



# Article Formation of Biochar Nanocomposite Materials Based on CoFe<sub>2</sub>O<sub>4</sub> for Purification of Aqueous Solutions from Chromium Compounds (VI)

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Abstract: The paper proposes a simple one-stage synthesis of organic-inorganic composite materials based on oxide compounds of iron (III) and cobalt (II) with a developed surface. The process of cobalt(II) ferrite (CoFe<sub>2</sub>O<sub>4</sub>) structure formation on the biochar surface was studied. As an organic component, biochar was obtained from agricultural waste, including sunflower husks, rice husks, and pea kernels. Composite materials cobalt ferrite/biochar were obtained for the first time using these wastes. The obtained materials were characterized using X-ray phase analysis, fourier transform infrared spectroscopy (FTIR), transmission electron microscopy, and N<sub>2</sub> adsorption-desorption. A mechanism for forming composite materials is proposed, including the stage of formation of chelate complexes of transition element cations with citric acid on the biochar surface and their subsequent thermal decomposition. High adsorption activity of the synthesized materials in the process of removing chromium (VI) ions from aqueous solutions was established. The sunflower husk biochar composite material based on CoFe<sub>2</sub>O<sub>4</sub> has the highest adsorption capacity of 6.98 mg/g. The results suggest that biochar composites based on CoFe<sub>2</sub>O<sub>4</sub> have great potential for the practical industrial wastewater treatment.

**Keywords:** Cobalt(II)-Iron(III) Oxy; spinel structure formation; carbon composite; synthesis; characterization; chromium nanostructured materials

## 1. Introduction

Complex oxide compounds based on transition metals have been the object of many years of intense study. This is due to the presence of a successful combination of a number of important technical properties and the relative ease of manufacture. Cobalt(II) ferrite (CoFe<sub>2</sub>O<sub>4</sub>) is obtained using various technological methods: solid-phase reaction [1], the sol-gel method [2–4], hydrothermal synthesis [5,6], and pyrolysis of precipitated hydroxides in an argon atmosphere [7]. To obtain efficient catalysts and adsorbents, it is necessary to synthesize materials with a developed surface. As a rule, oxide compounds of transition elements have a low specific surface area. To obtain new materials, the synthesis used, using starch [8], graphene oxide [9], sewage treatment plant sludge [10], and cellulose [11] as an organic carrier with a developed surface. Such compositions make it possible to obtain materials with a double effect: a developed surface due to a particular organic substance and magnetic or semiconductor properties due to an inorganic component [12–15]. With the use of these materials, polluted industrial effluents are effectively cleaned from dyes [13,14,16], heavy metals [8,17,18], pesticides [11,19], herbicides [20], and drug residues [21,22].

In recent years, more and more attention has been paid to waste processing by new technological chains with the formation of demanded products. One of the options for these wastes is the by-products of agricultural production—sunflower husks, rice husks,



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). and peas. Biochars can be prepared from these materials, allowing practically waste-free production. Numerous recent studies have been actively developing a process for using residual biomass to obtain a potential sorbent for purifying water contaminated with persistent pollutants.

It is known that biochar is obtainable from citrus peel [22], bamboo [16], melon peel [17] and banana [21], corn stalk [23], coconut shell and watermelon peel [24], pollen [25], and bark [18] pine, rice straw [20]. Biochar is an environmentally friendly and cost-effective adsorbent with a high specific surface area and porous structure. However, it has a low density and small particle size, which makes it difficult to remove them from the reaction system after the reaction. In this regard, a promising area of research in world science is the creation of organic-inorganic composite materials with the introduction of particles suitable for magnetic separation into biochar. The ferrites of transition elements with a spinel structure, with the general formula  $MeFe_2O_4$  (Me = Mn, Zn, Co, Mg, Fe, Cu) exhibit catalytic properties and exhibit adsorption activity. Among ferrites, the complex oxide of iron (III)-cobalt (II) ( $CoFe_2O_4$ ) is the preferred magnetic material since it is chemically and thermally stable and has high mechanical strength [17]. Different scientific groups have obtained composite organic-inorganic materials based on CoFe<sub>2</sub>O<sub>4</sub> compounds and used for a number of applications: biochar from orange peel is used for coagulation removal of fine silver particles [22], from bamboo [16]—for removal of organic dye, from melon peel [17], pine bark [18]—for sorption of  $Cu^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$  cations, from corn stalk [23]—for removal of lomefloxacin hydrochloride, from banana [21]-for removal of amoxicillin antibiotic, from sewage treatment plants sludge [10], pine pollen [25]-for the decomposition of bisphenol A.

One of the effective separation methods is solid-phase extraction. As its variation, magnetic solid-phase extraction can be distinguished when the sorbent used can be separated after the reaction by applying a constant magnetic field. This study aimed to develop a simple method for obtaining organic-inorganic magnetically detachable composite materials based on oxide compounds of iron (III)-cobalt (II) and several biochars for removing chromium compounds from aqueous solutions.

# 2. Materials and Methods

# 2.1. Materials

Starting materials—nitrates of cobalt (II) (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) and iron (III) Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (the content of components not less than 99%), ammonia solution NH<sub>3</sub>·H<sub>2</sub>O 25% (wt.), citric acid C<sub>6</sub>H<sub>8</sub>O<sub>7</sub> (analytical grade) used. Distilled water was used to prepare solutions. Rice and sunflower husks were obtained from private farmers in the South of Russia, pea kernels were provided by Agrokholod company, Russia.

#### 2.2. Pyrolysis of Biochars

The biomass of sunflower husks, rice husks, and pea kernels was washed with distilled water to remove surface contaminants, then dried in oven at 100 °C until a stable weight was reached. The resulting dry biomass was placed in a muffle furnace for pyrolysis in a sealed metal vessel to exclude oxidation. The reaction was carried out stepwise at temperatures of 100–700 °C, with a temperature change step of 200 °C. The total reaction time was 2 h 45 min, holding time in intermediate phases 20 min, and holding time at final temperature 45 min. The temperature rise rate was 11 °C/min. The resulting biochars were stored in sealed containers for further use.

#### 2.3. Synthesis of Composite Materials

Synthesis of the composite material was carried out in one stage with the formation of an composition in situ. Cobalt(II) ferrite was formed on the biochar surface according to the method developed by the authors and described in [26,27].

For the experiment, biochars prepared from sunflower husks, rice husks, and peas were used. Then, with continuous stirring, 25 mmol of  $Co(NO_3)_2$  and 50 mmol of  $Fe(NO_3)_3$ 

(in the form of solutions with a concentration of 1 mol/L) were simultaneously added. Then, 200 mmol of ammonia (in the form of a solution with a concentration of 25%) and 156 mmol of citric acid (in the form of a solution with a concentration of 6.25 mol/L) were introduced. The mixture was then heated until complete evaporation of the liquid. With further heating, the process of intensive decomposition occurred, accompanied by the release of gaseous substances and the glow of the reaction system. Heating was continued until the end of the evolution of gaseous products of thermolysis of metal nitrates. The end of the reaction was monitored visually. The resulting composite materials are designated as cobalt (II) ferrite/Sunflower (FS), cobalt (II) ferrite/Rice (FR), and cobalt (II) ferrite/Peas (FP).

#### 2.4. Characteristic

Various methods were used to characterize the obtained composite materials, including X-ray diffraction (XRD), Fourier transforms infrared spectrometry (FTIR), transmission electron microscopy (TEM), Brunauer-Emmett-Teller analysis (BET), thermogravimetric analysis (TGA). The phase composition was studied on an ARL X'TRA X-ray diffractometer (Thermo Scientific, United Kingdom) (monochromatized Cu-K $\alpha$  radiation was used) by point-by-point scanning (step 0.01°, accumulation time at a point 2 s) in the range of  $2\theta$ values from 15° to 70°. The crystallite size along the line (400) was using the Scherrer Equation (1) [28]:

$$D = 0.94\lambda / (B \cdot \cos\theta),\tag{1}$$

where *D* is the average crystal size, nm,  $\lambda$  is the X-ray wavelength, nm, *B* is the width of the peak line at half its height, rad,  $cos\theta$  is the value of the cosine of the angle for the peak.

The surface area was determined on a ChemiSorb 2750 V apparatus (Micromeritics, Norcross, GA, USA). Nitrogen physical adsorption isotherms were obtained at 77 K. Prior to measurement, the samples were degassed.

The FTIR absorption spectra of the samples were obtained on a Varian 640 IR-Fourier spectrometer (Agilent Technologies, Santa Clara, CA, USA) using the method of frustrated total internal reflection, the prism material was diamond.

The samples were prepared by pressing with potassium bromide (1% (wt.)). A Tecnai G12 BioTwins transmission electron microscope (FEI, Philips, Czech Republic) in bright field mode was used at an accelerating voltage of 100 kV to provide the TEM images.

## 2.5. Study of Adsorption Activity

The adsorption activity of the synthesized materials was studied on a model solution of potassium dichromate with a concentration of 5 mmol/L. In this case, 5 mL of the initial potassium dichromate solution was passed through a reaction column containing 2 cm<sup>3</sup> of the adsorbent. Next, 5 mL of deionized water was passed through the column, and the content of dichromate ions in the washing solution was determined. The determination was carried out by the intrinsic color of the solution by the photocolorimetric method using a KFK-2-UHL 4.2 device (Yurga, Russia) with a wavelength of 364 nm. The degree of purification (*N*) was calculated by the Equation (2):

$$N = n \cdot 216/m_0 \tag{2}$$

where *n* is the amount of desorbed  $Cr_2O_7^{2-}$  ions, mol; 216 g/mol is the molar mass of dichromate ions; *m*<sub>0</sub> is the mass of the used composite, g.

#### 2.6. Recycling

At the end of the experiment, the adsorbent was washed three times with distilled water, dried at room temperature, and the adsorption activity was re-examined. The composite was separated using a permanent magnet, and reused.

## 3. Results

### 3.1. Study of the Structure and Morphological Features of Samples

In all cases, the synthesized material had a porous structure. X-ray diffraction patterns of the synthesized samples of composite materials are shown in Figure 1. The X-ray patterns show spectra characterizing the phase of the cubic spinel  $CoFe_2O_4$ .



**Figure 1.** X-ray pattern of samples of composite materials (designated as cobalt (II) ferrite/Sunflower (FS), cobalt (II) ferrite/Rice (FR), and cobalt (II) ferrite/Peas (FP)).

For iron (III)-cobalt (II) oxide compounds of the CoFe<sub>2</sub>O<sub>4</sub> type, the structure can be described as a cubic close-packed lattice of oxygen ions, in which there are octahedral (denoted B) and tetrahedral (denoted A) voids (Figure 2). The degree of inversion of cobalt ferrite was determined using the calibration curve method [29]. Since the radius of the  $Co^{2+}$ ion (0.078) is larger than that of the  $Fe^{3+}$  ion (0.067), the cobalt ion, taking the place of the iron ion in the B-sublattice, pushes the surrounding  $O^{2-}$  anions apart, which leads to an increase in the lattice constant. In this regard, the lattice parameter has higher values for the reversed spinel. One of the ways to control the degree of conversion is the synthesis method. Thus, cobalt (II) ferrite obtained by the mechanochemical method at different annealing temperatures has different values of the lattice parameter [29]. The normal spinel structure is formed at low temperature annealing and is characterized by the value of the lattice parameter a = 0.8288 nm, reversed—at a higher annealing temperature, a = 0.8377 nm. The calculated values of the parameters of cobalt (II) ferrite samples synthesized in this study have intermediate values, according to the graph  $\lambda(a)$ , the degree of reversibility can be determined. The calculated values of the lattice parameters and reversibility are given in Table 1.

Cobalt(II) ferrite in composites with biochars from sunflower and rice refers to practically inverted spinels (the reversal parameter is 0.9 and 0.85, respectively). On the contrary, in a composite with peas, it is close to normal spinels (reversal parameter 0.1). The values of the average crystallite size (calculated by the Scherrer method) are given in Table 1. According to the obtained results, the synthesized cobalt (II) ferrite/rice composite has the smallest crystallite size, followed by the composite with sunflower biochar and, finally, pea biochar.

The TEM images in Figure 3 of the synthesized composites show regular octahedral crystals typical of  $CoFe_2O_4$ . The particle size distribution shows that the rice composite is almost monodisperse with a particle size of 50–100 nm, for the sunflower composite, the



main particle size falls within the same range; for the pea composite, the particles are larger, 300–400 nm.

**Figure 2.** Distribution of cations over A- and B-positions of oxide spinel CoFe<sub>2</sub>O<sub>4</sub> for normal and reversed structures.

<b>Table 1.</b> Characterization of synthesized composite materia
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Sample	a, nm	Reversibility Parameter $\lambda$	Spinel Formula	D, nm	$S_{BET}, m^2 \cdot g^{-1}$
FS	0.8376	0.9	(Co <sub>0.1</sub> Fe <sub>0.9</sub> )[Co <sub>0.9</sub> Fe <sub>1.1</sub> ]O <sub>4</sub>	121	83.2
FR	0.8370	0.85	(Co <sub>0.15</sub> Fe <sub>0.85</sub> )[Co <sub>0.85</sub> Fe <sub>1.15</sub> ]O <sub>4</sub>	104	87.1
FP	0.8297	0.1	$(Co_{0.9}Fe_{0.1})[Co_{0.1}Fe_{1.9}]O_4$	208	115.9



Figure 3. TEM images of synthesized composite materials: (a,d) is FS, (b,e) is FR, and (c,f) is FP.

The photographs clearly show the hexagonal structures of spinels formed on the surface of the sorbents. It is also seen that spinels attach to certain places of the sorbent and separate the layers, partially overlapping the surface of the coals.

Data on the structure of the material were supplemented by the results of FTIR spectroscopy (Figure 4). For all synthesized materials, the presence of peaks in the region of 3380–3440 cm<sup>-1</sup> was noted, which are associated with vibrations of the –OH group [30,31]. The peak in the region of 1616–1710 cm<sup>-1</sup> is attributed to vibrations of the C–C group [31,32]. In the region of 1000–1200 cm<sup>-1</sup>, an intense band of C–O stretching vibrations is visible [30]. A small peak at about 810 cm<sup>-1</sup> indicates C–H deformation [30].



**Figure 4.** FTIR spectra for the synthesized composite materials (**a**) with detailing of the oscillation region for the oxide component (**b**).

According to the results of thermographic analysis, for all samples there is a sharp change in mass in the region of 400-550 °C (Figure 5). In the same region, according to the data of differential scanning calorimetry, an exothermic effect was noted. These experimental data may be associated with the decomposition of the organic component of composite materials. For all samples, the decomposition start temperature is 350 °C. The decomposition end temperature increases from FS (570) through FR (580) to FP (650). The thermal effects for FS and FR are close in value (the area under the peak of the thermal effect is 848 and 944 relatively for composites units). For the FP sample, the thermal effect is more significant (on 26–34%) and more strongly affected in the temperature range. This may be due to the nature of the organic component of the composite: pea biochar is denser and has the highest bulk density (0.132 g/mL for FS, 0.215 g/mL for FR, 0.294 g/mL for FP). By the value of the residual mass, one can judge the ratio of the organic and oxide components in the composite material. The TGA data obtained indicate that the FR composite contains the largest amount of the inorganic component. This may be due to the shape of biochar particles; transition metal ions are more easily fixed on the surface of such particles, followed by oxy-spinel formation.



Figure 5. TG and DSC data for synthesized composites: (a) is FS, (b) is FR, and (c) is FP.

#### 3.2. Study of Adsorption Activity

The synthesized composite materials were tested in the process of sorption of  $Cr_2O_7^{2-}$  ions from an aqueous solution. The experimental data are given in Table 2.

**Table 2.** Adsorption properties of composite materials.

Sample	Sample Weight, g	n, μmol	N, mg $\cdot$ g $^{-1}$
FS	0.263	8.50	6.98
FR	0.430	9.75	4.90
FP	0.588	3.32	1.22

According to the results obtained, the composite based on cobalt (II) ferrite and sunflower biochar (FS) has the highest sorption capacity. Its sorption capacity exceeded the similar values for the FR and FP composites by 29.8 and 82.5%, respectively.

## 4. Discussion

The distribution of cations over the A- and B-positions may vary. There are two extreme cases of such a distribution—normal and inverted spinels. In normal spinel,  $Co^{2+}$  cations are inside the tetrahedron, and  $Fe^{3+}$  ions are inside the octahedron (Figure 2). The formula can be written as (Co)[Fe<sub>2</sub>]O<sub>4</sub>. In the inverted structure, half of the Fe<sup>3+</sup> ions are located at A sites, half at B sites, and Co<sup>2+</sup> ions occupy B sites (Figure 2); the formula can be written as (Fe)[CoFe]O<sub>4</sub> [33]. In real oxide spinels, the distribution of cations is of an intermediate nature and is determined by the reversal parameter  $\lambda$  (it shows the number of Co<sup>2+</sup> cations occupying B sites).

In terms of specific surface area (Table 1), the composite with peas has the highest value, followed by composites with rice and sunflower. The correlation between the values of the specific surface area of the synthesized composites and the value of the inversion parameter should be noted: the higher the degree of inversion of the oxy-spinel based on  $CoFe_2O_4$ , the lower the specific surface area of the composite. In addition, the values of the specific surface area for FS and FR differ slightly (by a value of about 4.5%), and with the value for FP the difference becomes more significant (up to 28%). A similar effect can be noted for the value of the inversion parameter: for FS and FR the difference is about 5.5%, and the value for FP increases to 80%. This experimental fact may be related to the nature of the surface of biochars: in the case of sunflower and rice, the particles have an elongated shape, while in peas, it is close to round. Under these conditions, the sorption of intermediate synthesis products on the biochar surface probably occurs differently, which leads to differences in the structural features of the oxide component of the composite.

The process of formation of cobalt (II) ferrite can be represented as consisting of a number of stages. The cations of transition elements in solution, formed as a result of the dissociation of the initial salts according to Equations (3) and (4).

$$Co(NO_3)_2 = Co^{2+} + 2NO_3$$
 (3)

$$Fe(NO_3)_3 = Fe^{3+} + 3NO_3$$
(4)

They are sorbed by the biochar surface. In the presence of an ammonia solution, precipitates of the hydroxides of the form of the corresponding metal (Equations (5) and (6)):

$$Co^{2+} + 2OH^{-} = Co(OH)_2$$
 (5)

$$Fe^{3+} + 3OH^{-} = Fe(OH)_3 \tag{6}$$

When citric acid is introduced into the reaction system, the formation of citrates is possible according to the reactions (Equations (7) and (8)):

$$Co(OH)_2 + C_6 H_8 O_7 = Co(C_6 H_6 O_7) + 2H_2 O$$
(7)



Followed by the formation of chelate complexes having a bulk structure (Figure 6):

 $Fe(OH)_3 + C_6H_8O_7 = Fe(C_6H_5O_7) + 3H_2O_7$ 

Figure 6. Possible structure of the intermediate citrate complex of transition elements.

In the process of thermolysis, the complexes are decomposed with the formation of a dispersed powder of spinel with the composition  $CoFe_2O_4$ . In this case, the effect of inheritance of the precursor shape is observed. A similar phenomenon was observed earlier [34,35], under interaction of ethylene glycol with iron and cobalt oxalates when heated in air. The authors found that the heat treatment of mixtures of oxalate powders with ethylene glycol leads to the formation of new compounds (solvates), in the structure of which the positions of water molecules are occupied by ethylene glycol molecules. The crystals of the formed solvates have an extended shape, which is transferred to the thermolysis products.

According to many observations, the region of  $250-600 \text{ cm}^{-1}$ , oscillations of the oxide component of the composite material appear [30,32,35] (Figure 4). It is customary to attribute the highest-valence cation vibration to the most intense spectral band [36]. In this regard, it can be assumed that a clear peak in the 580–600  $\text{cm}^{-1}$  corresponds to the vibrations of the trivalent iron cation in the A-positions. The line in the region 450–470 cm<sup>-1</sup> characterizes the vibrations of the divalent cobalt cation in the B positions. This band is not typical for the FP composite, which has an almost normal spinel structure. The peak, at  $380-410 \text{ cm}^{-1}$ , can be attributed to Fe<sup>3+</sup> vibrations in the B positions. Peaks in the lowest frequency region 220–250  $\rm cm^{-1}$  can be associated with the manifestation of vibrations of  $Co^{2+}$  cations in A-positions. For an almost normal spinel structure of the FP composite, this peak is intense; for FS and FR, in which the cobalt (II) ferrite has an inverted spinel structure, these peaks have a significantly lower intensity. It is known [37] that the structure of inverted spinel is characterized by diffuse peaks, their splitting, and the presence of shoulders. If we compare the spectra for FP and FS and FR, it can be noted that are three distinguished peaks for FP. In the case of FS and FR, additional elements are visible in the form of splitting of peaks, and the presence of a plateau, which confirms the earlier assumption about a high degree of inversion of cobalt (II) ferrite in FS and FR composites.

The results obtained are comparable with the literature data on the sorption of  $Cr_2O_7^{2-}$  (Table 2). Thus, in the study [38] a result of 8–18 mg/g was achieved depending on the reaction conditions, in the study [39] a result of 2 mg/g was reported. However, the complexity and duration of the synthesis of the sorbent (33 and 48 h) in these studies and the need to use precursors harmful (dimethylformamide, toxic aniline was used) to health should be noted. Compared with similar compounds [38,39], the proposed method for synthesizing composites from production waste is fast, does not require the use of complex equipment, proceeds in one stage. Composites exhibit increased adsorption activity and can be separated from the reaction system using a simple permanent magnet.

(8)

Thus, the composite materials proposed by us have an undoubted advantage in the simplicity of synthesis and the absence of the need to use precursors hazardous to health while exhibiting significant adsorption activity in the process of removing chromium compounds from an aqueous solution.

The increased adsorption activity of synthesized composites may be associated with the production of bifunctional materials having a developed surface due to the presence of a biochar in the composition, and a functional group due to the presence of an inorganic spinel phase. The presence of cobalt (II) ferrite on the surface of the biochar leads to the formation of active centers and an increase in the sorption strength of chromium ions.

A noteworthy experimental fact is an observed increase in adsorption activity with an increase in the reversal parameter of the oxide component of the composite. This experimental fact requires further verification. After the completion of the reaction, adsorption active materials were re-examined. The samples withstood five successive cycles of use without loss of activity (Figure 7).



Figure 7. Repeated sorption cycles.

#### 5. Conclusions

A simple one-stage method for obtaining a number of organic-inorganic composite materials based on oxide compounds of iron (III)-cobalt (II) is proposed. This method, unlike analogs, allows the synthesis of composite materials with the formation of an oxide component on the surface of the biochar in situ, which significantly reduces the complexity of the process. Using thismethod, cobalt (II) oxy-ferrites were obtained on the surface of biochars prepared from agricultural waste: sunflower husks, rice husks, and peas.

It was found that the synthesized materials have high specific surface area values of  $83-116 \text{ m}^2/\text{g}$ , and are suitable for use in the process of adsorption of pollutants from an aqueous solution.

It is shown that the oxide material is formed on the biochar surface in the form of octahedral crystals and corresponds to the structure of the cubic spinel  $CoFe_2O_4$ . The calculated values of the reversal parameter showed that cobalt (II) ferrite has the structure of a partially inverted spinel with a reversal parameter of 0.1–0.9.

The mechanism of sample formation is discussed, including the stage of formation of chelate complexes of transition element cations with citric acid and their subsequent thermal decomposition.

The adsorption activity of the synthesized composite materials was established in the process of removing chromium ions from an aqueous solution. The composite material showed the most pronounced adsorption activity with biochar from sunflower husks; for it, the adsorption capacity was 6.98 mg/g. The results can be used to obtain materials suitable for industrial wastewater treatment processes using chromium compounds in production cycles.

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