

## EQUILIBRIUM, KINETIC AND THERMODYNAMIC STUDIES ON REMOVAL OF Cd(II), Pb(II) AND As(V) FROM WASTEWATER USING CARP (CYPRINUS CARPIO) SCALES

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Unmodified farming carp (*cyprinus carpio*) scales were used as a biosorbent for the removal of Cd(II), Pb(II) and As(V) ions from aqueous solutions. The adsorption studies were conducted as a function of pH, contact time and temperature. The best sorption of cadmium, lead and arsenate ions was achieved for pH between 6.0 and 8.0. The adsorption data for cadmium, lead and arsenate at 20, 30 and 40 °C are fitted to Langmuir, Freundlich, Sips, Dubinin-Radushkevich (D-R), Jovanovic, Jovanovic-Freundlich (J-F), Temkin, Toth and Koble-Corrigan (K-C) isotherm models. Experimental data were used to model adsorption kinetics using pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion kinetic models. The results showed that the adsorption of Cd(II), Pb(II) and As(V) ions onto carp scale followed the pseudo-second-order kinetic model. Thermodynamic parameters, including the Gibbs free energy ( $\Delta G^0$ ), enthalpy ( $\Delta H^0$ ), and entropy ( $\Delta S^0$ ) changes, indicated that the present adsorption process was feasible, spontaneous and endothermic in the temperature range of 20-40 °C.

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### 1. Introduction

Cadmium, lead and arsenic are classified as prevalent toxic elements and major environmental health problems [1-4]. They can act in a harmful manner causing severe health problems after they enter the food chain through drinking water and crop irrigation by blocking essential functional groups, displacing other metal ions or modifying the active conformation of biological molecules [5]. Due to their immutable nature, metals and metalloids presents pollutants of much concern. According to US Environmental Protection Agency, the maximum contaminant level for cadmium, lead and arsenic is 0.005 mg dm<sup>-3</sup>, 0.015 mg dm<sup>-3</sup> and 0.010 mg dm<sup>-3</sup> respectively [6].

Using fish scale as adsorbent for heavy metals and metalloids is relatively new idea [7-11]. Generally, scales, along with gills and mucous tissues, are most susceptible to heavy metal and metalloid pollution in water which is directly associated with the osmoregulatory alterations [12] thus showing that scales reacts with ionic metal species. Due to the presence of a significant amount of foreign ions and non-stoichiometric formula, the biological apatites of fish scales have a small degree of crystallinity and high surface area, which contributes to their high reactivity. Consequently, they are more prone to display a variety of chemical substitutions [13].

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Scales of bony fish have consisted of two principal parts. A thin, hard, external, well mineralized layer which is composed mainly of calcium-deficient dahllite-type hydroxylapatite containing small amounts of sodium and magnesium, as well as carbonate anions in the phosphate sites of the apatite structure, which overlays a thick poorly mineralized layer composed largely of collagen known as the basal or fibrillar plate [14]. Collagen presents heterotrimeric, long, fibrous structural protein responsible for scale strength and elasticity. Tough bundles of collagen called collagen fibres are a major component of the extracellular matrix that supports tissue and gives cells structure from the outside [15].

The main goal of this research is to describe the effectiveness of carp scales of the species *Cyprinus carpio* to bind with cadmium, lead and arsenate ions. Fish scales are a suitable adsorbent due to its developed structure and number of different functional groups present at the surface. Because of the availability of the material in large quantity, the scales are at the moment considered only as a bio waste [16], and the development of the technology for the hazardous material removal from water provide multiple contribution to environmental protection.

## **2. Experimental approach**

### **2.1. Materials**

The fish scales were collected from farmed carp (*Cyprinus carpio*), grown in Ečka fish farm, Serbia. Scales were sonicated in a 5% solution of hydrogen peroxide and triple rinsed in with deionized (DI) water and dried. Pure dried carp scales were grinded and sieved to obtain material with narrower distribution of  $100 \pm 50 \mu\text{m}$  grain. Standard solutions were prepared from analytical-grade cadmium nitrate (Baker), lead nitrate (Baker) and  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  (Sigma-Aldrich). Stock solutions containing  $1000 \text{ mg dm}^{-3}$  were prepared, and additionally diluted with DI water to the required concentrations for the adsorption experiments.

### **2.2. Adsorption experiments**

Cd(II), Pb(II) and As(V) adsorption capacities of carp scale were determined in a batch reactors. Batch sorption experiments were performed using  $100 \text{ cm}^3$  vial with addition of 0.5 mg of grinded carp scale and  $5 \text{ cm}^3$  ( $m/V=100 \text{ mg dm}^{-3}$ ) of Cd(II), Pb(II), As(V) solution of initial concentrations ( $C_0$ ) 0.1, 0.5, 1, 2, 5 and  $10 \text{ mg dm}^{-3}$ . The bottles were placed in an ultrasonic bath. In order to evaluate the effect of pH on adsorption, the initial pH values of the solutions were set at 3.0, 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0 by adjustment with 0.01 and 0.1  $\text{mol dm}^{-3}$  NaOH, and 0.01 and 0.1  $\text{mol dm}^{-3}$   $\text{HNO}_3$ , at 25 °C. The optimal pH was found to be 6 for Cd(II), 8 for Pb(II), and 4 for As(V), and these pH was used throughout all the adsorption and kinetic experiments. Time-dependent sorbate concentration changes were examined in the range 1–240 minutes, and it was found that the optimal time (45 min) was sufficient to achieve equilibration of the system. The mixtures of carp scale and ionic solutions, after sonication was filtered through a  $0.2 \mu\text{m}$  PTFE membrane filter, acidified and analysed.

### **2.3. Adsorbent characterization**

Fourier-transform infrared (FTIR) spectra were recorded in transmission mode using a BOMEM (Hartmann & Braun) spectrometer. FTIR spectra were recorded before and after adsorption at initial sorbate concentrations of  $10 \text{ mg dm}^{-3}$ . Samples for FTIR determination were ground with spectral grade KBr in an agate mortar. All FTIR measurements were carried out at room temperature. Elemental analysis was performed by using Elemental Vario EL III microanalyzer for determination of C and N, and phosphorus was determined according to ISO 14869-1.

Nitrogen adsorption/desorption isotherms were obtained by using ASAP 2020 instrument (Micromeritics, USA) at a temperature of liquid nitrogen. The textural parameters of the carp scale were examined using the BET method for the determination of the specific surface area and the BJH method for the determination of the mesoporosity parameters.

Scanning electron microscopy (FEG–SEM) was used with field emission gun TESCAN MIRA3 electron microscope. Sputtering (with Au-Pd) has been performed on Fisons Instruments Polaron SC502 Sputter Coater.

Cd(II), Pb(II) and As(V) were analysed by the inductively coupled plasma mass spectrometry (ICP-MS) according to the literature method using an Agilent 7500ce ICP-MS system (Waldbronn, Germany) equipped with an octopole collision/reaction cell, Agilent 7500 ICP-MS ChemStation software, a MicroMist nebulizer and a Peltier cooled (2 °C) quartz Scott-type double pass spray chamber. Standard optimization procedures and criteria specified in the manufacturer's manual were followed.

### 3. Results and discussion

#### 3.1. Carp scale characterization

FTIR analysis shows the important functional groups of fish scale, such as hydroxyl, amides, phosphate, and carbonate, exists as available adsorptive sites for Cd(II), Pb(II) and As(V) removal. The FTIR spectra of carp scale (CS) before and after adsorption CS/Cd(II), CS/Pb(II) and CS/As(V) are given in Fig. 1. An analysis of FTIR spectrum of carp scale shows presence of phosphate groups in the apatite lattice specified by strong absorption bands at 600 and 1080  $\text{cm}^{-1}$ , and peaks at 872 and 1453  $\text{cm}^{-1}$  corresponding to carbonate anions substituted for phosphate ions in the apatite lattice [17]. Similar data have been reported for fish scale of *Pagrus major* [18] and *Leporinus elongatus* [19]. Three absorption bands attributed to amides I, II, and III [17] were observed at 1651, 1540, and 1234  $\text{cm}^{-1}$ , respectively. Stretching vibrations of N-H and O-H groups originated from collagen and hydroxyapatite shows broad band at  $\approx 3400 \text{ cm}^{-1}$ . These results indicate that the carp scale is a composite material consisting of type I collagen and calcium-deficient apatite containing carbonate ions.

Differences between bands structure in spectra of pure carp scale and after adsorptions of Cd(II) and Pb(II) could be noticed. Broad band at  $\approx 3411 \text{ cm}^{-1}$  (Fig. 1a), ascribed to OH and  $\text{NH}_2$  stretching vibrations, asymmetric and symmetric, is significantly affected by adsorbed ions, especially for Cd(II) which became notably narrower. This band changes suggest that the hydroxyl and amino groups are involved in a binding of cation. In addition, changes in the vibrational bands of amide group (amide I) at 1650  $\text{cm}^{-1}$  found for native adsorbent, after adsorption gave a slightly resolved peaks at  $\approx 1680$  and 1664  $\text{cm}^{-1}$  in a spectrum of CS/Pb(II), and even larger separation at  $\approx 1680 \text{ cm}^{-1}$  and  $\approx 1643 \text{ cm}^{-1}$  in a spectrum CS/Cd(II) were noticed. It means that stretching vibrations of amide groups (amides I, II and III) is highly affected by bounded Cd(II) and Pb(II) ions. Small intensity increase and shifting are also noted for a peaks at  $\approx 878$  and  $\approx 825 \text{ cm}^{-1}$  for Cd(II) and Pb(II), respectively [20]. Peaks at 1453 and 1398  $\text{cm}^{-1}$  associated to the carbonate anions substituted for phosphate ions in the apatite lattice are shifted and slightly increased.

Broad band at  $\approx 3411 \text{ cm}^{-1}$  (Fig. 1b), ascribed to OH and  $\text{NH}_2$  stretching vibrations, asymmetric and symmetric, is not significantly affected by adsorbed arsenic. As a consequence of the amino group protonation (pH 4), and probably due to interaction with arsenic species, new bands at  $\approx 3050 \text{ cm}^{-1}$ ,  $\approx 2020 \text{ cm}^{-1}$  and 1450  $\text{cm}^{-1}$  appeared, indicating that stretching and bending vibrations of ammonium group are influenced by arsenic adsorption [21].

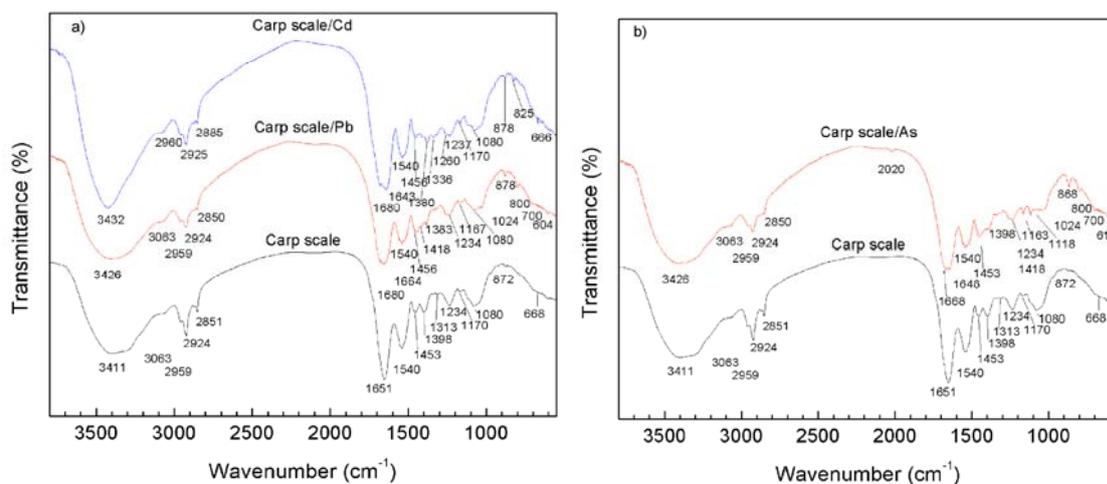


Fig. 1. FTIR spectra of carp scale and carp scale after adsorption in an aqueous solutions ( $m/V=100 \text{ mg dm}^{-3}$ ,  $T=20 \text{ }^\circ\text{C}$ ) of Pb(II) ( $C[\text{Cd}^{2+}]_0=10 \text{ mg dm}^{-3}$ ) at pH 6,  $C[\text{Pb}^{2+}]_0=10 \text{ mg dm}^{-3}$ ) at pH 8, (a), and As(V) ( $C[\text{As(V)}]_0=10 \text{ mg dm}^{-3}$ ) at pH 4 (b).

SEM images of carp scales showed characteristic fibrous and porous nature with clearly visible calciferous collagen molecule structure and plate like apatite crystals (Fig. 2).

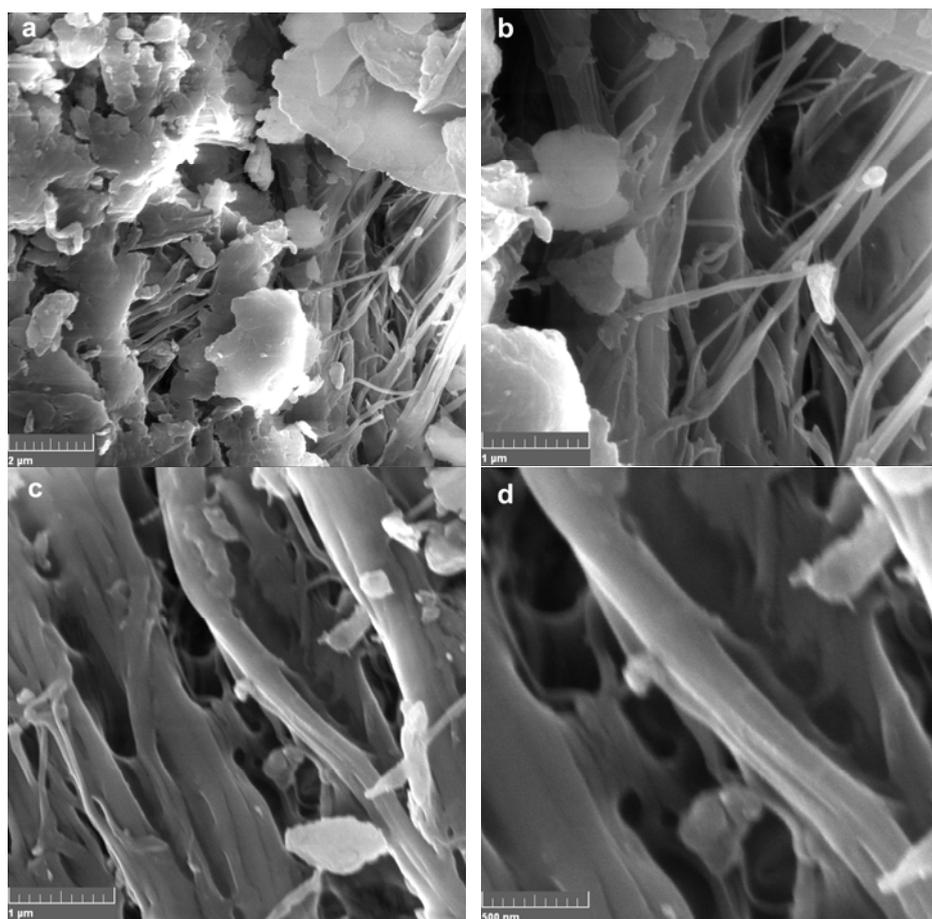


Fig. 2. Overview of carp scale FEG-SEM images: (a) 20.0 kx magnification, (b) and (c) 50.0 kx and (d) 100 kx magnification.

BET specific surface area and porosity of carp scale, as well as  $\text{pH}_{\text{PZC}}$  are given in Table 1.

Table 1. BET specific surface area and porosity of carp scale

Adsorbent	Specific surface area ( $\text{m}^2 \text{g}^{-1}$ )	Average pore volume ( $\text{cm}^3 \text{g}^{-1}$ )	Average pore diameter (nm)	$\text{pH}_{\text{PZC}}$
Carp scale	18.5	0.356	26.7	7.2
Carp scale/Pb	12.4	0.288	25.4	-
Carp scale/Cd	13.2	0.296	26.2	-
Carp scale/As	13.3	0.312	26.5	-

Results of elemental analysis, of carp scale are given in Table 2.

Table 2. Elemental analysis of carp scale

Sample	C (%)	N (%)	Ca (%)	P (%)	Mg (%)	Average mineral content (%)
Carp scale	26.5	11.1	14.5	6.7	0.3	46.2

### 3.2. The effect of pH on adsorption

Carp scale adsorption behaviour dependency of Cd(II), Pb(II) and As(V) ions on pH has been investigated over the pH range from 3.0 to 9.0.

Fig. 3 illustrates the influence of solution initial pH on degree of removal Cd(II), Pb(II) and As(V) in (%). Obviously, carp scale have the somewhat higher affinity for Cd(II) ions under the examined conditions, followed by Pb(II) ions and As(V).

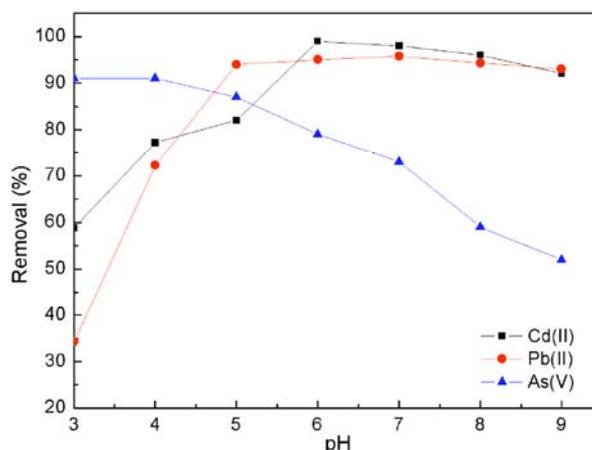


Fig. 3. Influence of solution initial pH on degree of removal Cd(II), Pb(II) and As(V) ( $C_{[\text{Cd(II)}, \text{Pb(II)} \text{ and } \text{As(V)}]} = 0.100 \text{ mg dm}^{-3}$ ,  $m/V = 100 \text{ mg dm}^{-3}$ ).

The solution pH affects the surface charge, surface properties, the degree of ionization of the groups present at carp scale surface, as well as ions speciation in aqueous solution at appropriate pH. The degree of adsorption of Cd(II) steeply increases with increasing pH, from 58% at pH 3 to 99% at pH 6, and then slowly decreases in the pH range from 6 to 9, reaching 95% at pH 8. The degree of adsorption of Pb(II) rapidly increases with increasing pH, from 35% at pH 3 to about 94% at pH 8, and then decreases to 90% at pH 9. Such results indicate acidic oxygen-containing groups behave as ion-exchange sites for the retention of Cd(II) and Pb(II) creating ligand surface complexes, and their adsorption capacities reach maxima at pH 6 and 8 respectively. The soft Cd(II) and large Pb(II) cation show strong bonding affinity to amino groups, while Pb(II) also could binds to phenols, hydroxyl and even ether groups [22].

The highest degree of As(V) adsorption was obtained at pH 4 (91% of initial arsenate concentration), slow decreased was observed in a region from pH 4 to 7, and after larger decrease of arsenate removal was noticed, achieving 47% of arsenate removal at pH 9. For carp scale at  $\text{pH} < \text{pH}_{\text{PZC}}$ , the positively charged surface of adsorbent electrostatically attracts the negatively

charged arsenate ions,  $\text{H}_2\text{AsO}_4^-$ , while at  $\text{pH} > \text{pH}_{\text{PZC}}$  electrostatic repulsion between arsenate ions and negatively charged surface takes place, causing the decrease of the amount of arsenate sorbed. At lower pH values, the surface charge is neutralized by the attraction of  $\text{H}_3\text{O}^+$  ions, and adsorption of arsenic species takes place. For the pH range 4-5,  $\text{H}_2\text{AsO}_4^-$  ions are dominant in the water solution (Fig. 3.). The adsorption free energy of  $\text{H}_2\text{AsO}_4^-$  ion may be lower than that of  $\text{HAsO}_4^{2-}$  and  $\text{AsO}_4^{3-}$ , and this would explain why  $\text{H}_2\text{AsO}_4^-$  adsorption is more favourable than  $\text{HAsO}_4^{2-}$  and  $\text{AsO}_4^{3-}$ .

From the presented results it could be concluded that adsorption capabilities of carp scale surface functional groups, as potential binding sites for divalent cations, depend on the adsorption condition, primarily on solution pH. Adsorption capabilities of carp scale with respect to As(V) is higher at lower pH, *i.e.* pH 4, due to protonation of functional groups and more favourable electrostatic interaction with arsenate anion.

### 3.3. Adsorption from real water samples

In order to examine the influence of ionic species present in a real water samples, the experiment with carp scale was performed using drinking water spiked with an addition of Cd(II), Pb(II) and As(V) (Table 3).

The ions commonly present in the real water sample (Table 3) are potential interfering agent which could contribute to decrease of CS adsorption efficiency. Presence of interference ions showed negligible effect on the Cd(II) and Pb(II) ions removal, while larger effect was found for As(V) removal capabilities by CS, and obtained results are presented in Table 3.

Table 3. The characteristics of spiked sample before and after adsorption.

The tested samples	pH	Removal (%)	The content of other ions ( $\mu\text{g dm}^{-3}$ )								
			Cr	Mn	Ni	Cu	Zn	Cd	Pb	Si	P
$\text{C}_0$ (spiked drinking water)		-	0.2	6.2	2.3	25.6	733	3.3	47	2700	10
Cd(II) ( $\text{C}_0=105 \mu\text{g dm}^{-3}$ )	6	98%	0.1	5.9	2.1	23	400	-	-	2700	9.4
Pb(II) ( $\text{C}_0=135 \mu\text{g dm}^{-3}$ )	8	94%	0.1	4.6	1.8	21	341	-	-	2500	9.2
As(V) ( $\text{C}_0=98 \mu\text{g dm}^{-3}$ )	4	71%	0	1.7	1	14	108	0.5	4	2300	7.4

It is obvious that the adsorption capacity of divalent cations in the presence of ions commonly found in real water have low influence on adsorption capacity Cd(II) and Pb(II) ion. It is opposite to the situation for arsenate solution which is significantly affected by the presence of other ions. The change in surface properties and arsenic species present in solution, along with the precipitation of different hydroxide on the adsorbent, caused a change in adsorption capacity. The change of concentration of phosphorous and silica was negligible during Cd(II) and Pb(II) removal, but significant decrease of Cu and Zn concentration was observed. This result indicate large competitive potential of present cation on Cd(II) and Pb(II) removal capabilities. It should be emphasized that significant decrease of concentration of Cu, Zn, Cd and Pb takes place simultaneously with arsenate separation. The results obtained indicate that carp scale have significant potential for use as adsorbent for divalent cations, Cd(II) and Pb(II), and lower for arsenate removal from real water sample.

### 3.4. Adsorption kinetics

In order to investigate the kinetics of adsorption of Cd(II), Pb(II) and As(V) on carp scale, adsorption kinetic models: pseudo-first order, pseudo-second order, Roginsky-Zeldovich-Elovich equation and second-order rate equation, and adsorption diffusion models: liquid film linear driving force rate equation, liquid film diffusion mass transfer rate equation, homogeneous solid diffusion model, parabolic or Weber-Morris model, Dunwald-Wagner model and double exponential model, were used [23].

Non-linear regression of experimental data, using Origin 8.0, showed that the best fitting kinetic model is pseudo-second order model giving the highest values of correlation coefficients than the other investigated models (Fig. 4). Therefore, this model could be used for the description of the adsorption kinetic of Cd(II), Pb(II) and As(V) on carp scale. Separation of the variables in differential form of the pseudo-second order equation and integration gives Eq. 1 [24]:

$$t/q_t = 1/(2K'q_e^2) + (1/q_e)t \quad (1)$$

where  $q_e$  and  $q_t$  are the amounts of adsorbed ions ( $\text{mg g}^{-1}$ ) at equilibrium and at time  $t$ , respectively.  $K'$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) is the pseudo-second order rate constant of adsorption. Kinetic parameters of the pseudo-second order equation for Cd(II), Pb(II) and As(V) adsorption on carp scale are given in Table 4.

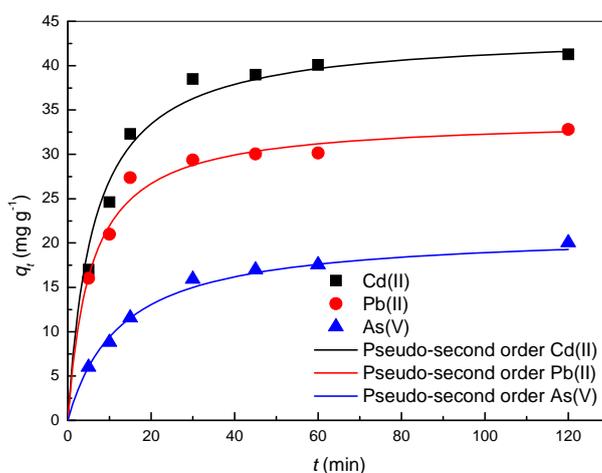


Fig. 4. Adsorption kinetics of Cd(II), Pb(II) at  $\text{pH } 6.0 \pm 0.1$  and As(V) at  $\text{pH } 4.0 \pm 0.1$  on carp scale adsorbent in a  $100 \text{ mg dm}^{-3}$  suspension and initial ionic concentrations  $5 \text{ mg dm}^{-3}$

Table 4. Kinetic parameters of the pseudo-second order equation for Cd(II), Pb(II) and As(V) adsorption on carp scale.

Adsorbate	$q_e$ ( $\text{mg g}^{-1}$ )	$K_2$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )	$R^2$
Cd(II)	43.76	0.4152	0.998
Pb(II)	34.05	1.1050	0.998
As(V)	21.31	0.2778	0.997

### 3.5. Adsorption isotherms

Several adsorption isotherm models were used in order to describe adsorption process, and to calculate various adsorption parameters according to: Langmuir, Freundlich, Sips, Jovanovic, Jovanovic-Freundlich, Dubinin–Radushkevich, Radke-Prausnitz, Redlich-Peterson, Temkin, Koble-Corrigan and Fritz-Schlünder isotherms. It was found that the best fitting data were obtained using Langmuir (L) isotherm (Fig. 5).

The Langmuir adsorption model [25] was used for determination of adsorption capacity and non-dimensional constant  $K_L$  used further for thermodynamic parameters calculation of studied process. Langmuir equation and its linearized forms is given by equation (2):

$$q_e = \frac{q_m K_L C}{1 + K_L C} \quad (2)$$

where  $q_e$  ( $\text{mg g}^{-1}$ ) is the amount of ions adsorbed per unit of carp scale,  $q_m$  ( $\text{mg g}^{-1}$ ) is the maximum adsorption capacity,  $c_e$  ( $\text{mg dm}^{-3}$ ) is the equilibrium concentration of ions, and  $K_L$  ( $\text{dm}^3 \text{mg}^{-1}$ ) is a Langmuir constant. The Langmuir isotherm theory assumes that the sorption takes place at specific homogeneous sites within the adsorbent.

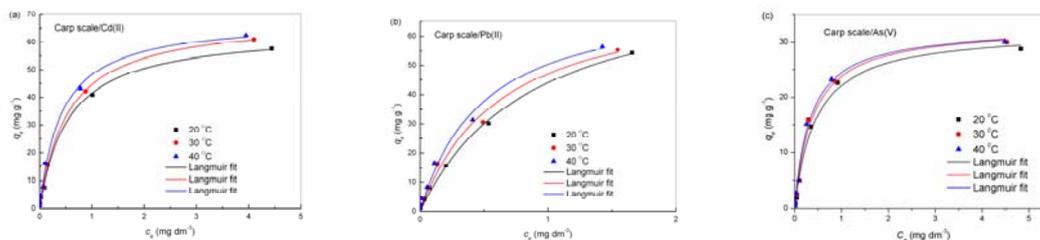


Fig. 5. Langmuir adsorption isotherms of Cd(II) at pH 6 (a), Pb(II) at pH 8 (b), and As(V) at pH 4 (c) on the carp scale at 20, 30 and 40 °C. ( $C_0 = 0.10, 0.20, 0.50, 1.0, 2.0, 5.0,$  and  $10.0 \text{ mg dm}^{-3}$ ,  $m/V = 100 \text{ mg dm}^{-3}$ ).

The results of experimental data fitting to Langmuir isotherms, using nonlinear method, are given in Table 5.

Table 5. Langmuir parameters for Cd(II), Pb(II) and As(V) removal on carp scale.

Isotherm	Cd(II)			Pb(II)			As(V)		
	20 °C	30 °C	40 °C	20 °C	30 °C	40 °C	20 °C	30 °C	40 °C
$q_m$ ( $\text{mg g}^{-1}$ )	64.4	68.6	69.0	55.4	56.8	62.5	28.8	32.0	32.1
$K_L$ ( $\text{dm}^3 \text{mg}^{-1}$ )	1.81	1.83	2.36	1.15	1.59	2.01	2.32	2.38	3.05
$R^2$	0.996	0.993	0.992	0.995	0.982	0.985	0.992	0.988	0.984

### 3.6. Error functions

In order to measure the quality of fitting the validation of adsorption isotherms were accomplished using different error functions alongside with the correlation coefficient  $R^2$ . Using nonlinear regression instead of linear incorporates the minimization or maximization of error distribution between the experimental data and the predicted isotherms based on its convergence criteria [26]. The data analysis was accomplished using Marquardt's percent standard deviation (MPSD); hybrid fractional error function (HYBRID); average relative error (ARE); average relative standard error (ARS); sum squares error (ERRSQ/SSE); normalized standard deviation (NSD); standard deviation of relative errors ( $s_{RE}$ ); spearman's correlation coefficient ( $r_s$ ), nonlinear chi-square test ( $\chi^2$ ) and root mean square error (RMSE) (Table 6).

Table 6. Values of correlation coefficients and error functions for Cd(II), Pb(II) and As(V) adsorption on carp scale for Langmuir isotherm at 20 °C.

	Cd(II)	Pb(II)	As(V)
MPSD	56.3	58.2	54.9
HYBRID	61.6	67.5	71.2
ARE	33.6	33.0	33.6
ARS	0.514	0.531	0.501
ERRSQ	11.1	10.9	22.0
NSD	51.4	53.1	50.1
S <sub>RE</sub>	35.7	34.8	35.7
r <sub>s</sub>	0.956	0.957	0.913
χ <sup>2</sup>	3.08	3.38	3.56
RMSE	1.26	1.25	1.77
R <sup>2</sup>	0.996	0.995	0.992

### 3.7. Thermodynamic study

The Gibbs free energy ( $\Delta G^0$ ), enthalpy ( $\Delta H^0$ ) and entropy ( $\Delta S^0$ ) of adsorption were calculated using the Van't Hoff thermodynamic equations:

$$\Delta G^0 = -RT \ln(b) \quad (3)$$

$$\ln(b) = \Delta S^0 / R - \Delta H^0 / (RT) \quad (4)$$

where  $T$  is the absolute temperature in  $K$  and  $R$  is the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ).  $\Delta H^0$  and  $\Delta S^0$  can be obtained from the slope and intercept of  $\ln(b)$  versus  $1/T$  plot, assuming the sorption kinetics to be under steady-state conditions. The calculated thermodynamic values (Table 7) give appropriate information on the adsorption mechanism operative in investigated system.

Table 7. Calculated Gibbs free energy of adsorption, enthalpy and entropy for Cd(II), Pb(II) and As(V) adsorption on carp scale at 293, 303 and 313K.

Adsorbate	$\Delta G^0$ (kJ mol <sup>-1</sup> )			$\Delta H^0$ (kJ mol <sup>-1</sup> )	$\Delta S^0$ (J mol <sup>-1</sup> K <sup>-1</sup> )
	293 K	303 K	313 K		
Cd(II)	-40.7	-42.7	-44.8	18.5	202
Pb(II)	-45.6	-48.3	-50.5	27.3	249
As(V)	-40.3	-42.2	-44.2	17.6	197

The negative adsorption standard free energy changes ( $\Delta G^0$ ) and positive standard entropy changes ( $\Delta S^0$ ) at all temperatures indicate that the adsorption reactions are spontaneous. For all adsorbate the adsorption process are endothermic ( $\Delta H^0$ ). The decrease of Gibbs free energy ( $\Delta G^0$ ) with increasing temperature indicates that spontaneity of the reaction increases.

## 4. Conclusions

In this work, scales of carp fish *Cyprinus carpio* were characterized and used for adsorption of Cd(II), Pb(II) and As(V) from aqueous solution. The FTIR spectra of carp scales, before and after dyes adsorption, suggest that the hydroxyl, phosphate, amides I, II, and III, and carbonate groups are the potential sites of adsorption. The observed adsorption order was

Cd(II)>Pb(II)>As(V) with adsorption capacity at 30 °C of 68.6, 56.8 and 32.0 mg g<sup>-1</sup> respectively. The experimental data were successfully modelled to the Langmuir adsorption model. The results suggest that carp fish scale is a new and suitable sorbent material for the adsorption of Cd(II), Pb(II) and As(V) from aqueous solutions.

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