

# The Influence of Chemical Modification on the $\text{Co}^{2+}$ Ion Sorption Process by Anaerobic Sludge

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## Abstract

Modification by chemical agents affected the sorption capacities of sludge from municipal wastewater treatment plants (WWTPs). We tried to characterize changes in sorption capacity of dried anaerobic sludge (DANS) after chemical modification by formaldehyde, methanol, and hydrochloric acid. Modified sludges were characterized by FT-IR spectroscopy, cation exchange capacity, and electrothermal atomic absorption spectrometry (ETAAS) analysis. Maximum sorption capacities  $Q_{max}$  at pH 6.0 for  $\text{Co}^{2+}$  ions calculated from Langmuir isotherm model were  $175 \pm 5$   $\mu\text{mol/g}$  for unmodified DANS,  $170 \pm 2$   $\mu\text{mol/g}$  for  $\text{CH}_2\text{O}$ -modified DANS,  $12 \pm 0.2$   $\mu\text{mol/g}$  for  $\text{CH}_3\text{OH}$ -modified DANS, and  $15 \pm 0.3$   $\mu\text{mol/g}$  for HCl-modified DANS. Our paper established the crucial role of carboxyl functional groups against amino and hydroxyl groups in sorption process of cobalt ions.

**Keywords:** anaerobic sludge, sorption,  $\text{Co}^{2+}$ , chemical modification FT-IR

## Introduction

Production of unseparable sludges in wastewater treatment plants (WWTPs) as a result of industrial intensification presents a serious problem for environmental protection. Sludge utilization is limited by content of heavy metals. Generally, these wastes can be utilized as soil fertilizers and conditioners. The Ministry of the Environment of the Slovak Republic (2010) showed that the total annual production of sewage sludge in SR is around 55,000 t of dry matter per year. The major part of sludge production is composted. Most authors [1-4] described the utilization of sewage sludges from WWTPs as an efficient sorbent of heavy metals and emerging organic compounds from liquid wastes and industrial waste waters. Anaerobic sludges contain vari-

able amounts of bacteria, protozoa, and extracellular polymeric substances [5]. Extracellular polymers are a matrix of proteins, carbohydrates, humic, and nucleic acids [6]. These components play an important role in the formation of anaerobic sludge structures and are rich in active centers of xenobiotic binding. Conventional methods for toxic metals removal from aqueous solutions as precipitation, ion-exchange, electrochemical pretreatment, or ultrafiltration are not all fully effective and have a lot of limitations. The main disadvantages of classical methods are low efficiency of the removal process when toxic metal concentrations are in the range of 1-100 mg/L [7] and production of toxic sludges. Sorption as a potential alternative to the classical toxic metal removal has several advantages [8].

Our paper [9] shows different modes of the sorption process such as nonactive metal uptake by biomass. Utilization of microbial sorbents and extracellular polymer

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substances has a crucial role in sorption processes and sorbent preparation. Authors [10, 11] refer to the ability of living organisms to uptake cobalt ions from liquid wastes. Both living and dead microbial biomass shows high sorption capacity. The toxic effect of high concentration of heavy metals to living cells is one of the limitations of biosorption and bioaccumulation utilization in remediation studies. To overcome the disadvantages, dead biomass is preferred in removal of toxic compounds and metals [12]. Many authors [13-15] showed the importance of superficial functional groups of organic matter in sorption processes of heavy metals. The presence of carboxyl (-COOH), hydroxyl (-OH), aldehyde (-COH), sulfhydryl (-SH), and amino (-NH<sub>2</sub>) is decisive for binding bivalent ions. Acidic functional groups of sorbents are involved in metal binding and there exists a positive correlation between their total concentration and the process of biosorption [16]. Sorption capacities of sorbents can be changed by a wide range of treatments methods. Modification of biomass using physical methods such as heating, autoclaving, freezing, drying, boiling, and chemical treatment such as effects of acids, alkalis, and organic chemicals showed reduction in heavy metal sorption [17]. Chemical pretreatments of sludge can predict sorption behavior of sorbent under reaction conditions of chemical agents present in waste waters. In addition, dried anaerobic sludge could provide economic sorbent, however, solubilization and leaching of organic compounds can cause the pollution in the second step.

Thus, it is preferable to treat sludge by chemical modification agents that influence the concentration of solubilized sludge fractions as well as capacity of sorption material. The main aim of this paper was to point out the influence of chemical modification on Co<sup>2+</sup> ions sorption process by dried anaerobically digested sludge. A lot of scientific discussions show the ability of specific chemical agents to block typical functional groups of sorbents. We tried to characterize sorption mechanisms of Co<sup>2+</sup> ions as a model of bivalent heavy metal ions from a single metal system by dried anaerobic sludge before and after chemical modification by formaldehyde, methanol, and hydrochloric acid.

## Materials and Methods

### Biosorbent Preparation and Modification

Biomass of anaerobically digested sludge was obtained from municipal WWTP (Zeleneč, Slovak Republic). After washing twice in deionized water, sludge was oven dried at 90°C for 48 h, ground, and sieved. Powdered dried anaerobic sludge (DANS 1) of particle size <450 µm was used for Co<sup>2+</sup> ion sorption studies. For chemical modification of sludge biomass, solutions of CH<sub>2</sub>O (DANS 2), 96% CH<sub>3</sub>OH (DANS 3), 0.1 mol/L HCl (DANS 4) were used. Preparation of modified sorbents was carried out by suspending dried anaerobically digested sludge (fraction <450 µm) in chemical agents (ratio w/v sludge: agent, 1:40) and agitation for 6 h at 22°C, 150 rpm. After reaction time, liquid phase was removed and washed sediment of modified

sludge sorbents was dried at 90°C for 48 h. Powdered modified anaerobic sludges of particle size <450 µm were used for Co<sup>2+</sup> ion sorption studies. Chemical reagents used to modify anaerobic sludge including formaldehyde, anhydrous methanol and hydrochloric acid were all purchased from Merck (SK). All agents were analytical grade and without further purification.

### Biosorbent Characterization

Soluble fractions in 0.9% NaCl at 22°C of the sludges were characterized by determinations of soluble protein [18], carbohydrate [19], -SH contents [20], and soluble inorganic salt contents determined by ion chromatography (IC) using Dionex ICS-5000 RFIC, Reagent-Free™ Ion Chromatography (Dionex – Thermo Fisher Scientific, USA). Solid fractions of sorbents prepared from DANS were characterized for cobalt initial content by ETAAS analysis using a Shimadzu AA-6300 (USA).

Cation exchange capacities (CEC) were estimated according to the Slovak Institute of Metrology modified by Frišták et al. [1]. Sludge sorbents (DANS 1-4) were suspended (83.3 g/L) in 0.1 mol/L BaCl<sub>2</sub> and mixed on a laboratory shaker for 1 h at 22°C at 150 rpm. Phases were separated after centrifuging (5 min at 5,000 rpm). This procedure was repeated twice. The next step of CEC determination consisted of resuspending sludge sediments in 3 ml of 0.025 mol/L BaCl<sub>2</sub> and of agitation for 19 h at 22°C. After phase separation, 3 ml of 0.02 mol/L MgSO<sub>4</sub> was added to sediments. After agitation (19 h at 22°C), centrifuging and phase separation, CEC by standardized 0.02 mol/L Na<sub>2</sub>EDTA was determined. The CEC values were determined by chelatometric determination of Mg<sup>2+</sup> ions in liquid phase and calculated according to:

$$CEC = \frac{(M_0V_0 - MV_v)}{10^{-3}} \varepsilon \quad (1)$$

... where CEC is cation exchange capacity (meq 100 g<sup>-1</sup>), M<sub>0</sub> is molar concentration of magnesium added to the sample (mol·L<sup>-1</sup>), V<sub>0</sub> is volume of solution of magnesium added to the sample (L), M is molar concentration of the magnesium in the leachate (mol·L<sup>-1</sup>), V<sub>v</sub> is volume of obtained extract (L), and ε is the conversion factor that has for the bivalent ions and amount 0.25 g of sorbent value 800 meq (100 g·mol<sup>-1</sup>).

### Sorption Experiments

Batch sorption experiments from a single metal system were carried out by suspending DANS 1-4 biomass (2.5 g/L, d.w.) in water solutions of CoCl<sub>2</sub> in concentration 1000 µmol/L spiked with radionuclide <sup>60</sup>Co (70 kBq/L) and adjusted to desired pH 6. Flasks were agitated on reciprocal shaker (120 rpm) at 22°C for 4 h and samples were taken for equilibrium study. Biomass was filtered out, washed twice in deionised water, and radioactivity of sludges was measured. The batch experimental set-up to determine the sorption capacity of sludges was described in detail previ-

Table 1. Equations of adsorption isotherms.

Isotherm model	Equation	Parameters
Langmuir model	$Q_{eq} = \frac{bQ_{max}C_{eq}}{1 + bC_{eq}}$	$Q_{eq}$ – amount of sorbed sorbate at equilibrium
		$B$ – coefficient related to the affinity between metal ion and the sorbent
		$Q_{max}$ – maximum metal uptake capacity
		$C_{eq}$ – equilibrium concentration in metal solution
Freundlich model	$Q_{eq} = KC_{eq}^{(1/n)}$	$Q_{eq}$ – amount of sorbed sorbate at equilibrium
		$C_{eq}$ – equilibrium concentration in metal solution
		$K, n$ – Freundlich empirical constants indicating sorption capacity and intensity of sorption

Table 2. Physico-chemical characteristics of studied sorbents DANS 1-4.

Sorbent	Solid fraction		Soluble fraction <sup>a)</sup>			
	CEC <sup>b)</sup> [meq/100g]	Co content <sup>c)</sup> [μg/g]	Proteins <sup>d)</sup> [mg/g]	Carbohydrates <sup>e)</sup> [mg/g]	Thiols <sup>f)</sup> [μmol/g]	Anions <sup>g)</sup> [μg/L]
DANS 1	25	<1	9.6	5.1	6.1	<LOD
DANS 2	24	<1	<0.5	4.5	<1	<LOD
DANS 3	0.5	<1	<0.5	4.2	<1	<LOD
DANS 4	2	<1	<0.5	5.0	<1	<LOD

<sup>a)</sup> extracted by 0.9% NaCl at 22°C; <sup>b)</sup> cation exchange capacity determined by BaCl<sub>2</sub>; <sup>c)</sup> initial concentration of cobalt (ETAAS); <sup>d)</sup> determination of soluble proteins; <sup>e)</sup> determination of carbohydrates by anthrone reagent; <sup>f)</sup> determination of thiols by 5,5-dithiobis-(2-nitrobenzoic acid); <sup>g)</sup> determination of soluble inorganic salts by IC (values of LOD for anions used (μ/L): fluorides 6, chlorides 7, nitrites 20, bromides 29, sulphates 25, nitrates 24, phosphates 7)

ously [1]. All experiments were performed in triplicate. The metal uptake was calculated as:

$$Q_{eq} = (C_0 - C_{eq}) \frac{V}{M} \quad (2)$$

...where  $Q$  is the uptake (μmol/g),  $C_0$  and  $C_{eq}$  are the liquid-phase concentrations of metal at initial and equilibrium (μmol/L),  $V$  is the volume (L), and  $m$  is the amount of dried biosorbent (given in grams).

### Radiometric Analysis and FT-IR Analysis

The gamma spectrometric assembly using a well-type scintillation detector 54BP54/2-X, NaI(Tl) (Scionix, the Netherlands) and Scintivision 32 data processing software (ORTEC, USA) were used for <sup>60</sup>Co determination in DANS 1-4 at the energy of γ- photons: <sup>60</sup>Co – 1,173.24 keV. Standardized <sup>60</sup>CoCl<sub>2</sub> solution (5.181 MBq/ml; 20 mg CoCl<sub>2</sub>/L in 3 g·dm<sup>-3</sup> HCl) was obtained from the Czech Institute of Metrology. The spectrometric analysis of sorbents in infrared region (FT-IR) was carried out to identify the chemical functional groups present on non-treated and pretreated sorbents and to explain the sorption mechanism. FT-IR spectra of unloaded and Co-loaded sorbents were performed by KBr technique using Nicolet NEXUS 470 spectrometer.

### Data Analysis

Data analysis of adsorption equilibrium was done using Langmuir and Freundlich adsorption isotherm equations (Table 1). To calculate maximum sorption capacity of sorbents and the corresponding parameters of adsorption isotherms, non-linear regression analysis was performed by ORIGIN 8.0 Professional (OriginLab Corporation, Northampton, USA).

## Results and Discussion

### Physico-Chemical Characterization of Sorbents

Characterization of unmodified and modified sorbents DANS 1, DANS 2, DANS 3, and DANS 4 used in paper are present in Table 2. The initial concentrations of cobalt in studied sorbents were lower than the detection limit (LOD) of ETAAS detector, which was 1 μg of Co per g of d.w. It suggests the ability of free binding sites for Co<sup>2+</sup> ions. The cation exchange capacity of unmodified DANS 1 was 25 meq per 100 g of d.w., which is higher than CEC of dried activated sludge from industrial WWTP [1]. According to Eq. 1 values of CEC decreased in the order DANS 1 > DANS 2 > DANS 4 > DANS 3. The effects of chemical modification by CH<sub>2</sub>O (DANS 2) caused minimal changes

Table 3. Langmuir and Freundlich equilibrium parameters ( $\pm$  standard deviation of the mean) for  $\text{Co}^{2+}$  ions sorption by studied sorbents obtained by non-linear regression analysis.

Sorbent	Model	$Q_{max}$ [ $\mu\text{mol/g}$ ]	$b$ [ $\text{L}/\mu\text{mol}$ ]	$K$ [ $\text{L/g}$ ]	$1/n$	$R^2$
DANS 1	Langmuir	175 $\pm$ 5	0.003 $\pm$ 0.001	—	—	0.966
	Freundlich	—	—	21.91 $\pm$ 4.01	0.25 $\pm$ 0.13	0.756
DANS 2	Langmuir	170 $\pm$ 2	0.004 $\pm$ 0.001	—	—	0.987
	Freundlich	—	—	18.45 $\pm$ 3.54	0.24 $\pm$ 0.13	0.747
DANS 3	Langmuir	12 $\pm$ 0.2	0.0003 $\pm$ 0.0001	—	—	0.989
	Freundlich	—	—	3.14 $\pm$ 0.17	0.14 $\pm$ 0.02	0.886
DANS 4	Langmuir	15 $\pm$ 0.3	0.0002 $\pm$ 0.0001	—	—	0.998
	Freundlich	—	—	3.39 $\pm$ 0.12	0.16 $\pm$ 0.04	0.921

in exchange capacity of sludge. Methylation of DANS amino and hydroxyl functional groups by formaldehyde as a crosslinking agent had a non-significant effect on CEC value. On the other hand, esterification of carboxylic functional groups of DANS by methanol caused a decrease of CEC value of about 98%. Cation-exchange capacity equally decreased after hydrochloric acid modification by more than 90%. Inorganic acids can cause irreversible damage of sorbent surface that in turn decreased the concentration of exchangeable ions. As shown in Table 2, concentrations of water-soluble proteins and carbohydrates sorbents used in the experiments decreased after chemical modification. Contents of soluble proteins and thiols of DANS 2, DANS 3, and DANS 4 were lower than LOD of used methods. In addition, determination of soluble inorganic salts by IC at ambient temperature confirmed the absence of fluorides, chlorides, nitrites, bromides, sulphates, nitrates, and phosphates in salt solutions of sorbents.

### Sorption Process and Role of Functional Groups

Sorption capacity of the sorbent is one of the most important factors for its practical utilization. Physical, chemical, or biological pretreatments can increase or decrease capacity for uptake of toxic metals by sewage sludge-based sorbents [21]. A number of modification reagents such as hydroxides and carbonates (NaOH,  $\text{CaOH}_2$ ,  $\text{Na}_2\text{CO}_3$ ), mineral and organic acids (HCl,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , EDTA,  $\text{C}_6\text{H}_8\text{O}_7$ ), organic compounds (ethylene, formaldehyde, methanol, acetone), oxidant ( $\text{H}_2\text{O}_2$ ), and dyes (Orange 13) can be used for chemical modifications [22]. Modification of sorbent surfaces by chemical agents is a possibility of sorption capacity changes [23]. Increased surface area of sludge is related to increased concentration of weak acidic functional groups of sorbents. In pursuance of our previous papers [1, 4, 24], we defined that the sorption of cobalt ions by DANS is a rapid process in which the equilibrium is reached within 2 h (Fig. 1). Experimentally estimated sorption capacities of DANS 1-4 for cobalt ions

were calculated according to Eq. 2. and fitted to nonlinear forms of the Langmuir and Freundlich adsorption isotherms. Coefficients of determination indicated that the Langmuir model fits obtained data better in comparison with the Freundlich model (Table 3).

To determine maximum sorption capacities ( $Q_{max}$ ) of studied sorbents the theoretical Langmuir isotherm was used.  $Q_{max}$  value of unmodified DANS for  $\text{Co}^{2+}$  ions was 175  $\mu\text{mol/g}$ . We found the effects of chemical modifications to  $Q_{max}$  values of studied sorbents for  $\text{Co}^{2+}$  ions. Bhatti et al. [25] showed that formaldehyde can enhance uptake capacity of sludge biomass by increasing the surface area and porosity of original samples, but our sorption data for DANS 2 did not confirm this fact.

We found modification of sludge biomass by formaldehyde and thus the blocking of hydroxyl and amino functional groups caused a non-significant decrease in cobalt

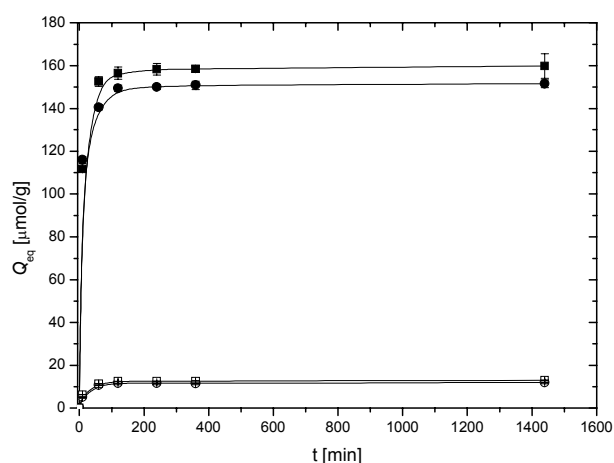


Fig. 1. Effect of contact time on sorption of  $\text{Co}^{2+}$  ions by DANS 1 (■), DANS 2 (●), DANS 3 (○), DANS 4 (□) in a single metal system. Experimental conditions:  $c_0 = 1000 \mu\text{mol/L}$   $\text{CoCl}_2$ , amount of sorbent 2.5 g/L,  $^{60}\text{CoCl}_2$  70 kBq/L, pH 6, reaction time of 10-1,440 min, at 22°C. All experiments were performed in triplicate. Error bars represent standard deviation of a mean ( $\pm$ SD).

Table 4. Comparison of maximum sorption capacity ( $Q_{max}$ ) of select sludge sorbents for  $Co^{2+}$  ions.

Sorbent	$Q_{max}$ [ $\mu\text{mol}\cdot\text{g}^{-1}$ ]	Reference
Activated sludge from distillery WWTP	256±9	[1]
Anaerobically digested sludge from distillery WWTP	209±5	[2]
Anaerobically digested sludge from municipal WWTP	175±5	This paper
Methylated anaerobically digested sludge from municipal WWTP	170±2	This paper
Esterified anaerobically digested sludge from municipal WWTP	12±0.2	This paper
0.1 HCl treated anaerobically digested sludge from municipal WWTP	15±0.3	This paper

sorption. Comparison of  $Q_{max}$  values of DANS 1 and DANS 2 (Table 3) showed the absence of hydroxyl and amino functional groups in sorption process of  $Co^{2+}$  ions by DANS. Pérez-Marín et al. confirmed the negligible effect of hydroxyl groups on Cd, Cr, and Zn sorption onto orange waste [26]. Hydrochloric acid (DANS 4) removed not only impurities from sludge surface but also released extracellular polymers after rupturing the cell-membrane and causing significant damage to sorbent [11]. Esterification of carboxyl functional groups by methanol (DANS 3) caused a significant decrease of  $Q_{max}$ , about more than 94%. Sorption capacities of dried activated sludge for  $Cd^{2+}$  and  $Zn^{2+}$  ions

before and after methanol treatment are not similar [4]. Authors showed reduction of both  $Zn^{2+}$  and  $Cd^{2+}$  ions adsorbing about 43% and 34% by esterified carboxyl groups of sludge surface. Kılıç et al. also found out effect of carboxyl group modification by esterification. Authors showed the decreasing of sludge sorption capacity after chemical modification and confirmed the major role of carboxylic groups in  $Pb^{2+}$  ions sorption [27].  $Q_{max}$  values of modified and unmodified anaerobically digested sludges are comparable to other sludge sorbents (Table 4). Hullebusch et al. found maximum sorption capacity of anaerobic sludge granules for  $Co^{2+}$  ions as 209  $\mu\text{mol/g}$ .

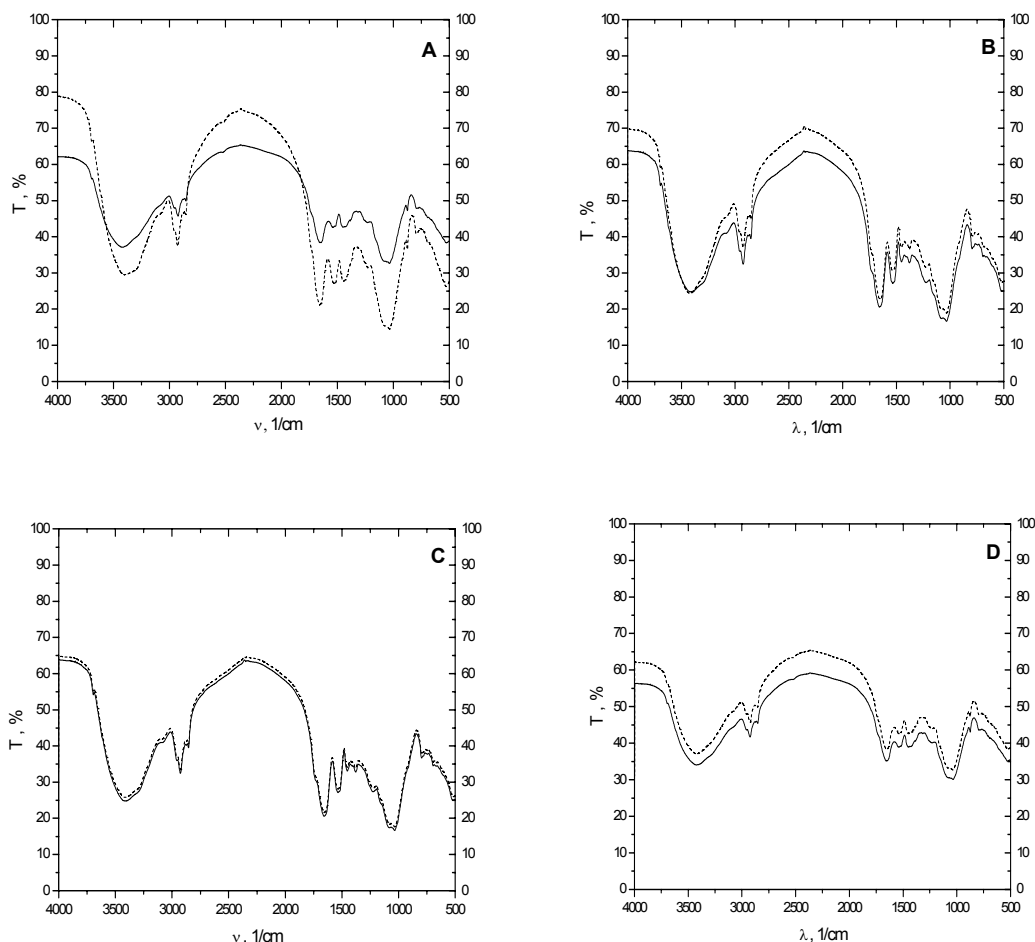


Fig. 2. FT-IR spectra of DANS 1(A), DANS 2 (B), DANS 3 (C), DANS 4 (D) before (solid line) and after (dashed line) sorption of  $Co^{2+}$  ions ( $c_0 = 4,000 \mu\text{mol/L CoCl}_2$ , DANS 2.5 g/L d.m., reaction time 4 h).

Table 5. Wavenumber values  $\nu/\text{cm}^{-1}$  of unmodified (DANS 1) and modified sorbent (DANS 2-4) with expected functional groups; FT-IR spectra in Figs. 2 a, b, c, and d.

Type of vibration/ functional group	$\nu/\text{cm}^{-1}$							
	DANS 1		DANS 2		DANS 3		DANS 4	
	Before sorption*	After sorption*	Before sorption*	After sorption*	Before sorption*	After sorption*	Before sorption*	After sorption*
Valence vibration –OH, –NH	3,423	3,429	3,421	3,420	3,399	3,399	3,422	3,422
Asymmetric vibration aliphatic $\text{CH}_2$ , $\text{CH}_3$	2,924	2,925	2,927	2,925	2,924	2,925	2,921	2,920
Symmetric vibration aliphatic $\text{CH}_2$ , $\text{CH}_3$	2,852	2,854	2,854	2,854	2,855	2,856	2,845	2,846
Valence vibration $\text{C}=\text{O}$ (carboxylates)	1,745	1,747	1,748	1,750	1,748	1,748	1,740	1,742
Valence vibration $\text{C}=\text{O}$ , $\text{C}-\text{N}$ (amide I)	1,657	1,658	1,658	1,658	1,658	1,658	1,654	1,654
Valence vibration $\text{C}=\text{O}$ , $\text{C}-\text{N}$ (amide II)	1,536	1,538	1,539	1,538	1,539	1,539	1,531	1,531
	1,518	1,517	1,517	1,517	1,518	1,518	1,516	1,516
Valence vibration $\text{C}=\text{O}$ , –OH (phenols)	1,452	1,448	1,448	1,449	1,450	1,450	1,450	1,450
Valence vibration $\text{C}=\text{O}$ , –OH	1,230	1,220	1,219	1,223	1,221	1,220	1,229	1,226
Valence vibration –OH, $\text{C}-\text{O}-\text{C}$ (esters)	1,078	1,090	1,090	1,090	1,092	1,092	1,074	1,074

\*before and after sorption of  $\text{Co}^{2+}$  ions (4,000  $\mu\text{mol/L}$   $\text{CoCl}_2$ , 4 h, pH  $6\pm 0.05$ ,  $22^\circ\text{C}$ ) by DANS 1-4 (2.5 g/L).

To confirm obtained experimental data, FT-IR analysis of studied sorbents before and after  $\text{Co}^{2+}$  ion sorption in the range of  $4000\text{--}400\text{ cm}^{-1}$  was used. DANS spectra are sketched out in Fig. 2 (a-d). The compounds deciphered could be identified based on the reports in previous study and are shown in Table 5. The profile in Fig. 2a portrays the FT-IR spectrum of unmodified sludge (DANS 1). The strong band at  $3,423\text{ cm}^{-1}$  reflected N–H and O–H stretching vibrations of hydroxyl and amine groups on the surface of the anaerobic sludge, while the band at  $2,924\text{ cm}^{-1}$  and the band at  $2,852\text{ cm}^{-1}$  represented asymmetric and symmetric vibrations of  $\text{CH}_2$  and  $\text{CH}_3$ . The band at  $1,745\text{ cm}^{-1}$  could be assigned to the valence vibration of  $\text{C}=\text{O}$  of carboxylates. A distinct band at  $1,657\text{ cm}^{-1}$  is the result of the valence vibration of  $\text{C}=\text{O}$  and  $\text{C}-\text{N}$  (amide I) peptidic bonds of proteins. Wavenumber of  $1,536\text{ cm}^{-1}$  band could be due to a combination of the valence vibration of  $\text{C}=\text{O}$  and deformation vibration  $\text{C}-\text{N}$  (amide II). The band at  $1,230\text{ cm}^{-1}$  could be attributed to the O–H stretching of phenols. Band at  $1,078\text{ cm}^{-1}$  could be attributed to the stretching vibration of –OH of esters.

After sorption of  $\text{Co}^{2+}$  ions were distinct shifts attributed to the vibration of carboxyl, amino, and hydroxyl groups (Table 5). Treatment of sludge with formaldehyde (DANS 2) changes the methylation of amine group (Fig. 2b). The band at  $3,421\text{ cm}^{-1}$ ,  $1,658\text{ cm}^{-1}$  and  $1,539\text{ cm}^{-1}$  got wider and the apex was lower compared to DANS 1. This modification demonstrates that O–H and N–H groups were reduced. In addition, FT-IR spectrum of DANS 2 after sorption process of  $\text{Co}^{2+}$  ions confirmed insignificant shifts of amide I and amide II bands. There was a substantial decrease in adsorption intensity of carboxyl groups at  $1,748\text{ cm}^{-1}$  and  $1,219\text{ cm}^{-1}$ . Comparison of sorption experiments and FT-IR analysis of DANS confirmed only minimal effect of methy-

lation of amino and hydroxyl groups to sorption process of  $\text{Co}^{2+}$  ions. On the other hand, modification of sludge with methanol (DANS 3) changes the esterification of carboxyl groups (Fig. 2c).

Observed bands at  $1,748\text{ cm}^{-1}$  and  $1,450\text{ cm}^{-1}$  substantially shifted and the two bands became wider and lower, which may be attributed to the esterification of carboxyl groups in the anaerobic sludge. The FT-IR spectrum of DANS 3 after sorption  $\text{Co}^{2+}$  ions and experimentally obtained values of  $Q_{\text{max}}$  after esterification of carboxyl groups indicate that functional groups of carboxylates play a crucial role in the sorption process of cobalt ions. The effect of esterification of carboxyl groups on the biosorption process of heavy metals is very important [28]. Modification of DANS by hydrochloric acid can be used as a tool to lower the inorganic content of a carbonaceous material through partial dissolution of the inorganic fraction [29]. The analysis of FT-IR spectrum of DANS 4 (Fig. 2d) revealed that hydrochloric acid as a chemical agent caused the crucial changes in width and intensity of bands of amide I and II. After sorption of  $\text{Co}^{2+}$  ions, minimal shifts of carboxyl groups at  $\nu$   $1,740$  and  $1,229\text{ cm}^{-1}$  were detected (Table 4). Less significant shifts of carboxyl functional groups after metal sorption can occur due to the presence and interaction of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions in the ion exchange process of  $\text{Co}^{2+}$  ions [24].

Xu and Liu showed the influence of electrostatic interactions between the hydroxyl and carboxyl functional groups on sorption of  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Ni}^{2+}$  by aerobic granules [30]. Sorption experiments confirmed a decrease of sorption capacity of DANS 4. The treatment of sludge by hydrochloric acid can yield dramatic improvements in sludge surface areas [29] but can also significantly damage the sorption surface and released the oxygen complexes and

polymer substances (proteins and phosphates) [24, 25]. Sludge electronegativity decreases due to increased concentration of  $H^+$  ions present in the structures of DANS. Changes of biomass electronegativity caused the decrease of sorption capacity of sorbents [31]. Benguella and Benaissa showed that chemical treatment by inorganic acids also caused changes in sorption capacity of sorbents based on chitin for  $Cd^{2+}$  ions [32].

### Conclusions

Sewage sludge from municipal WWTP can be considered removable material for potential toxic metal sorption from liquid wastes. Data presented in our paper confirm the sorption capacity of dried anaerobic sludge for  $Co^{2+}$  ions up to 175  $\mu\text{mol}$  per g of d.w. We found out that the effect of methylation by formaldehyde caused insignificant change in sorption capacity of sludge. On the other hand, esterification of carboxyl groups by methanol and modification of sludge surface by hydrochloric acid caused significant decrease in sorption capacity of sorbent (more than 90%).  $^{60}\text{Co}$  gamma spectrometry and FT-IR analysis established the crucial role of carboxyl functional groups compared to amino and hydroxyl groups of anaerobic sludge in the sorption process of  $Co^{2+}$  ions.

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