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Development of nanostructured catalysts for catalytic oxidative water purification from organic impurities, including phenolic compounds

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Abstract

The purpose of this work was to create magnetic nanocatalysts that could be used for the oxidation of organic water pollutants – phenol and its derivatives – and to determine the physicochemical characteristics of the catalysts. The development of such active nanocomposite catalysts would solve the environmental problem in the Republic of Kazakhstan in the field of wastewater treatment from organic impurities, including phenols, and would also contribute to the subsequent creation of domestic production of oxygen-containing compounds, since almost the entire spectrum of oxygen-containing compounds for various industries is imported into the Republic. Nanosized magnetic composites based on Fe and Co were obtained by chemical deposition, in some cases, using polyethyleneimine and polyvinylpyrrolidone. It was shown that the interaction between nanoparticles and the polymer takes place in the case of a $CoFe_2O_4$ catalyst stabilized with polyvinylpyrrolidone or polyethyleneimine, which may indicate the efficient formation of nanocomposites. According to the IR study, for the $CoFe_2O_4$ nanocomposite stabilized with polyvinylpyrrolidone, the absorption bands at 735, 663, 649, 626 cm^{-1} are natural vibrations for the composite nanoparticles embedded in a polyvinylpyrrolidone matrix. The synthesized nanocomposites were tested in the oxidation of phenol with oxygen. The results demonstrate that the catalysts are promising both for the purification of industrial wastewater from phenol and for the synthesis of oxygen-containing compounds in the liquid phase under mild conditions.

Keywords

oxidation
catalysts
nanoscale magnetic composites
phenol wastewater
aromatic hydrocarbons
polyethylenimine
polyvinylpyrrolidone

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Key findings

- Nanocomposites of Fe_3O_4, Fe-Co/Al_2O_3 and $CoFe_2O_4$ as well as $CoFe_2O_4$ stabilized with polyethylenimine or polyvinylpyrrolidone were synthesized.
- The prepared nanocomposites were studied by physicochemical research methods and tested in the oxidation reaction of phenol with oxygen.
- The efficiency of using Fe_3O_4, $CoFe_2O_4$ and $CoFe_2O_4$ stabilized with polyethylenimine in the oxidation of phenol with oxygen was established.

1. Introduction

Many reservoirs are polluted by phenolic wastewater from petrochemical and oil refineries, pulp and paper mills, chemical industry enterprises producing phenol or using it for the synthesis of other substances, plants and factories of pharmaceutical and forestry industries, and enterprises producing building materials, rubber, adhesives, plastics,

pesticides, phenol-formaldehyde resins [1–6]. Catalysts based on various metals, metal oxides, deposited systems, and magnetic composites based on metal oxides show good efficiency in the oxidation of phenol with oxygen [3, 4, 7–14]. The most promising catalysts are nanodisperse catalytic systems for the purification of industrial waters from organic impurities, including phenolic compounds. Such catalysts can provide a high rate of oxidation of phenolic pollutants and effective oxidation of organic compounds with various functional groups. A significant number of publications are devoted to the study of the properties and applications of magnetic materials based on iron oxides in their common modifications – hematite, maghemite, and magnetite. This is due to the lower toxicity of nanoparticles and their acceptable magnetic properties when compared with similar compounds of nickel and cobalt [13, 15–19]. The oxidation of phenol with oxygen in the presence of a magnetically controlled ferromagnetic catalyst stabilized by polymers is characterized by higher efficiency, low activation energy and the absence of toxic compounds in aqueous solution. For example, Fe_3O_4 is an active particle of catalysts, and cobalt complexes forms stable π-complexes with aromatic compounds; due to the π-dative transfer of electrons from the central atom to π*-loosening C_6H_6 orbitals, they activate the multiple bonds of the ring more strongly and loosen the molecule. When the metal complex is bound to the polymer, some of the ligands in the complex are replaced by functional groups of the polymer chain. One of the most promising preparative methods is the synthesis of nanoparticles using polyethyleneimine (PEI) or polyvinylpyrrolidone (PVP) as a stabilizer due to their biocompatibility and hypoallergenicity. PEI coatings contain many amino groups and form cationic complexes that actively react with negatively charged surfaces and substances. PEI is a positively charged polymer. The authors of [20, 21] found the effectiveness of magnetofection in vivo when using iron oxide nanoparticles stabilized with PEI. The structural formula of PVP contributes to the fact that PVP acts as a surface stabilizer, dispersant and nanoparticle expansion modifier. PVP also has protective properties due to its unique structure. The PVP molecule contains a highly polar amide group, which provides hydrophilic properties, as well as non-polar methyl groups, both in the skeleton and in the ring, which provide hydrophobic properties [22].

The purpose of this work was to create magnetic nanocatalysts that could be used for the oxidation of organic water pollutants – phenol and its derivatives – and to determine the physicochemical characteristics of the catalysts.

2. Experimental

The following chemical reagents were used for the synthesis of magnetite and cobalt ferrite stabilized with PEI and PVP: iron (II) sulfate heptahydrate ($FeSO_4.7H_2O$) – “chemically pure”; iron (III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$) – “chemically pure”; $Co(NO_3)_2{\cdot}6H_2O$ – “chemically pure”; 25% aqueous solution of ammonia (NH_4OH) – “chemically pure”.

Co-deposition occurs in two stages: first, the nucleation of crystals (when critical supersaturation is reached); second, the slow crystal growth through the process of diffusion of dissolved substances to the crystal surface. These two stages should be separated in order to avoid the formation of crystals during the growth period [5, 16, 23, 24]. According to a number of works [25–27], the creation of polyethyleneimine coatings on magnetic iron oxide nanoparticles is a difficult task due to the aggregation during the adsorption of this polymer. To increase the efficiency of the catalytic system in the oxidation of organic compounds, the surface of magnetite was treated with cobalt nitrate. In the series of $MeFe_2O_4$ ferrites, where Me is Fe^{2+}, Co^{2+}, Ni^{2+}, $Cu^{2+}$and etc.), cobalt ferrite ($CoFe_2O_4$) has the highest cubic magnetocrystalline anisotropy, which is why cobalt nitrate was chosen.

Synthesis of $CoFe_2O_4$ was carried out through the following stages:

1) mixing of the aqueous solutions of $FeCl_3{\cdot}6H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$;

2) slow heating of the mixture to 353 K;

3) dripping 25% ammonia solution into the mixture with intense stirring and constant control of the crucial parameters (solution pH, mixture temperature);

4) mixing the resulting composite for another 40 minutes.

As a result, a very rapid formation of a dark brown suspension occurred.

Nanosized magnetic composites stabilized with PVP (M_w = 10,000) and based on Fe_3O_4, $CoFe_2O_4$ were obtained by chemical deposition. Nanocrystals of iron magnetite (Fe_3O_4) stabilized with PVP were obtained by chemical coprecipitation of the corresponding salts: ferrous and ferric iron ions in an alkaline solution [16, 28–30]. The synthesis was carried out separately in water in an aqueous solution with PVP (M_w = 10,000).

The composition and structure of the synthesized catalysts were determined by SEM, Mossbauer and IR-Fourier spectroscopy. A Vertex 70v IR Fourier spectrometer (Bruker, Germany) with a computer-based system for recording and processing spectra was used.

The reactions of phenol with oxygen on the nanocomposites stabilized with PEI were carried out according to a widely used method described in the scientific literature, including our previous works [5, 16, 23, 24], in a duck-type thermostated glass reactor. During and after the experiment, the samples of intermediate and final products were analyzed for the presence of phenol and benzoquinone by UV and IR spectroscopy.

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3. Results and discussion

3.1. Results of physicochemical studies

For the Fe-Co/Al_2O_3 sample (Figure 1), according to the SEM analysis, areas with an increased iron content were found, which confirms the results of the elemental analysis (Figure 2, Table 1).

In the diffraction pattern of the Fe-Co/Al_2O_3 sample (Figure 3), the signals related to iron oxide, cobalt in the region of 2θ = 50–55°, and a shoulder corresponding to the unknown phase in the region 2θ = 40–45° are seen. The diffraction peaks for cobalt oxide correspond to Co_3O_4 spinel [28, 29, 31–33] (Table 2).

Detection of hydrocarbon by elemental analysis in the case of a $CoFe_2O_4$ catalyst stabilized with PVP shows that there is an interaction between nanoparticles and polymer, indicating efficient formation of nanocomposites (Figure 4, Table 3) [34, 35]. According to an IR study, for the $CoFe_2O_4$ nanocomposite stabilized with PVP, the absorption bands in the region of 600–800 cm^{-1} are due to the stretching vibrations of the Fe–O bond in oxides. The absorption bands at 735, 663, 649, 626 cm^{-1} are natural vibrations for composite nanoparticles embedded in a polyvinylpyrrolidone matrix.

Table 1 Elemental analysis of the Fe-Co /Al_2O_3 sample.

Spectrum	Na_2O	Al_2O_3	Cl	Fe_2O_3	CoO	Total
1	0.21	71.33	0.00	19.90	8.56	100.00
2	0.34	94.07	0.00	4.20	1.39	100.00
3	0.36	93.36	0.00	4.63	1.66	100.00
4	0.23	95.77	0.00	1.38	2.62	100.00
5	0.36	98.29	0.00	0.09	1.26	100.00
6	0.23	98.30	0.00	0.08	1.38	100.00
Average	0.29	91.95	0.00	5.05	2.81	100.00

Table 2 The diffraction date of the Fe-Co /Al_2O_3 and nanocomposite with PEI samples.

Sample	Reflections, Å	Phase
Fe-Co/Al_2O_3	3.48, 2.37, 2.08, 1.74, 1.60, 1.51, 1.40, 1.37, 1.23, 1.18	Al_2O_3 (ASTM 71-1123).
	2.71, 2.51, 2.20, 1.84, 1.69, 1.59, 1.48, 1.45, 1.30	hematite α-Fe_2O_3 (ASTM 13-534).
	5.52, 4.28, 2.85, 2.76, 2.71, 2.55, 2.51, 2.37, 2.13, 2.06, 1.43, 1.23	Co_3O_4 (ASTM 80-1535).
nanocomposite with PEI	2.96, 2.53, 2.09, 1.71, 1.61, 1.48, 1.32, 1.27	γ-Fe_2O_3 (ASTM 5-637).
	2.70, 2.53, 1.84, 1.48, 1.45, 1.30, 1.18	α -Fe_2O_3 (ASTM 13-534)
	2.98, 2.73, 1.38	ε-Fe_2O_3 (ASTM 16-653)
	4.29, 2.87, 2.73, 2.65, 2.38, 2.36, 2.04, 1.43, 1.23	Co_3O_4 (ASTM 80-1535)

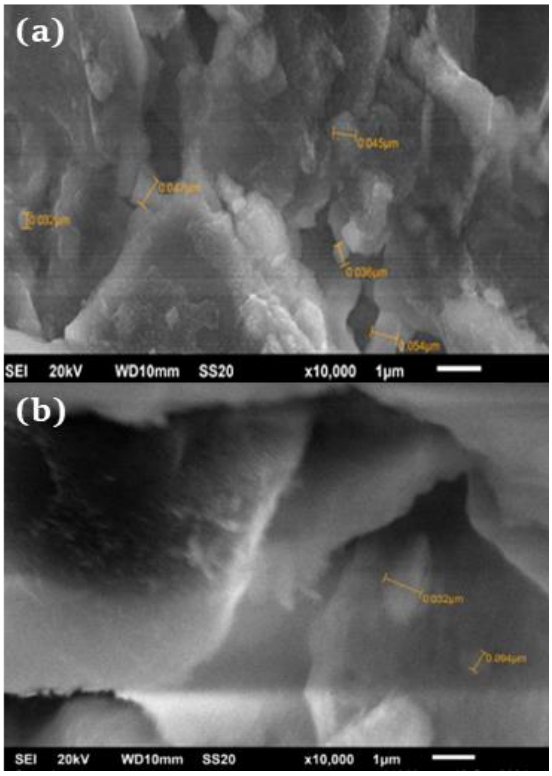

Figure 1 Results of SEM analysis: $CoFe_2O_4$ (a), Fe-Co/Al_2O_3 (b).

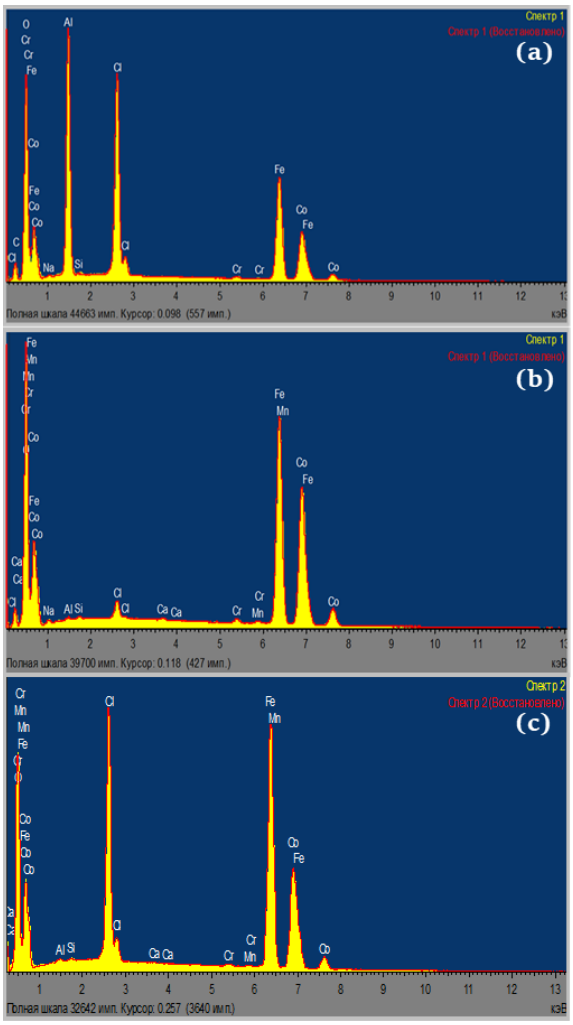

Figure 2 X-ray fluorescence analysis of the samples: Fe-Co/Al_2O_3 (a); $CoFe_2O_4$ (b); $CoFe_2O_4$/PEI (c).

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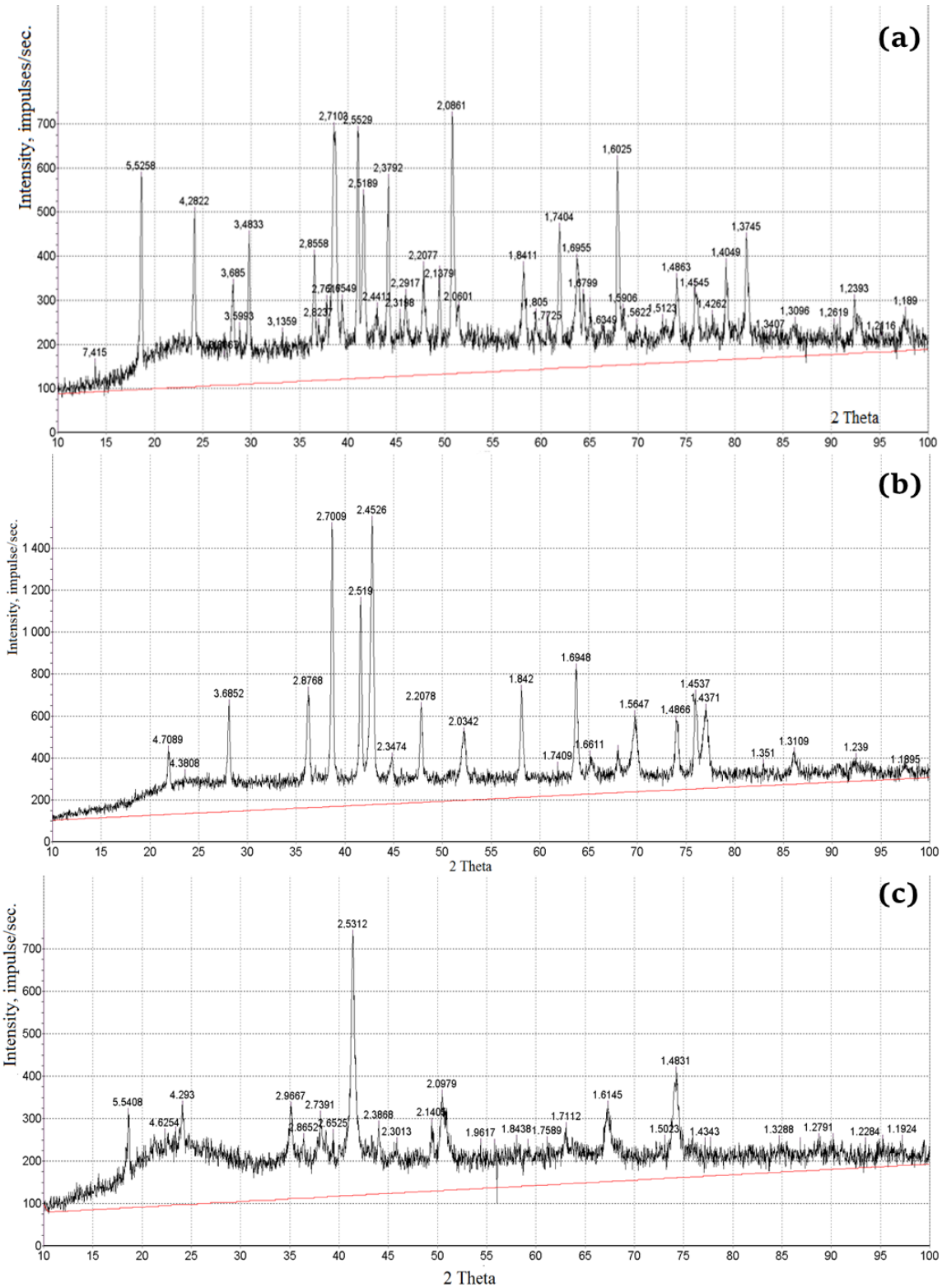

Figure 3 The diffraction patterns of: Fe-Co/Al_2O_3 sample (a); $CoFe_2O_4$ composite (b); $CoFe_2O_4$/PEI composite (c).

Table 2 Elemental analysis data of the $CoFe_2O_4$ catalyst stabilized with PVP.

Element number	Element symbol	Element name	Atomic conc.	Weight conc.
6	C	Carbon	24.869	10.600
8	O	Oxygen	42.794	24.300
26	Fe	Iron	23.157	45.900
27	Co	Cobalt	9.180	19.200

Bands characteristic of PVP at 1657 cm^{-1} (amide Raman band), 1498, 1461, 1423, and 1372 cm^{-1} (deformation vibrations of CH_2 groups in the pyrrolidone cycle) and 1287 cm^{-1} (Amide III–C–H bending vibrations) were found in the polymer matrix with slight shifts compared to pure PVP [36, 37]. This probably indicates that PVP forms a composite together with the ferrite nanocrystals. Thus, the inclusion of $CoFe_2O_4$ nanoparticles in the PVP matrix leads to a shift of some absorption bands in the nanocomposites.

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3.2. Testing of the synthesized nanocomposites in the oxidation of phenol

The synthesized nanocomposites were tested in the oxidation reaction of phenol with oxygen (Figure 5). Catalytic activity of the magnetic nanocomposites with composition Fe_3O_4, $CoFe_2O_4$ and $CoFe_2O_4$/PEI was checked in the process of phenol oxidation (C_{phenol} = 0.003 mol/L).

Brief interpretation of the IR spectra of phenol and reaction products after oxidation with oxygen in the presence of a $CoFe_2O_4$/PEI nanocomposite (Figure 6):

For phenol: IR spectrum: valence oscillations OH – in the area 3385–3610 cm^{-1}, 3390–3395 cm^{-1}; valence vibrations of C–O are in the fields of 1220–1232 cm^{-1} and 1240–1245 cm^{-1}.

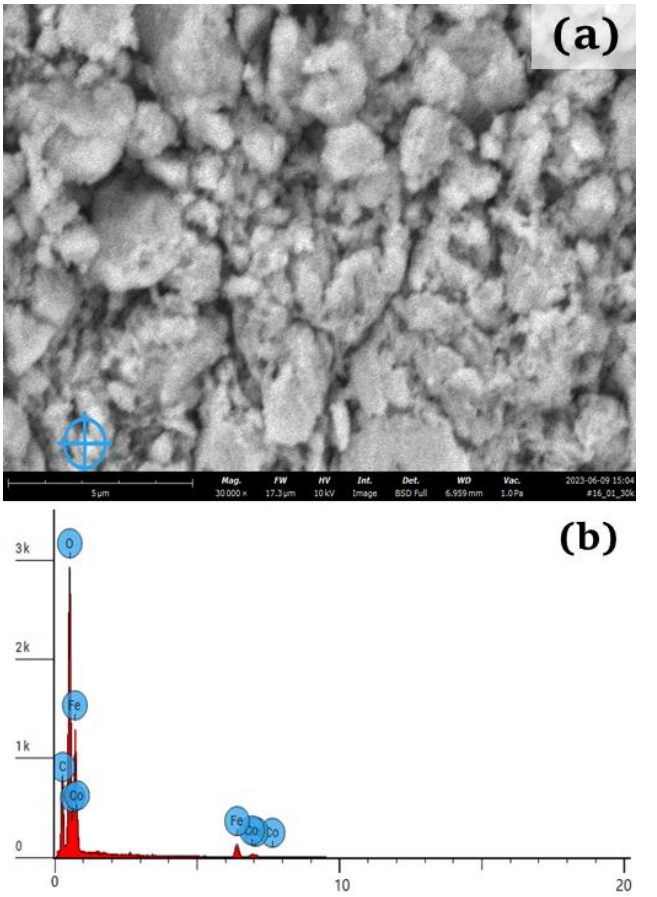

Figure 4 Results of physicochemical studies of the $CoFe_2O_4$ catalyst stabilized with PVP: SEM image (FW: 17 μm, Mode: 10 kV – Image, Detector: BSD Full) (a); X-ray fluorescence spectrum (b).

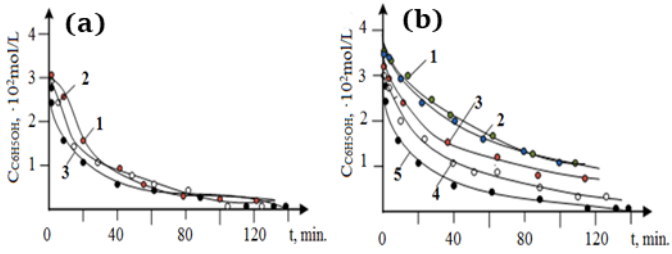

Figure 5 Oxidation of phenol with oxygen: oxidation on systems of different composition (a): Fe_3O_4 (1); $CoFe_2O_4$ (2); $CoFe_2O_4$/PEI (3); oxidation on $CoFe_2O_4$/PEI at different reaction temperatures (b): 303 K (1), 313 K (2), 323 K (3), 333 K (4) and 343 K (5).

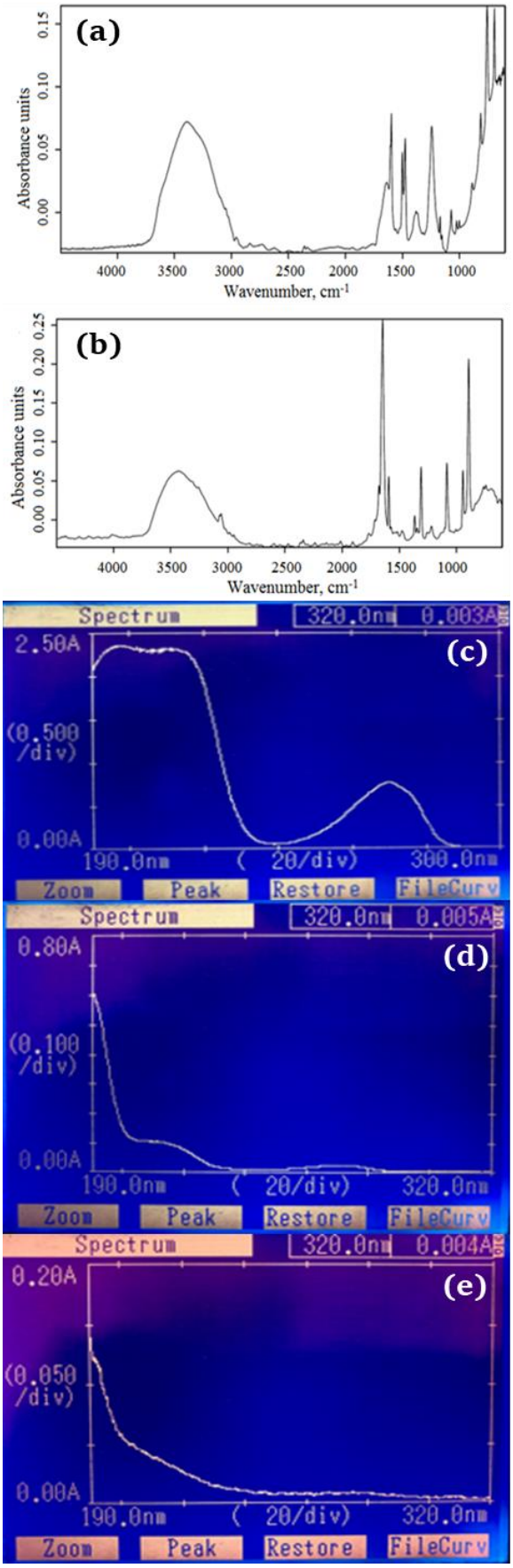

Figure 6 The results of the analysis of the reaction medium for the oxidation of phenol with oxygen: IR spectrum of the starting material, phenol, before the reaction (a); IR spectrum of the final sample after the phenol oxidation reaction (b); UV spectra: pure phenol (c); after 1 hour of oxidation (d); after 2 hour of oxidation (e).

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UV spectrum data: 210 (ε = 6200 L/mol·cm) and 270 nm (ε = 1450 L/mol·cm). There are absorption bands characteristic of phenol in the region 192–194/210–2011/265–270 nm (Figure 6a).

The results of IR and UV spectroscopy indicate the presence of CH in the aromatic ring and C=C double bonds, as well as valence vibrations of C=O groups of carbonyl compounds [16, 38–42].

The absorption band of double bonds C=C was found at 3050–3060 cm^{-1}. The oscillation band of hydroxyl groups of hydroquinone, the intermediate product of phenol oxidation is at 3420–3425 cm^{-1}. The vibrations in the C=O bonds of the carbonyl group of benzoquinones were at 1676 cm^{-1}, 1648 cm^{-1} (intense band).

The vibration bands of the C–H and C–C bonds of the quinone ring are at 1365 cm^{-1} and 1312 cm^{-1}.

The UV spectrum of the sample during the reaction shows bands in the 207–210/213 nm region (Figure 6b) and a plateau in the 270–275 nm region [16, 40–42].

Thus, according to the UV and IR spectroscopy data, the magnetic composites have good catalytic activity during the oxidation of phenol with oxygen. It was concluded that among the magnetic nanocomposites of the Fe_3O_4, $CoFe_2O_4$ and $CoFe_2O_4$/PEI compositions, the most efficient oxidation of phenol is observed in the presence of the $CoFe_2O_4$/PEI nanocomposite.

4. Limitations

The magnetic properties of stabilized magnetic composites are determined by many factors, such as the chemical composition, the type of crystal lattice, the size and shape of particles, and the interaction of particles with the surrounding polymer matrix.

By changing the size, shape, composition, and structure of nanoparticles, it is possible, within certain limits, to control the magnetic characteristics of materials based on them.

However, it is not always possible to control all these factors during the synthesis of nanoparticles of approximately the same size and chemical composition, which means that the properties of stabilized magnetic composites may differ.

During synthesis, magnetite can be oxidized to maghemite, but it tends not to oxidize completely even during prolonged heating. In the process of obtaining nanoparticles, the question of their stabilization always arises, which limits the further growth of the solid phase. Therefore, it is difficult to determine the optimal reaction conditions, including the type of reaction, solvent, temperature and surfactants, in particular polymers, which react selectively at the resulting phase boundary.

5. Conclusions

It is known that good results in the purification of industrial wastewater from phenol can be obtained by using catalysts. Among the most promising catalysts are nanodispersed catalytic systems and magnetic composites based on metal oxides. Within the framework of this research the nanocomposites of Fe_3O_4, Fe-Co/Al_2O_3 and $CoFe_2O_4$ were synthesized. The composites of $CoFe_2O_4$ stabilized with polyethylenimine or polyvinylpyrrolidone were prepared and used for oxidation of phenol with oxygen. According to IR-spectroscopy, there was the presence of C=O bonds of the carbonyl group of benzoquinone and C–H and C–C bonds of the quinone ring in the products of phenol oxidation with oxygen. Based on the results of phenol oxidation, it can be concluded that magnetic composites based on iron and cobalt immobilized by polymers are promising catalysts for wastewater treatment from organic compounds, including phenol, as well as for the targeted synthesis of oxygen-containing compounds.

• Supplementary materials

No supplementary materials are available.

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• Conflict of interest

The authors declare no conflict of interest.

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