q_e = \log K_f + \frac{1}{n} \log C_e \quad (9)$$

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16 Where q_e is the equilibrium amount of solute adsorbed per unit weight of activated
17 carbon (mg g^{-1}); K_f , the constant indicative of the relative adsorption capacity of the
18 activated carbon (mg g^{-1}); n , the constant related to intensity of the adsorption (-).
19 Temkin isotherm assumes that the fall in the heat of sorption is linear rather than
20 logarithmic. The linear form of the adsorption isotherm equation can be expressed as:

$$21 q_e = B \ln A_T + B \ln C_e \quad (10)$$

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24 A_T , the Temkin isotherm equilibrium binding constant (L g^{-1}) and B , the constant
25 related to the heat of sorption (J mol^{-1}).

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28 The linearized Langmuir, Freundlich and Temkin isotherms for modeling the
29 equilibrium sorption of Pb^{2+} , Cd^{2+} and Ni^{2+} on the CScPA are shown in Figs. S7, S8
30 and S9. Isotherms were determined at room temperature for a concentration range of
31 5-500 mg L^{-1} . The estimated adsorption model parameters for the different isotherms
32 are given in Table 3. From the values of correlation coefficients summarized in Table
33 3, it may be concluded that the adsorption of Pb^{2+} and Ni^{2+} on the CScPA is described
34 better ($R^2 > 0.96$) with Freundlich model as compared to Langmuir and Temkin
35 models under the concentration range studied. It should be emphasized, that even if
36 chemisorption is usually restricted to just one layer of molecules on the surface,
37 obtained results indicate that it may be followed by additional layers of physically
38 adsorbed species.

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41 According to the correlation coefficient ($R^2 > 0.99$), Cd^{2+} adsorption could well be
42 approximated more favorably by the Langmuir model as compared to Freundlich and
43 Temkin models. The observation suggests that monolayer sorption takes place on the
44 surface of the CScPA for Cd^{2+} , with the theoretical monolayer saturation capacity of
45 198.74 mg g^{-1} . The maximum experimentally obtained capacity was 168.25 mg g^{-1} ,
46 which corresponds to the initial concentration of 500 mg g^{-1} . The maximum
47 adsorption capacities for Pb^{2+} and Ni^{2+} were 180.26 mg g^{-1} and 77.71 mg g^{-1} ,
48 respectively. The maximum adsorption capacities that were obtained theoretically and
49 experimentally are in good agreement.
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1 Isotherm batch experiments showed that performed adsorption is greatly dependent on
2 the contact time, pH value and initial adsorbate and activated carbon concentrations.
3 The optimum adsorption capacity of CScPA for the removal of metal ions was
4 obtained within 30 minutes at pH 6, with initial adsorbate and activated carbon
5 concentrations of 500 mg L⁻¹ and 0.1 g (2 g L⁻¹), respectively.
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7 **Table 3**

8 Langmuir, Freundlich and Temkin isotherm constants for Pb²⁺, Cd²⁺ and Ni²⁺
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13 The essential features of the Langmuir isotherm may be expressed in terms of
14 equilibrium parameter R_L, which is a dimensionless constant referred to as separation
15 factor or equilibrium parameter:
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$$17 R_L = \frac{1}{(1 + bC_0)} \quad (11)$$

18
19 Where C_o is the initial concentration of Pb²⁺, Cd²⁺ and Ni²⁺. The R_L value indicates
20 the shape of isotherm. R_L values between 0 and 1 indicate favorable adsorption, while
21 R_L ≥ 1 or R_L = 0 indicate unfavorable and irreversible adsorption isotherms. R_L values
22 are given in Table 4. According to the R_L at different concentrations between 0 and 1,
23 Langmuir isotherm indicates a highly favorable adsorption.
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28 **Table 4**

29 The R_L values for CScPA
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35 3.8. Comparison of metal ions in binary and ternary systems

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37 In industrial aqueous wastes, contaminated with more than one heavy metal,
38 competitive adsorption appears, resulting in decreased adsorption of a considered
39 metal ion in comparison with its single solute adsorption. In order to assess the
40 multicomponent effects on separation efficiency, adsorption on CScPA in binary and
41 ternary metal systems was investigated. Simultaneous removal of Pb²⁺, Cd²⁺ and Ni²⁺
42 ions in binary- and ternary-metal solutions was performed at pH 6, initial
43 concentration 100 mg L⁻¹ for each metal ion, activated carbon dose 2.0 g L⁻¹, contact
44 time 30 min and reaction temperature 22 ± 1°C. The adsorption results of Pb²⁺, Cd²⁺
45 and Ni²⁺ by CScPA are shown in Fig. 5.
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54 **Fig 5. Interaction between metal ions in binary and ternary system**

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57 Results indicated that the separation efficiency of single metal ions in all multisolute
58 systems decreases with the increasing number of components. The presence of Pb²⁺
59 significantly suppressed Cd²⁺ and Ni²⁺ removal. Cd²⁺ removal efficiency in the
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1 absence of Pb^{2+} and Ni^{2+} was 92.4%, but decreased to 85.5% with the presence of
2 Pb^{2+} . Meanwhile Pb^{2+} and Cd^{2+} removal efficiency decreased slightly from 94.5% to
3 93.5% and 92.4% to 90.6%, respectively, with the presence of Ni^{2+} . These multisolute
4 adsorption results indicated that preferential affinity of metal ion by CScPA followed
5 the order: $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+}$.
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7 *3.9. Desorption study*

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9 The reusability of the activated carbon is one of the most important factors in
10 assessing of its commercial applications for wastewater treatment and economical
11 aspect. The regeneration of CScPA was investigated by performing three times
12 repeated batch adsorption-desorption cycles (C1, C2 and C3) of Pb^{2+} , Cd^{2+} and Ni^{2+} .
13 Fig. 6 presents the effects of HNO_3 on the metal ions desorption from CScPA in each
14 cycle. Based on the results, more than 85 % of the adsorbed Pb^{2+} and Cd^{2+} was
15 desorbed from the metal loaded CScPA during the first cycle. Desorption efficiency
16 of Ni^{2+} is lower compared to the other metals. Decrease of the adsorbent capacity with
17 increase in adsorption-desorption cycle shows that the metal ions adsorption on the
18 CScPA is a partially recoverable process (Petrović et al., 2016).
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28 **Fig. 6.** Adsorption/desorption study of Pb^{2+} , Cd^{2+} and Ni^{2+} per cycle (C1, C2 and C3)
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31 *3.10. Comparison with other activated carbons*

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33 A comparison of the adsorption results obtained in present study with those published
34 in literature for different adsorbents is summarized in Table 5. The value of maximum
35 adsorption capacity of CScPA is significantly higher than data reported for the most
36 other activated carbons. Presented data indicate that the CScPA is an efficient
37 activated carbon for the uptake of lead, cadmium and nickel ions in single, binary and
38 ternary systems.
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42 *3.11. Metal ions adsorption from real sample and cost factor*

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44 The production of alternative separation mediums from waste biological materials is
45 usually justified by two factors: the ability of these precursors for adsorption from real
46 waste systems and the possibility of adsorbent production at an affordable cost.
47 Expenditure on individual activated carbons varies, depending on the processing
48 employed and its local availability. In the present study, the sweet and sour cherry
49 kernels were collected from fruit plantation located in Novi Becej, province of
50 Vojvodina (Serbia), and this biomass (waste byproducts of the fruit industry) in
51 Serbia is available free of cost. Considering the expenses for transport, chemicals and
52 electrical energy, the cost of the final CScPA approximately would be 100 \$/tonne or
53 0.1 \$/kg (Michalak et al., 2013; Nadeem et al., 2016). The cost of commercial
54 activated carbon for separation of Pb^{2+} , Cd^{2+} and Ni^{2+} from aqueous wastes varies
55 from 5 to 6 \$/kg, approximately (Mathialagan et al., 2003).
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Table 5

Comparison of adsorption capacity of metal ions with other adsorbents

In order to assess the efficiency and suitability of CScPA to remove metals ions from a real system, the adsorption study with industrial wastewater samples after the secondary treatment in a batch mode was done. The results showed that about 5.0 g of activated carbon was sufficient to treat a wastewater volume of 10 L containing around 4 mg L⁻¹ metals (Cd²⁺, Pb²⁺ and Ni²⁺). The wastewater was treated till the metal concentrations reached the values established by Serbian legislations of 0.2 mg L⁻¹, 0.1 mg L⁻¹ and 1.0 mg L⁻¹ for lead, cadmium and nickel, respectively („Službeni glasnik RS”, br. 55/05, 71/05). Using CScPA, 1 kg of metal ions can be removed at about 0.1 \$ cost (Nadeem et al., 2016). Therefore, the present study confirmed that CScPA, as cost-effective, eco-friendly and viable activated carbon, could be justifiably used for the treatment of wastewater containing lead, cadmium and nickel.

4. Conclusion

The study presented in this work revealed that the thermochemical conversion of the sweet and sour cherry kernels can yield activated carbon characterized by a high surface area and a very well developed porosity, which can be effectively applied as a low-cost medium for Pb²⁺, Cd²⁺ and Ni²⁺ separation from aqueous solutions. A very important step in the synthesis of alternative adsorption medium was achieved by the synthesis of active coal of high separation performance in the complete absence of inert atmosphere (with the yield of 73%). The produced activated carbon has high carbon content (about 61%) and contained predominantly aliphatic compounds.

Isotherm batch experiments showed that performed adsorption is greatly dependent on the contact time, pH value, and initial adsorbate and activated carbon concentrations. The optimum adsorption capacity of CScPA for the removal of all metal ions were obtained within 30 minutes at pH 6, with activated carbon concentrations of 2 g L⁻¹. Metal removal efficacy decreases rapidly with the increase in the initial adsorbate concentration above 100 mg L⁻¹.

The Langmuir model provides a better fit of the equilibrium adsorption data than the Freundlich and Temkin one for the Cd²⁺ in the studied parameters range. Freundlich model provides a best fit for the Pb²⁺ and Ni²⁺ equilibrium adsorption data. The maximum adsorption capacities calculated from the Langmuir model are found to be 180.26 mg g⁻¹, 198.740 mg g⁻¹ and 77.71 mg g⁻¹ for the Pb²⁺, Cd²⁺ and Ni²⁺, respectively. The kinetic study of metal ions adsorption shows that the pseudo-second order model provides better correlation of the sorption data than the pseudo-first-order model. This suggests that the rate-limiting step might be chemisorption rather than diffusion, which is consisted by the best agreement with the Langmuir and Freundlich isotherm model.

The biomass employed in this work is widely locally available and represents a significant element of municipal waste. Thus, the obtained results are highly

beneficial for the development of alternative wastewater management technologies, as well as for modern organic waste disposal solution. The study resulted in an eco-friendly and economical alternative activated carbon that, due to its high separation capacity, can effectively be applied in so-called green wastewater processing technologies and thereby position itself as a serious competitor to the conventional approaches based on activated carbon.

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Supplementary materials

Evaluation of the adsorption potential of eco-friendly activated carbon prepared from cherry kernels for the removal of Pb^{2+} , Cd^{2+} and Ni^{2+} from aqueous wastes

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Fig. S1. Lignocellulosic raw material (left) and activated carbon CScPA (right)

Fig. S2. SEM micrographs (a) before (b) after adsorption and (c) EDX microanalysis of CScPA

Fig S3. FTIR spectra of CScPA

Fig S4. Pseudo-first order kinetics plot of Pb^{2+} , Cd^{2+} and Ni^{2+} onto CScPA

Fig S5. Pseudo-second order kinetics plot of Pb^{2+} , Cd^{2+} and Ni^{2+} onto CScPA

Fig S6. Intraparticle diffusion plot of Pb^{2+} , Cd^{2+} and Ni^{2+} onto CScPA

Fig S7. The linearized Langmuir isotherm of Pb^{2+} , Ni^{2+} and Cd^{2+} onto CScPA

Fig S8. The linearized Freundlich isotherm of Pb^{2+} , Cd^{2+} and Ni^{2+} onto CScPA

Fig S9. The linearized Temkin isotherm of Pb^{2+} , Cd^{2+} and Ni^{2+} onto CScPA

Table S1

Yield of activated carbons obtained at various activation temperatures and with different chemical agents

Table S2

Textural properties of the synthesized activated carbon

Fig 1

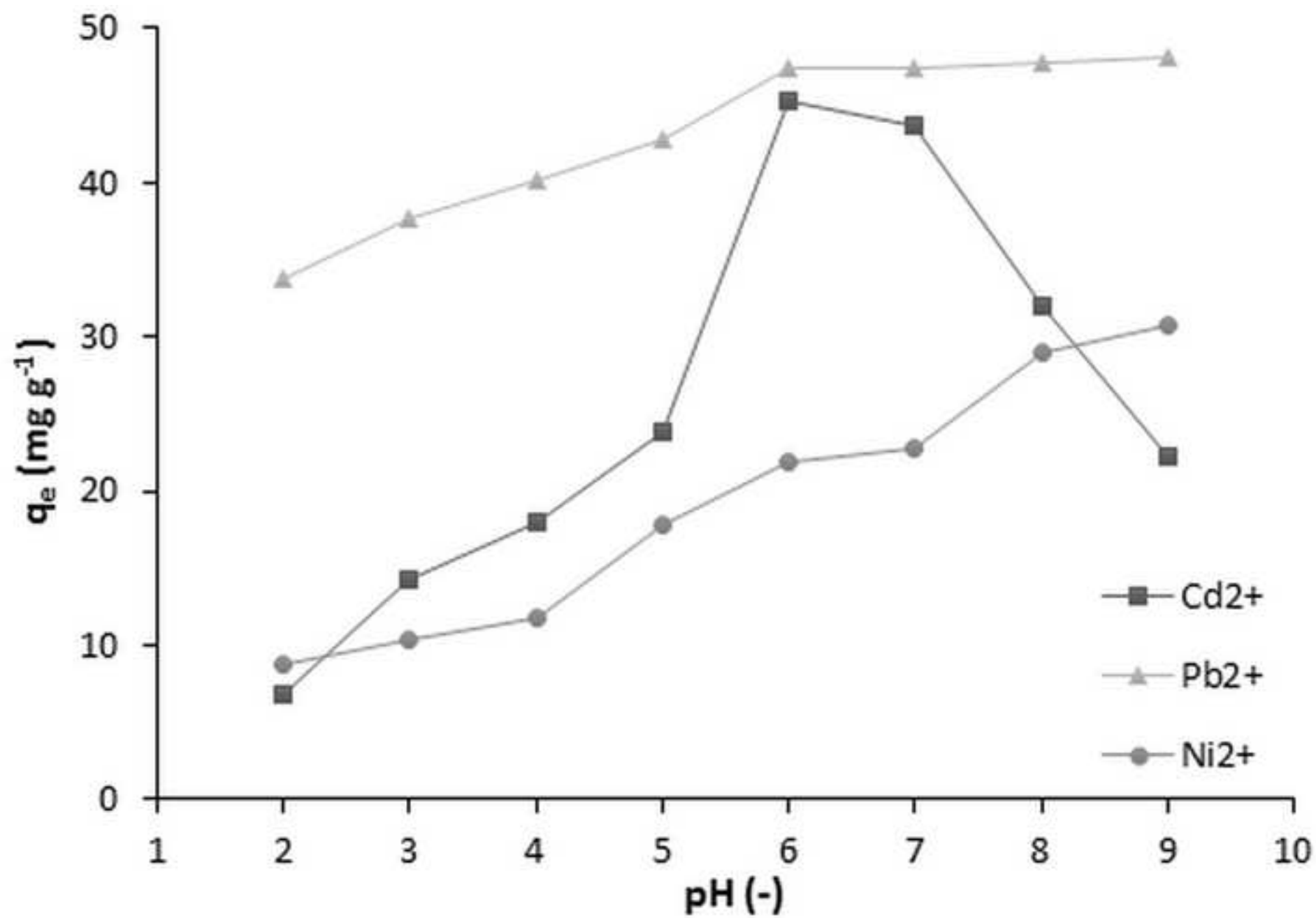
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Fig 2

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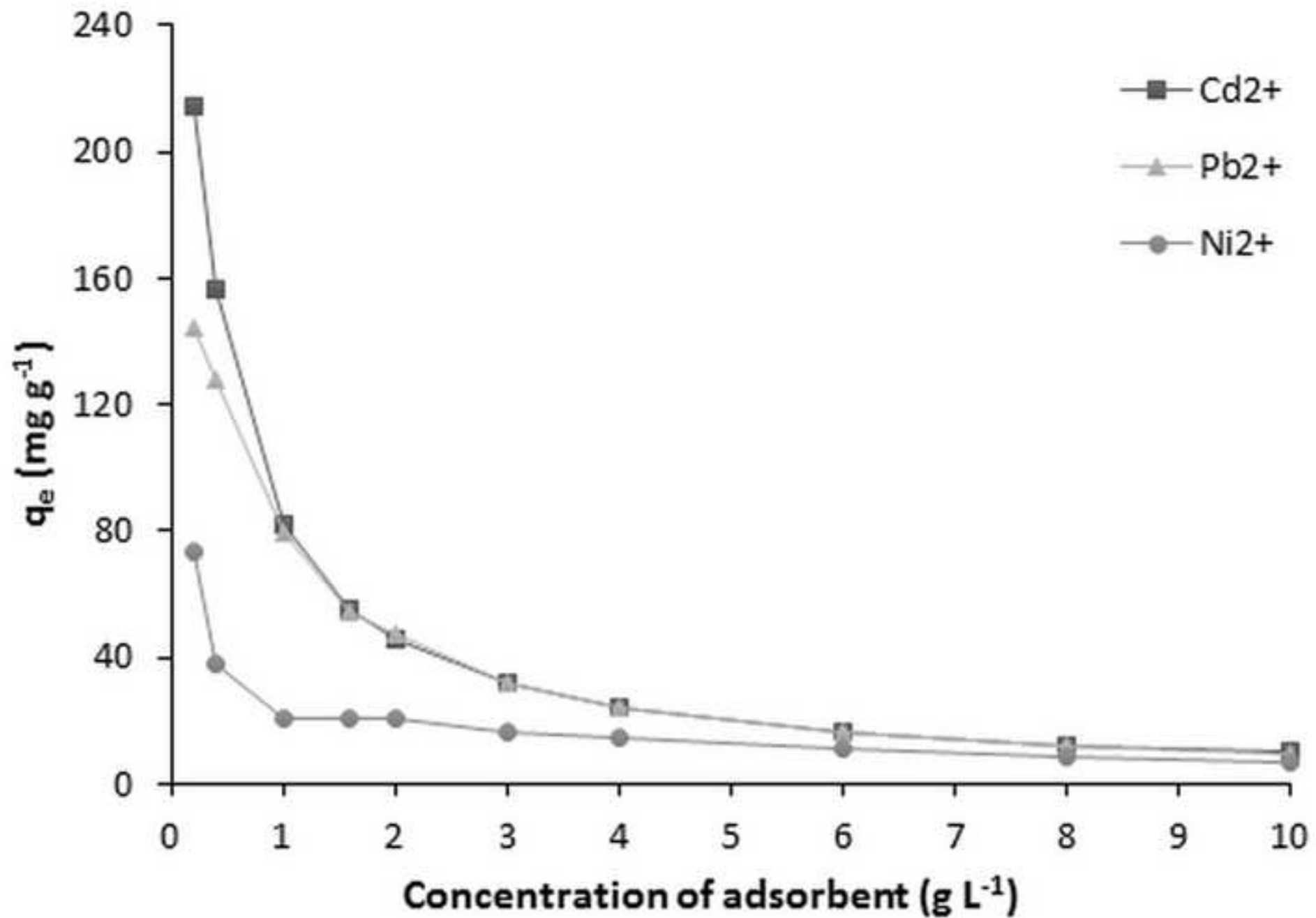


Fig 3

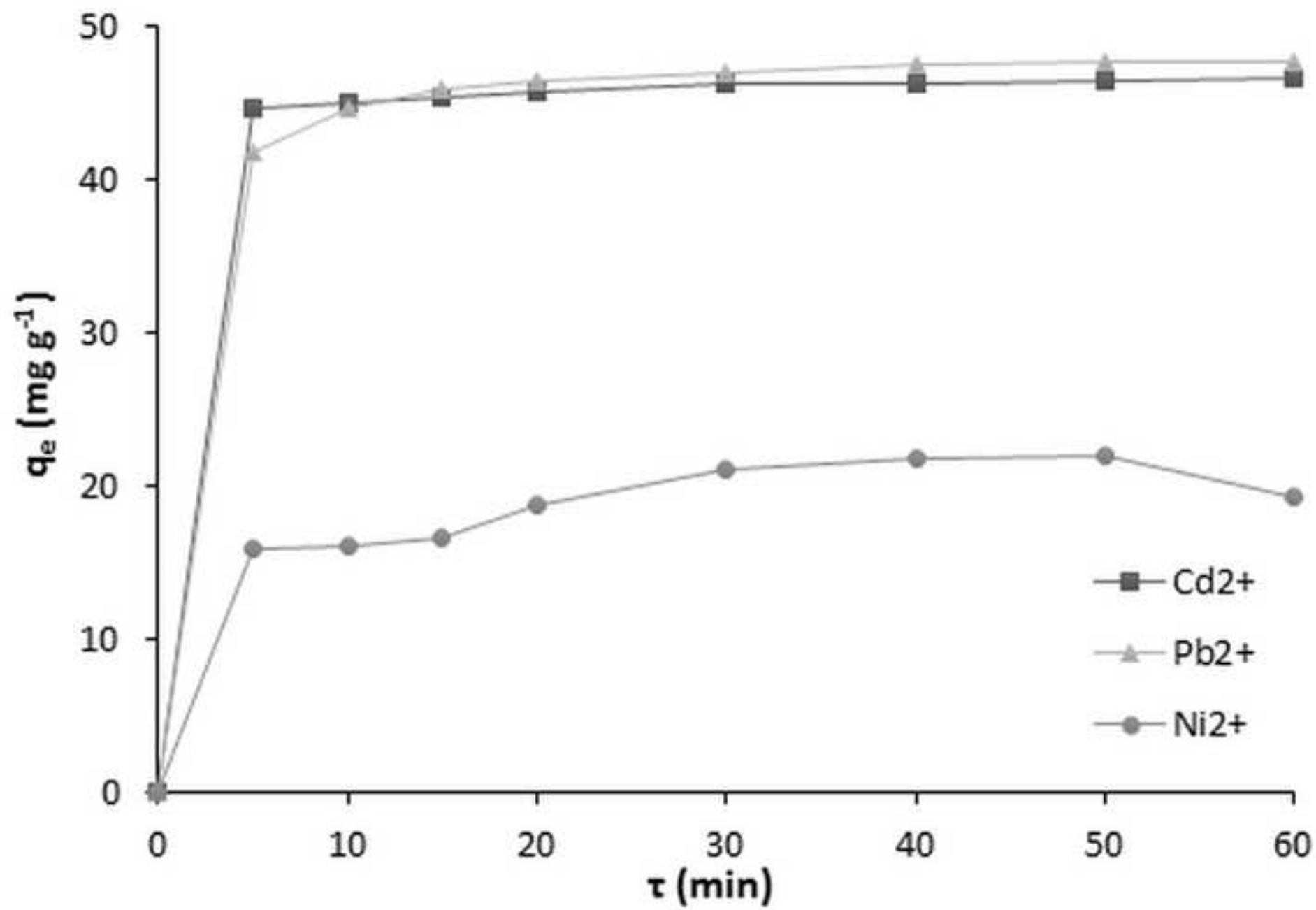
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Fig 4

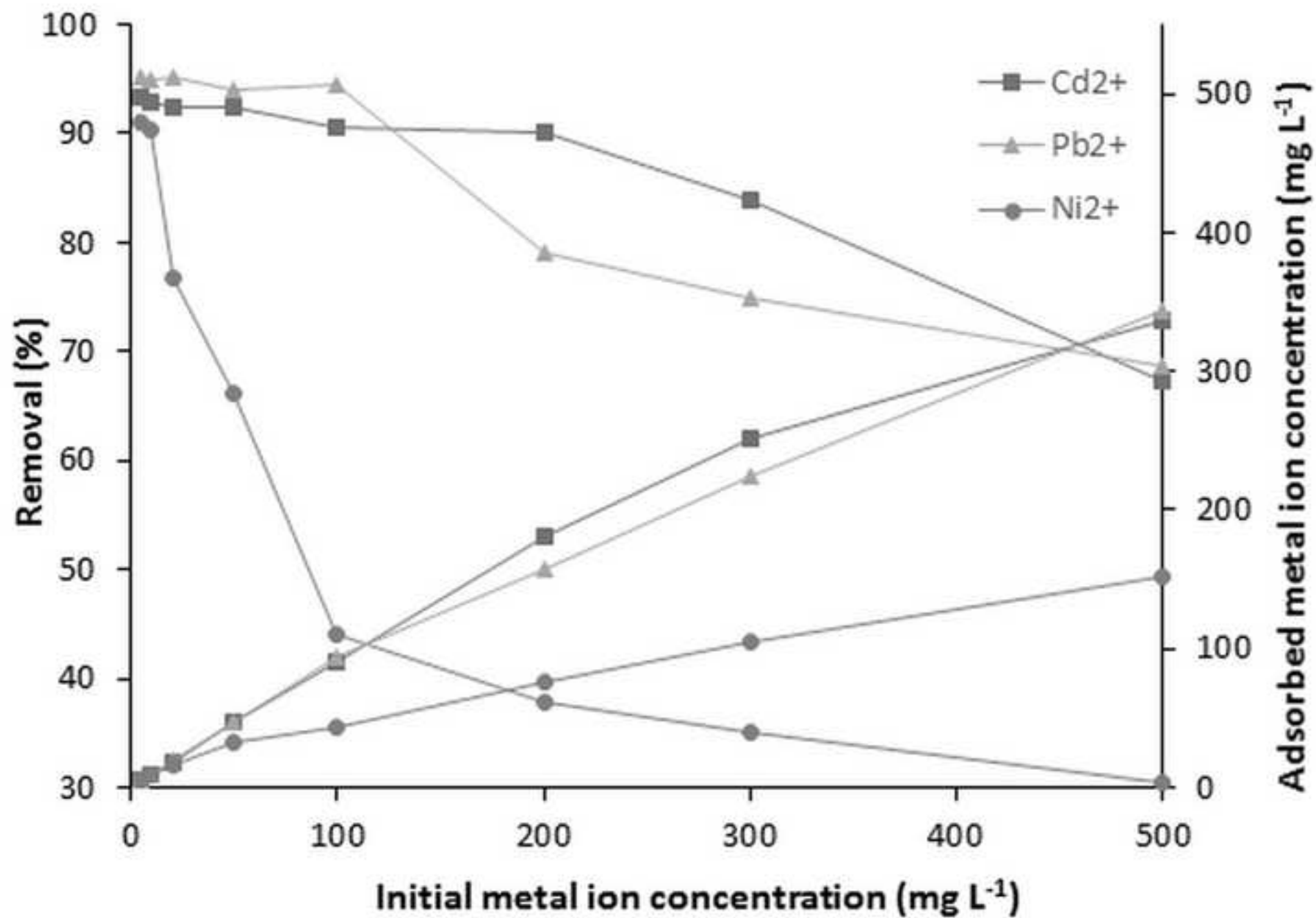
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Fig 5

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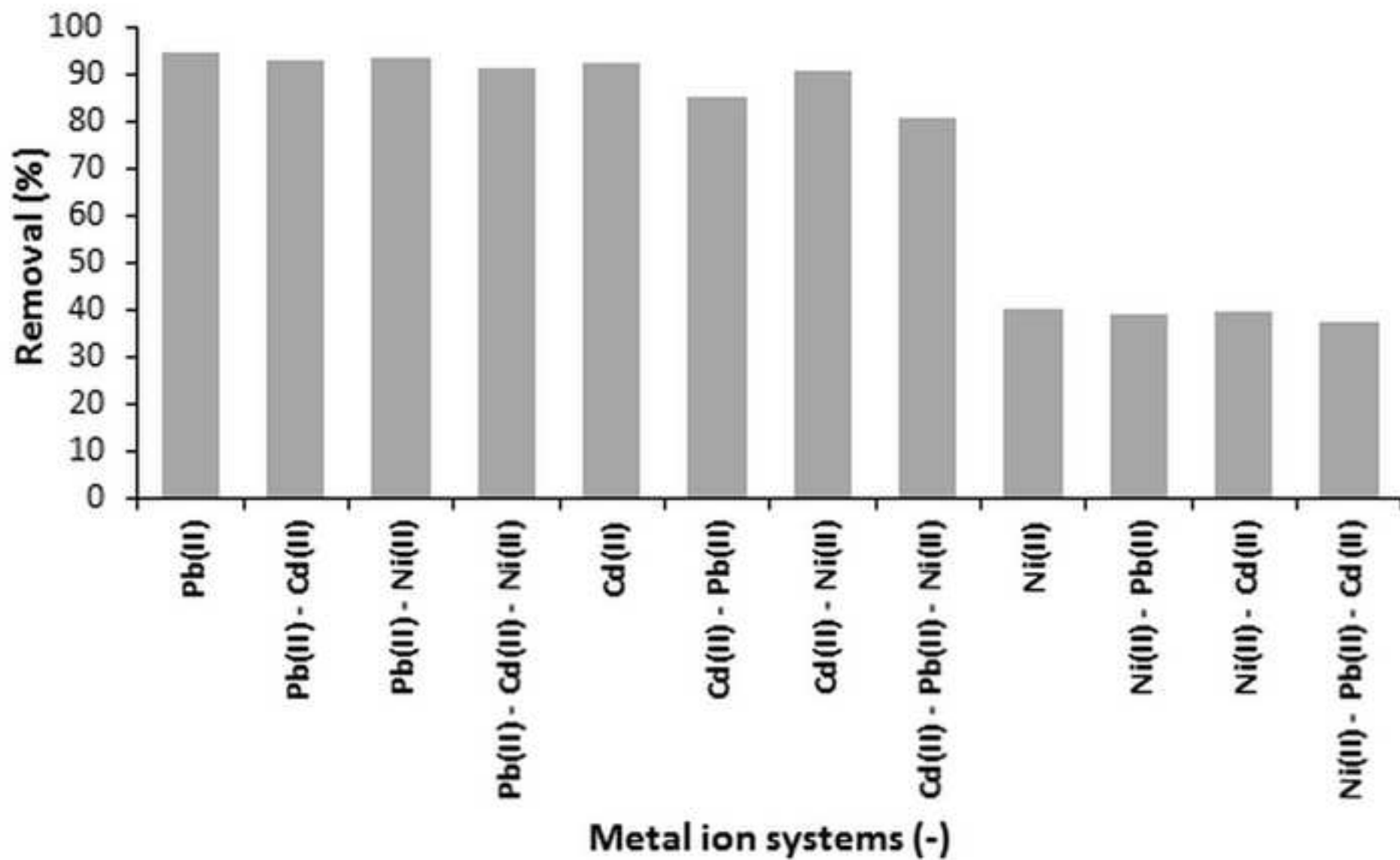


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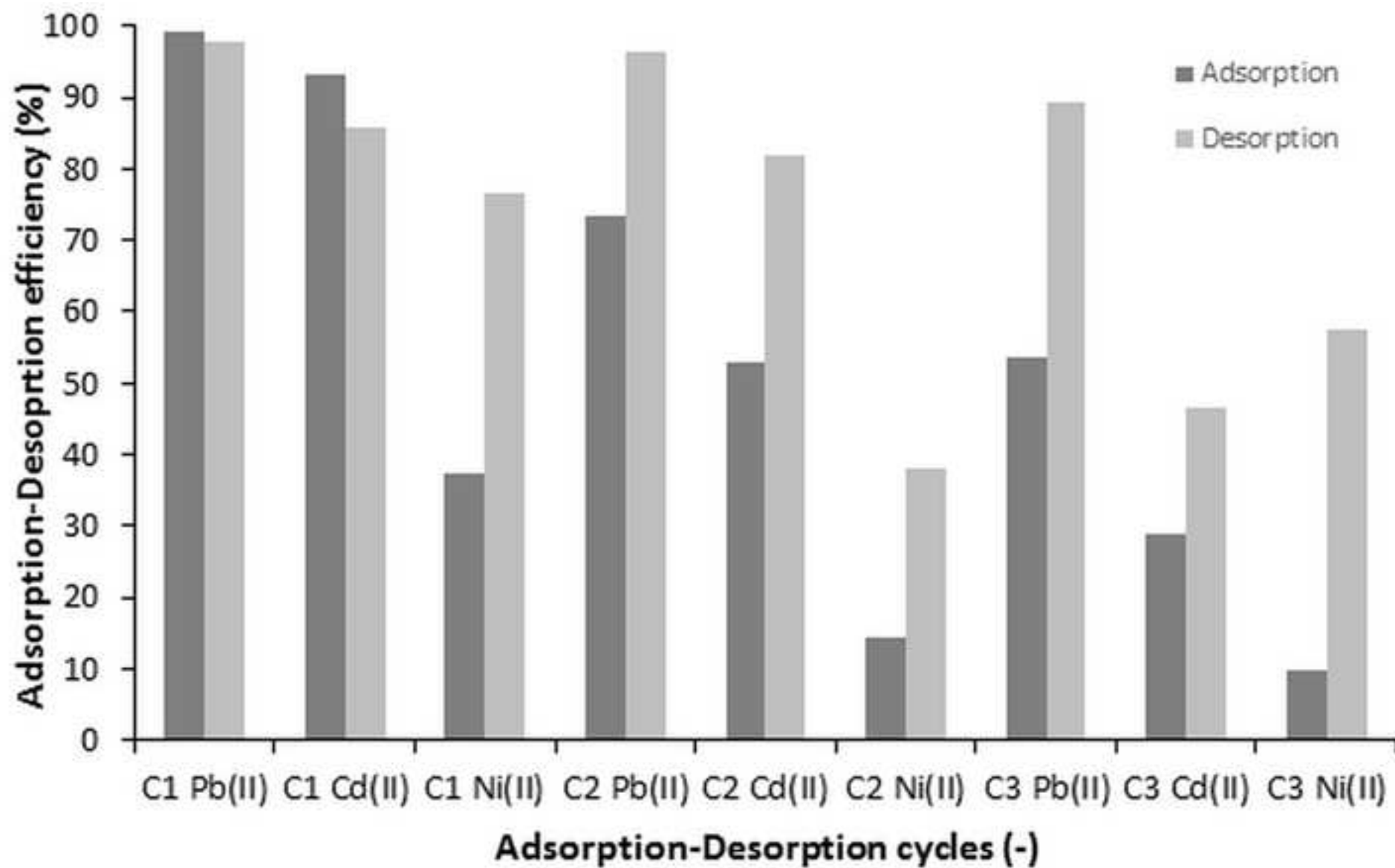
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Fig S1

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Fig S2

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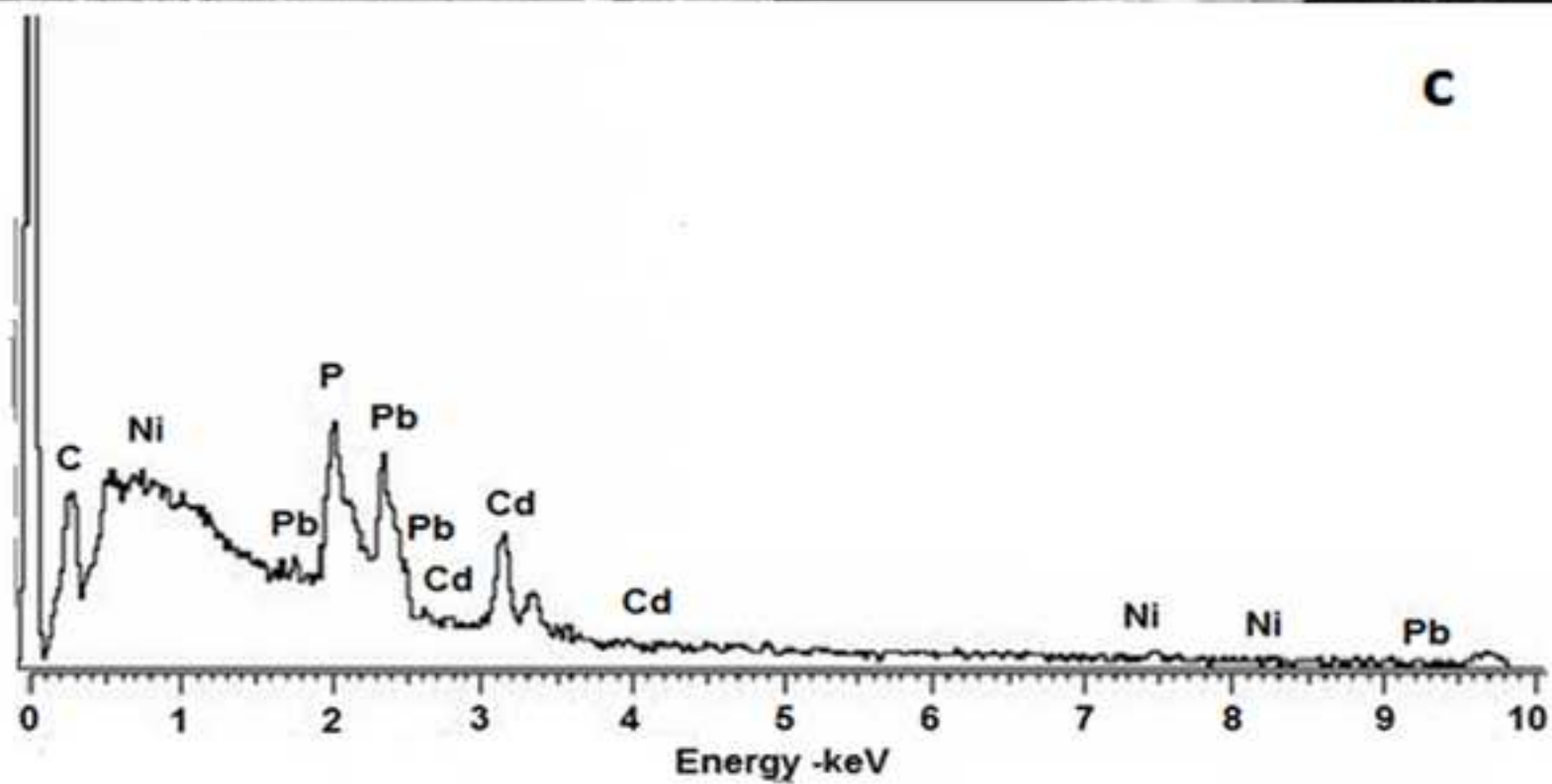
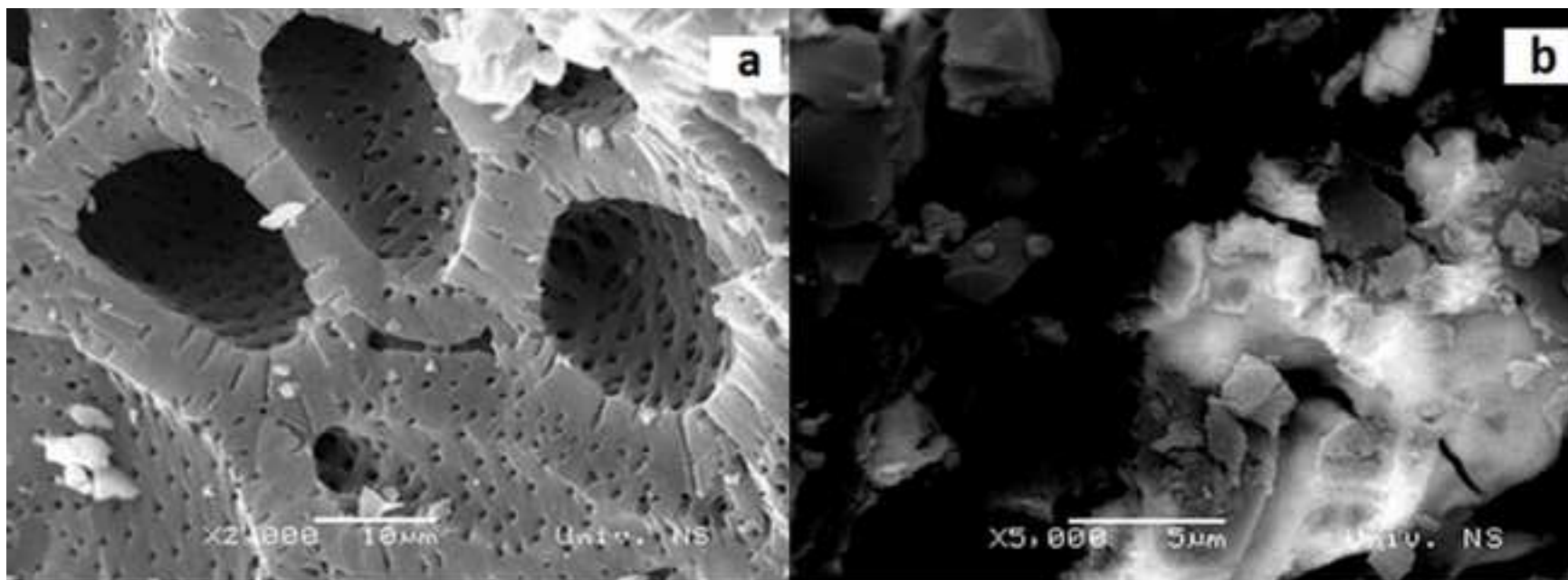


Fig S3

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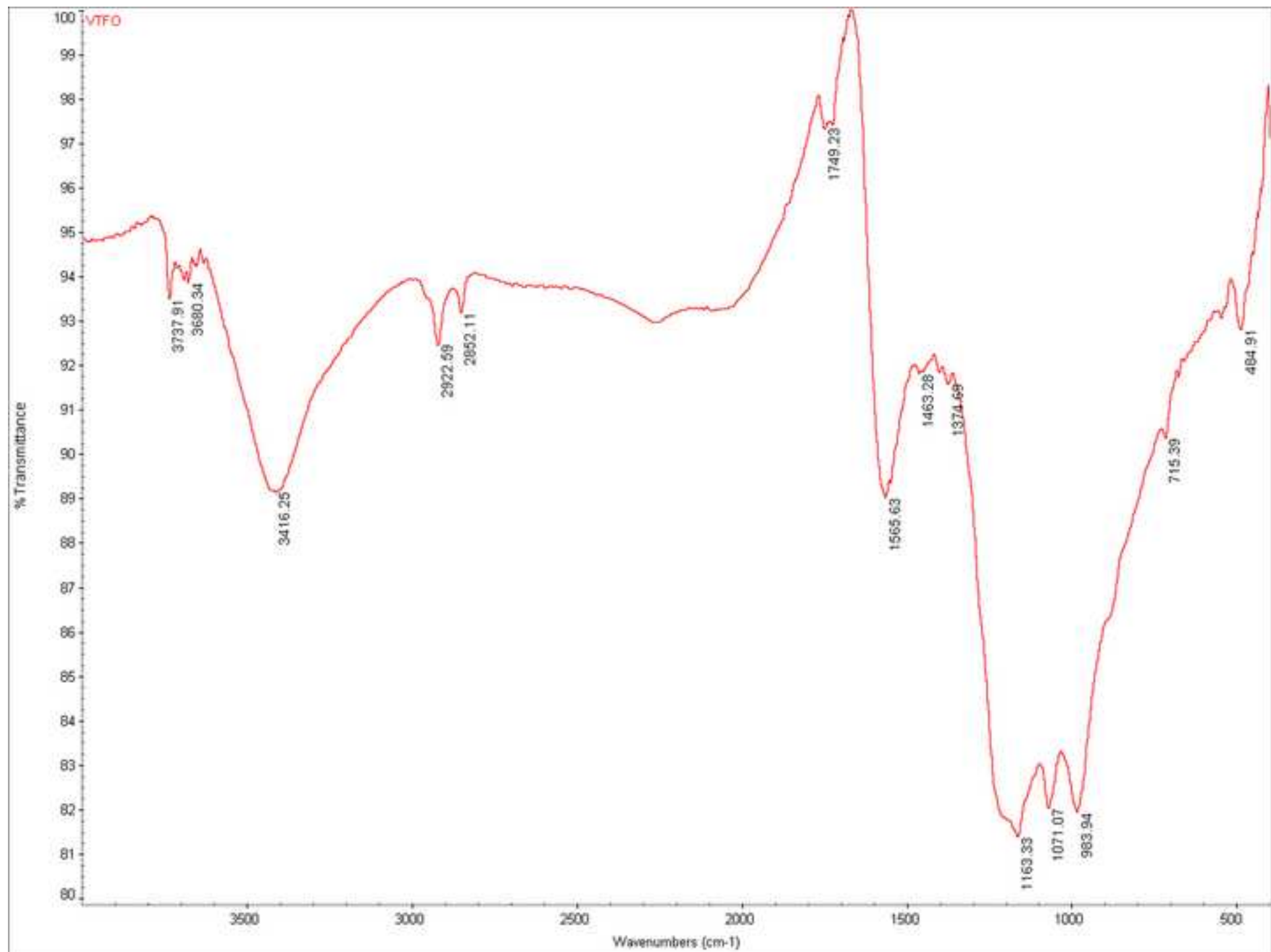


Fig S4

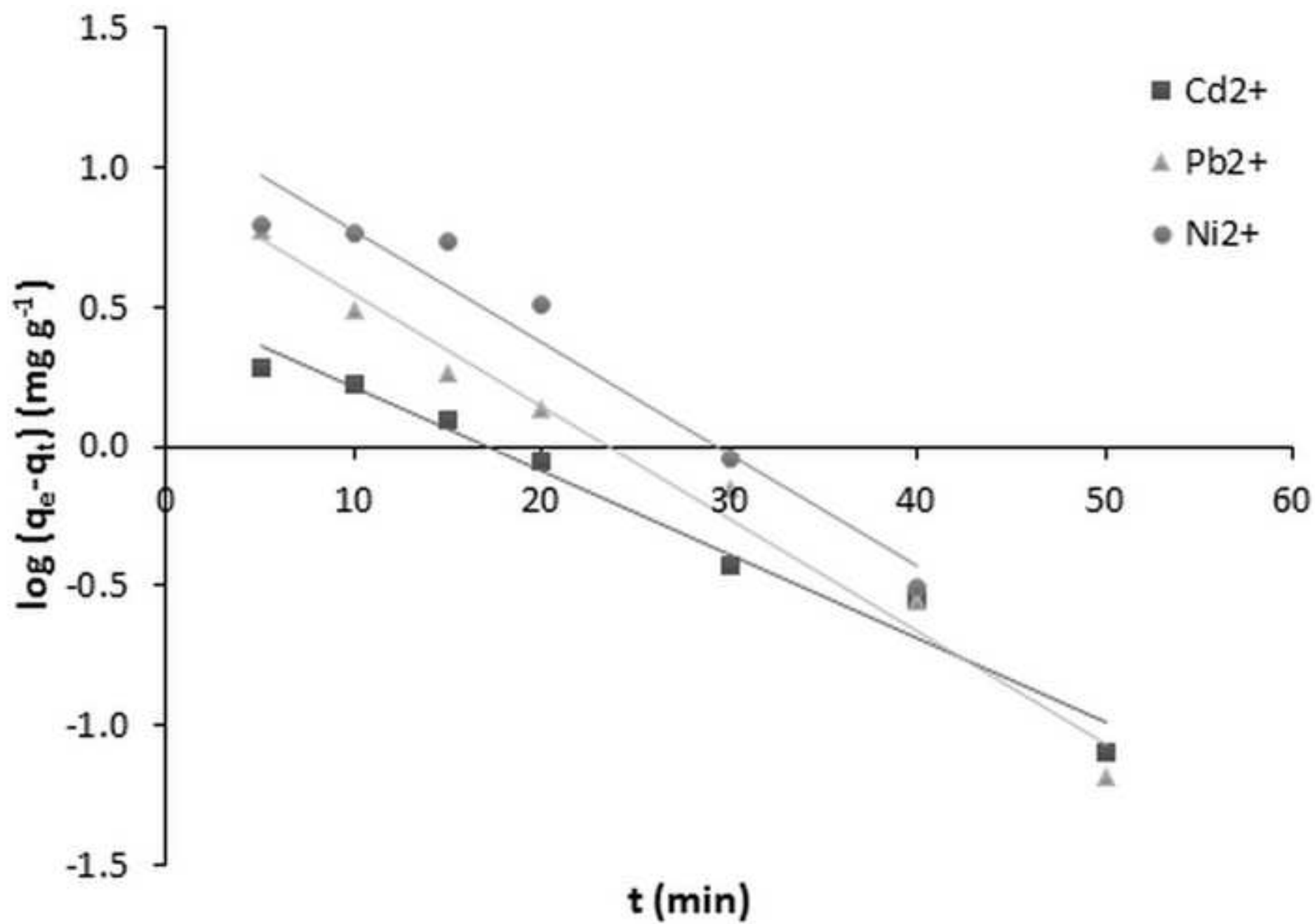
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Fig S5

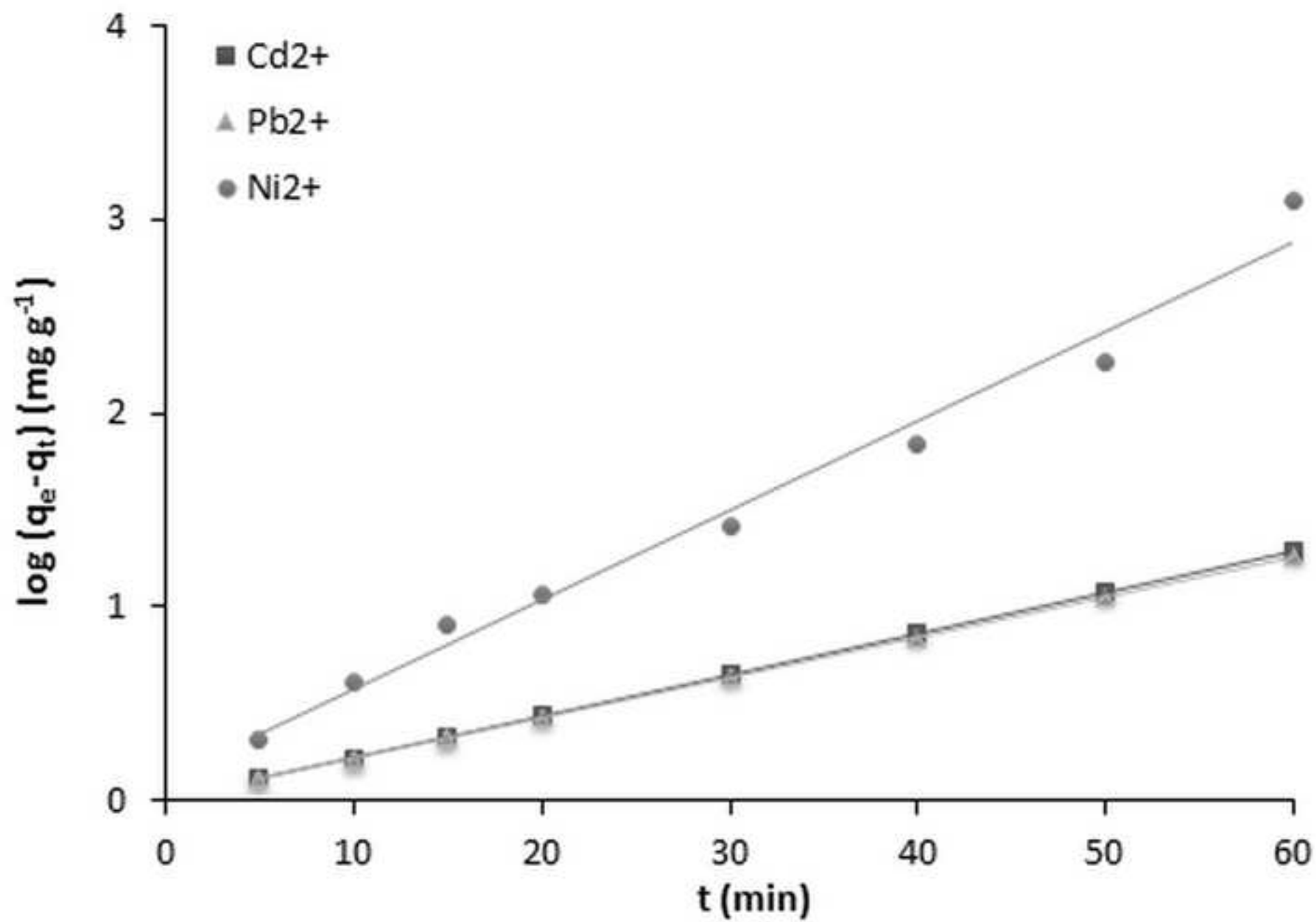
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Fig S6

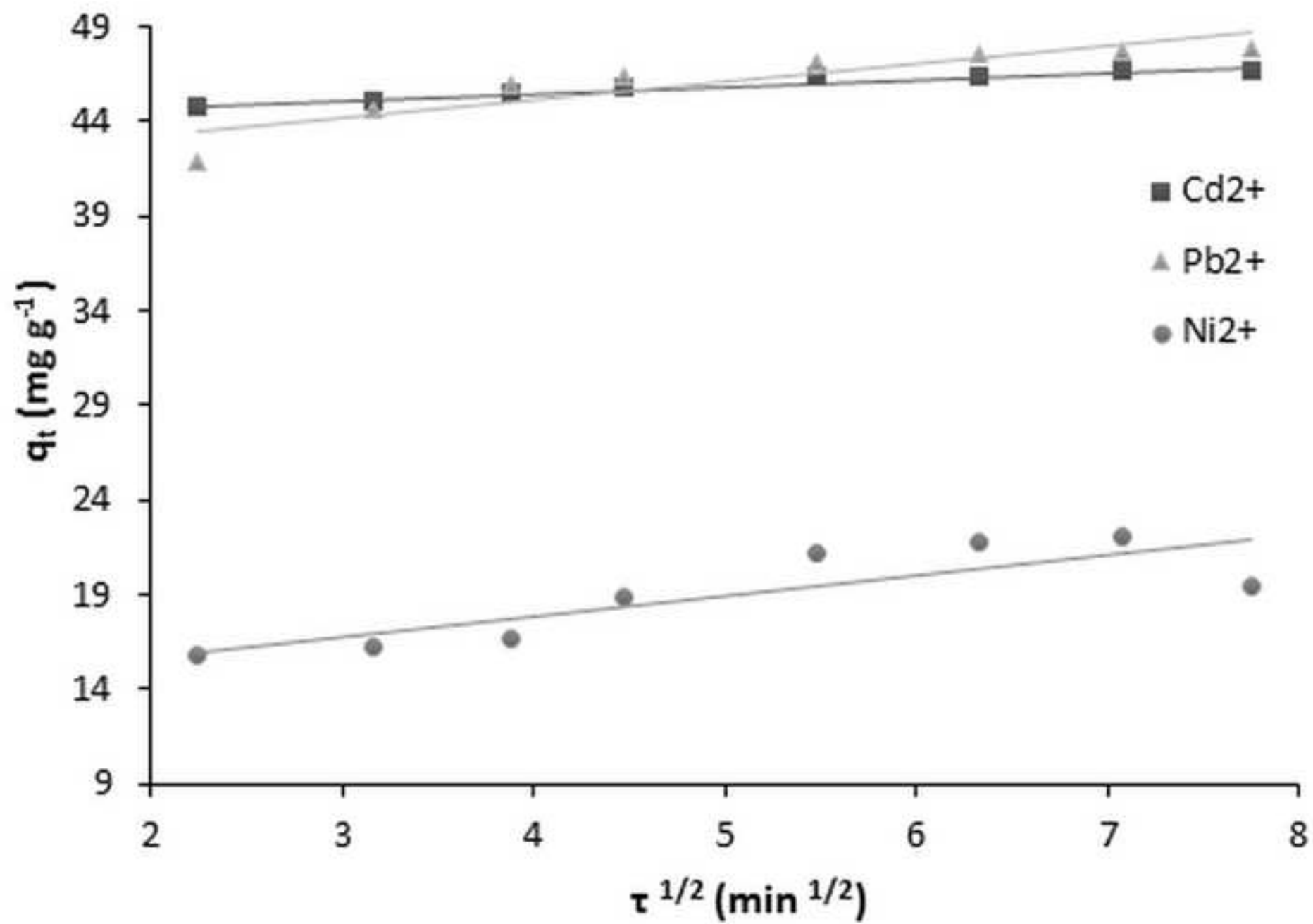
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Fig S7

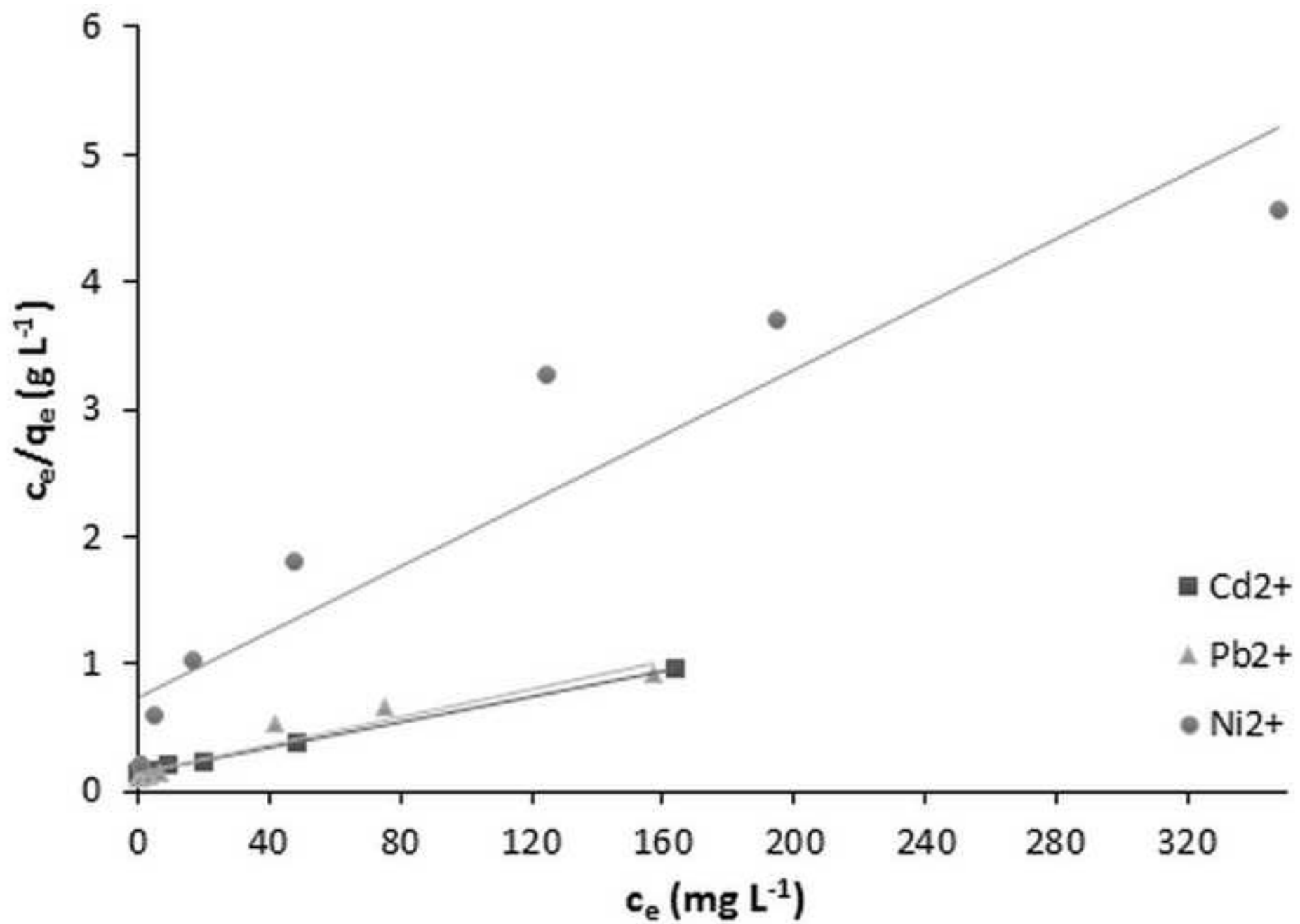
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Fig S8

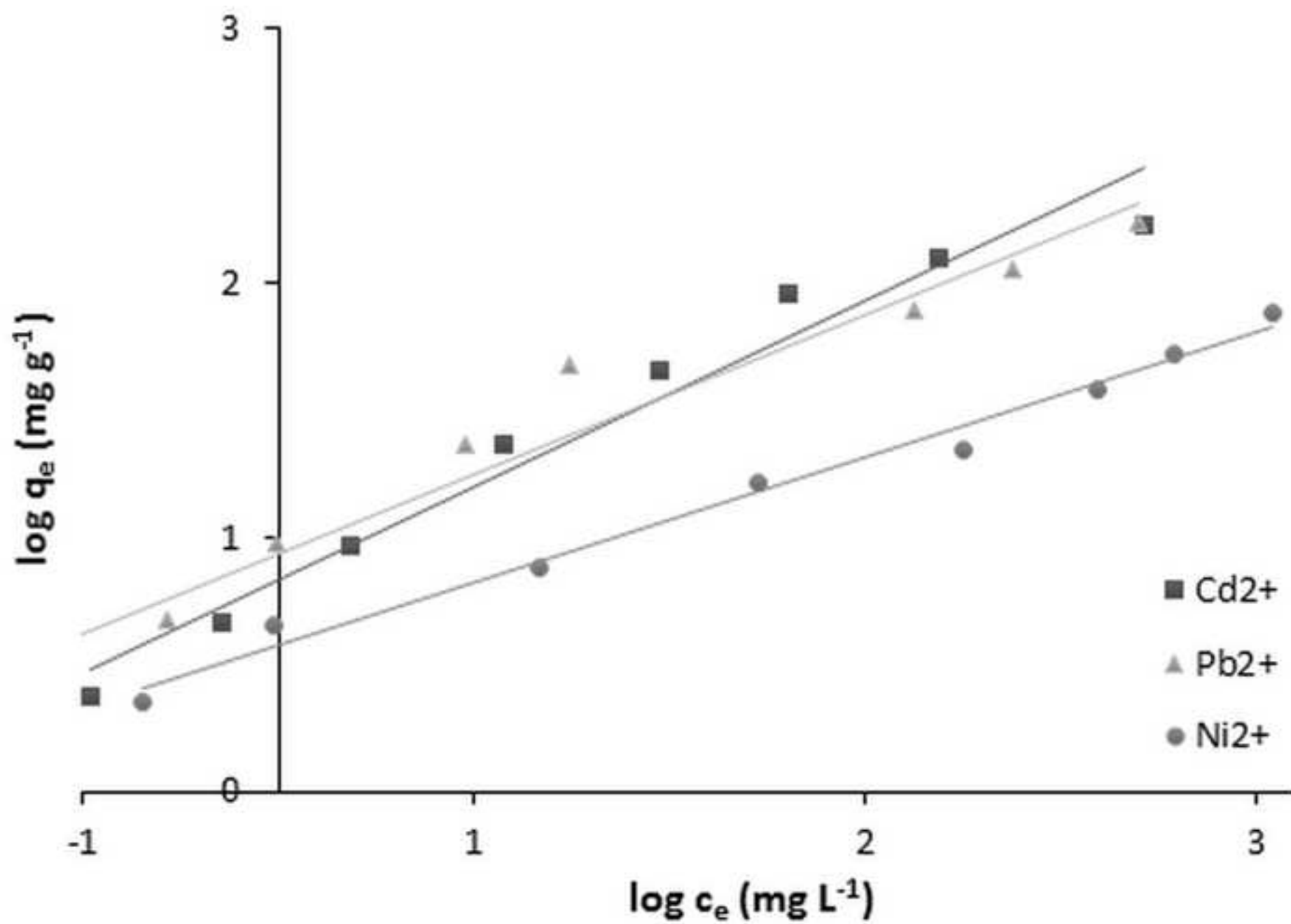
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Fig S9

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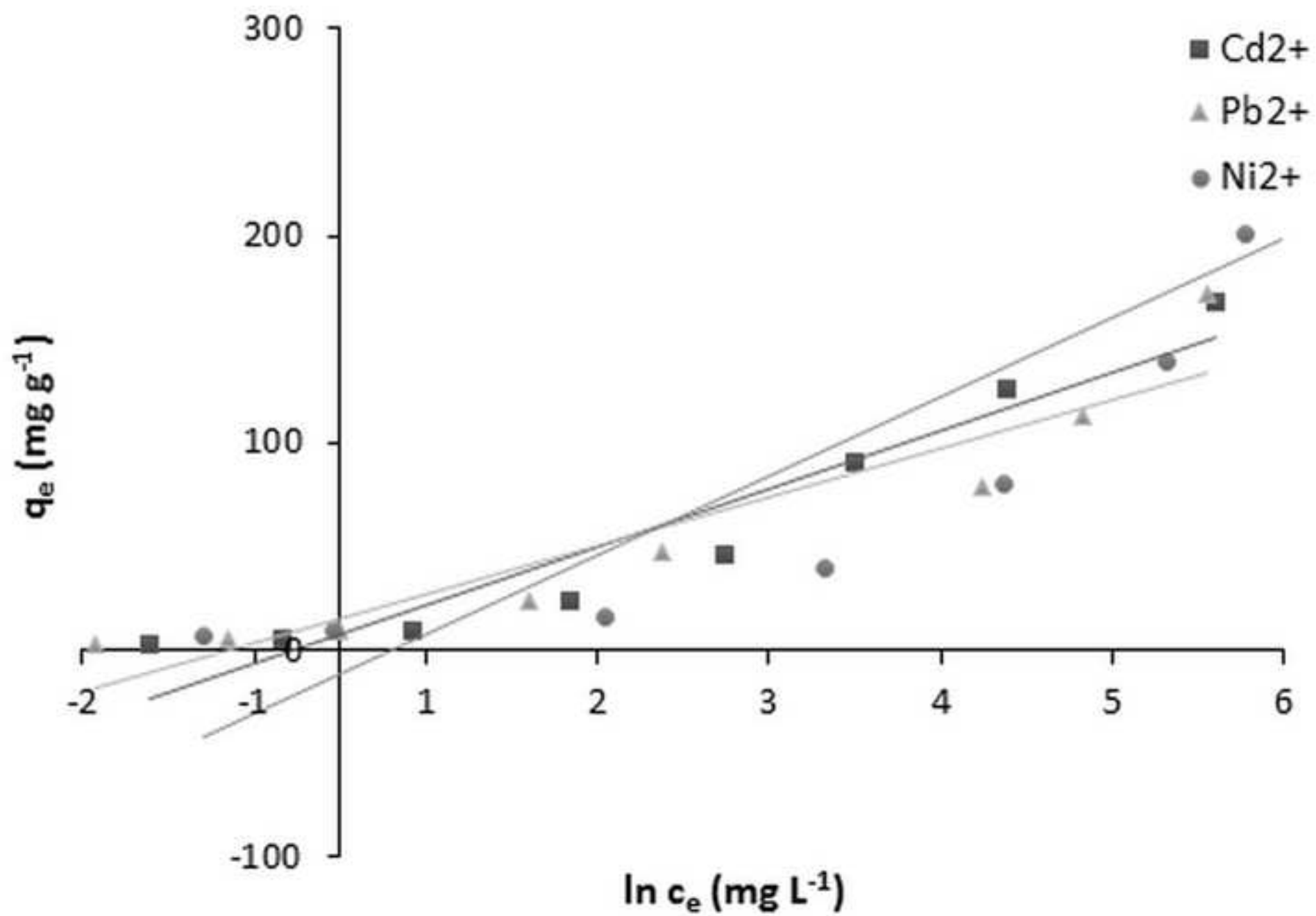


Table 1[Click here to download Table: Table 1.docx](#)**Table 1**

Chemical and physical characteristics of the CScPA and raw material

Material	Elemental analysis (%)					pH _{sus}	pH _{pzc}	Density (kg m ⁻³)	Moisture content (%)	Ash content (%)
Raw material	C	O ^a	S	N	H	-	-	-	-	-
	49.3	41.7	n.d. ^b	1.5	7.4					
CScPA	C	O ^a	S	N	H	2.17	3.14	583	3.39	4.26
	60.4	36.4	n.d. ^b	1.1	2.1					

^a By difference^b Not detected

Table 2[Click here to download Table: Table 2.docx](#)**Table 2**Kinetic parameters for the adsorption Pb^{2+} , Cd^{2+} and Ni^{2+} onto CScPA

Metal ion	$q_{e, \text{exp}}$ (mg g^{-1})	Pseudo-first order			Pseudo-second order			Intraparticle diffusion		
		$q_{e, \text{cal}}$ (mg g^{-1})	K_1 (1 min^{-1})	R^2	$q_{e, \text{cal}}$ (mg g^{-1})	K_2 ($\text{g mg}^{-1} \text{ min}^{-1}$)	R^2	K_i ($\text{mg g}^{-1} \text{ min}^{-1/2}$)	C (mg g^{-1})	R^2
Pb^{2+}	47.805	8.794	-0.093	0.982	48.892	0.025	0.999	0.940	41.395	0.806
Cd^{2+}	46.670	3.221	-0.069	0.971	46.947	0.051	0.999	0.371	43.995	0.958
Ni^{2+}	22.040	14.867	-0.092	0.943	21.596	0.020	0.983	1.088	13.473	0.690

Table 3[Click here to download Table: Table 3.docx](#)**Table 3**Langmuir, Freundlich and Temkin isotherm constants for Pb^{2+} , Cd^{2+} and Ni^{2+}

Metal ion	$q_{\text{max,exp}}$ (mg g^{-1})	Langmuir			Freundlich			Temkin		
		q_{max} (mg g^{-1})	b (L mg^{-1})	R^2	K_f (mg g^{-1})	$1/n$	R^2	A_T (L g^{-1})	B (J mol^{-1})	R^2
Pb^{2+}	171.400	180.260	0.040	0.926	8.455	1.585	0.963	14.802	23.647	0.886
Cd^{2+}	168.250	198.740	0.035	0.998	6.854	0.731	0.964	7.584	28.065	0.915
Ni^{2+}	76.270	77.707	0.018	0.884	3.826	0.499	0.993	0.191	9.535	0.817

Table 4[Click here to download Table: Table 4.docx](#)**Table 4**The R_L values for CScPA

Co (mg L ⁻¹)	Pb ²⁺	R_L Cd ²⁺	Ni ²⁺
5	0.8343	0.8529	0.9197
10	0.7157	0.7435	0.8514
20	0.5572	0.5917	0.7413
50	0.3348	0.3670	0.5340
100	0.2011	0.2247	0.3643
200	0.1118	0.1266	0.2227
300	0.0774	0.0881	0.1604
500	0.0479	0.0548	0.1028

Table 5[Click here to download Table: Table 5.docx](#)**Table 5**

Comparison of adsorption capacity of metal ions with other adsorbents

Pb ²⁺			Cd ²⁺			Ni ²⁺		
Activated carbon	q _{max} (mg g ⁻¹)	Ref.	Activated carbon	q _{max} (mg g ⁻¹)	Ref.	Activated carbon	q _{max} (mg g ⁻¹)	Ref.
Raw cherry kernels	10.84	Present study	Raw cherry kernels	11.23	Present study	Raw cherry kernels	6.79	Present study
Chemical treated cherry kernels	17.86	Present study	Chemical treated cherry kernels	19.67	Present study	Chemical treated cherry kernels	12.33	Present study
Apricot stone	21.38	Mouni et al., 2011	Papaya wood	17.22	Asma et al., 2005	Tea factory waste	15.26	Malkoc and Nuhoglu, 2005
Sago waste	46.64	Quek et al., 1998	Pomelo peel	21.83	Saikaew and Kaewsarn, 2009	<i>Padina australis</i>	27.03	Pahlavanzadeh et al., 2010
Tea waste	65.00	Amarasinghe and Williams, 2007	Grapefruit peel	42.09	Torab-Mostaedi et al., 2013	Grapefruit peel	46.13	Torab-Mostaedi et al., 2013
Red mud	88.20	Gupta et al., 2001	<i>S. platensis</i>	73.64	Celekli and Bozkurt, 2010	Cassava peel	57.07	Kurniawan et al., 2011
Green algae	140.00	Gupta and Rastogi, 2008	Red mud	106.04	Apak et al., 1998	<i>S. platensis</i>	69.04	Celekli and Bozkurt, 2010
CScPA	180.26	Present study	Fungus (<i>T. versicolor</i>) biomass	166.60	Subbaiah et al., 2011	CScPA	77.71	Present study
Neem leaf powder	300.00	Bhattacharyya and Sharma, 2004	CScPA	198.74	Present study	Marine macro algae	181.00	Kalyani et al., 2004

Table S1

Yield of activated carbons obtained at various activation temperatures and with different chemical agents

Activated carbon type	Yield on 400 °C (%)	Yield on 500 °C (%)
CScPA	84.0	72.8
CScSA	37.4	34.4

Table S2

Textural properties of the synthesized activated carbon

Activated carbon	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Micropore volume ($\text{cm}^3 \text{g}^{-1}$)	Mesopore volume ($\text{cm}^3 \text{g}^{-1}$)	Mesopore surface ($\text{m}^2 \text{g}^{-1}$)	Max. mesopore diameter (nm)
CScPA	657.1	0.196	0.051	46.739	32.50