CHAPTER 7

Impregnation of Iron and Magnetite Phases in Wood and Partial Pyrolized Wood

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ABSTRACT

Nanoiron-containing adsorbents have been widely used for cleaning of waters contaminated with organic and inorganic pollutants. Nanoiron can be spread over an organic and inorganic liner. Using renewable bioresources (timber, agricultural wastes, waste of biotechnological processes, etc.) to obtain sorbents containing nanoiron and iron oxide is quite promising. Iron-containing sorbents were obtained using *Alnus incana* wood. To avoid the emission of organic components from the wood into water, their partial pyrolysis was carried out with the formation of 1–3 mm coal layer. 13–17% of iron was impregnated in pyrolyzed and non-pyrolyzed samples. Impregnation was performed by 0.2 M $FeCL_3 \cdot 6H_2O$ and 0.2 M $Fe(NO)_3 \cdot 9H_2O$ solutions. Reduction of impregnated in the wood Fe^{+3} ions to nanoiron was carried out by $NaBH_4$ in an inert atmosphere. By this method, polyfunctional sorbents like Fe/wood and Fe^0/C/wood were obtained. Fe_3O_4/C/Wood type sorbents were obtained by pyrolysis of $Fe(NO_3)_3$–wood complexes. The nanoiron was spread on wood linen by passing steam of iron (0) pentacarbonyl at 150–200°. Wood–$Fe(CO)_5$ system fibers composed from spatial grains are formed in an autoclave during heating. Magnetite partially impregnated into

the wood. The obtained sorbents easily cause degradation of halogenated organic pollutants (1,4-dichlorbenzol and 4-bromanaline) and completely remove Cu^{+2} ion from model solutions.

7.1 INTRODUCTION

Various organic and inorganic substances dramatically increase pollution of soil, water, and air due to anthropogenic activity. One of the biggest problems of the modern world is water pollution by industrial, urban, and agricultural waste flows. The most of enterprises operating in Georgia do not remove organic and inorganic pollutants from wastewaters. Application of methods used in foreign countries is limited due to their high cost. However, these problems can be partially solved through the preparation of mono- and multifunctional sorbents in Georgia. The existing environmental situation, especially in terms of water pollution requires the installation of effective purification systems. Obtaining effective multifunctional sorbents is foreseen based on modern civilization experience. Application of unique properties of nanozerovalent iron (nZVI) is considered as one of the upcoming trends in technology for cleaning of wastewaters. It has been established that the nZVI in water undergoes some transformations by the following scheme:

$$2Fe^0_{(s)}+4H^+_{(aq)}+O_{2(aq)}\rightarrow 2Fe^{2+}_{(aq)}+2H_2O_{(l)}Fe^0_{(s)}+2H_2O_{(l)}\rightarrow 2Fe^{2+}_{(aq)}+2H_{2(g)}+2OH^-_{(aq)}4Fe^{2+}_{(aq)}+4H^+_{(aq)}+O_{2(aq)}\rightarrow 4Fe^{3+}_{(aq)}+2H_2O_{(l)}4Fe^{2+}_{(aq)}+2H_2O_{(l)}+O_{2(aq)}\rightarrow 2Fe^{3+}_{(aq)}+2H_{2(g)}+2OH^-_{(aq)}$$

nZVI acts as a reducing agent because of its standard reduction potential (E°_{h} = 0.44 V). Standard reduction potential for dehalogenation half-reaction of various alkyl halides ranges from +0.5 to +1.25 V at pH = 7, so the reaction goes to the following direction:

$$Fe^0 + RX + H^+ \rightarrow Fe^{2+} + RH + X^+$$

As a result, chloro-organic compounds are converted into hydrocarbons, which are easily degraded by biochemical processes or removed from water by physical procedures. Iron nanoparticles with the surface of 500–2000 m^2/g represent reducing agents for heavy metal ions and easily participate in redox reactions. For example, reduction of $Cr_2O_{7-}{}^2$ or $CrO_{4-}{}^2$ is implemented by the following scheme [1–8]:

$$Cr^{6+} + Fe^{0} \rightarrow Cr^{3+} + Fe^{3+}(1\text{-}x)Fe^{3+} + xCr^{3+}$$
$$+ 3H_2O \rightarrow CrxFe(_1\text{-}x)(OH)_{3\downarrow} + 3H^{+}$$

Part of these issues is a well-known worldwide practice, but to achieve their final practical application in our conditions (and also in our neighborhood regions) it is necessary to conduct comprehensive scientific research for the development of new technological processes.

The content of inorganic and organic pollutants in the environment depends on different types of production and the quality of the water pollution. Therefore, in each case, appropriate sorbents and purification technologies must be adopted. It is possible to remove inorganic and organic pollutants from wastewaters separately or simultaneously through mono- and multi-functional sorbents, which will be hybrid systems containing organic-inorganic or inorganic components. It is well known that biosorbents obtained from renewable bio-resources can remove ions of heavy metals from polluted water [9–21]. Biosorbents obtained by us from wastes of oak (*Quercus*), hornbeam (*Carpinus*), poplar (*Populus italic*, *populous pyramidalis*), plane tree (*Platanus*) and beech (*Fagus*) wood processing) have been tested for removing of Crions from waters [22–24]. Removal of chromium from wastewaters of the tannery is a topical challenge: chromium sulfate (basic) is used in the leather production technology of Georgian tanneries. Only 60–70% of chromium is used in leather, all the rest appear in the wastewaters. From the local inorganic mineral resources, it is possible to use aluminosilicates (zeolite tuffs, clays, etc.); renewed bioresources often are used as heavy metal adsorbents, but they have less degradation ability for organic pollutants. For assigning of multi-functional properties to natural biosorbents, the necessary components should be added, which will increase their ability to absorb heavy metal ions and degraded organic pollutants. It is necessary to impregnate nZVI or iron-containing compounds (oxides, hydroxides) into biosorbents and as a result, inorganic-organic sorbents will be created. Mild chemical modification of biosorbents (including partial pyrolysis of wood) is also necessary with the aim of making lining inert towards active component–nanoiron and to avoid its deactivation. This article applies to the development of methods for impregnation of ultradispersed powders of iron and magnetite into the wood and partially pyrolyzed wood.

7.2 EXPERIMENTAL

$FeCl_3{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $NaBH_4$, $Fe(CO)_5$ purchased from Sigma Aldrich were used. The microstructure of the samples was studied by optical and

scanning electron microscopes (Nikon ECLIPSE LV 150, LEITZ WETZLAR and Jeol JSM–6510 LV-SEM). Samples X-ray diffraction (XRD) patterns were obtained with a DRON–3M diffractometer (Cu-Kα, Ni filter, 2°/min). Fe content has been established by ISO–11047–1998 standard with atomic-absorption spectrophotometer AA 350. Water sampling and pre-processing was carried out in accordance with the ISO 11466 standard.

1. **Partial pyrolysis of wood**: Partial pyrolysis of wood was carried out by the flame and in a high-temperature Kejia tube furnace at 300–1000°C. Duration of flame pyrolysis was 5–30 sec. Pyrolysis in the inert area was carried out in a previously heated furnace for 10–30 min. A volume of sample was 1–3 cm^3 and charcoal deepness–0.5–3.4 mm.
2. **Impregnation of Iron (III) compounds in the wood:** Impregnation of Iron (III) compounds in the wood, and charcoaled wood samples were carried out by using 0.2 M solution of $FeCl_3 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ during 48 h. After filtration, samples were dried at room temperature. Crystallization of salts on the surface of the sample was not noticed.
3. **Reduction of impregnated iron compounds using sodium borohydride:** Reduction was carried out in desiccator like a reactor, with three-necked removable lid. Samples were placed in a glass reactor with a 50% Ethanol-water solution. Samples were sinking in solution by using a hollow plastic plate. The reactor was cooled with ice water, and 0.5 M $NaBH_4$ were added. Mole ratio Fe^{+3}:$NaBH_4$=1:15. Reduction time 8–10 h. Samples were separated from the solution, washed with ethanol and dried in vacuum at 50°C 8 hours. Ultra-dispersed iron powder separated from samples was washed with ethanol and dried in vacuum for 2 h.
4. **$Fe(NO_3) \cdot 9H_2O$-wood, and $Fe(NO_3) \cdot 9H_2O$-partially pyrolyzed wood samples reduction in hydrogen flow**: Samples reduced in hydrogen flow were carried out into a high-temperature vacuum furnace (Kejia Furnace). Samples were placed in the furnace and 5 min after argon, and then argon/hydrogen mixture (50:50) were inputted. The temperature was increased up to 250–450°C with a heating rate of 10°C min^{-1}. Reduction of samples continued for 30 min at the highest temperature, and rapid cooling was achieved by moving samples in a cool part of the furnace.
5. **Impregnation of nanoiron in supports by using iron (0) pentacarbonyl:** Impregnation of supports with iron was carried out

at low temperature (150–200°C) by passing a vapor of $Fe(CO)_5$. 5ml of $Fe(CO)_5$ was placed in the gas bubbler and heated to 50–55°C in the area of argon. Carbonyl vapor flows through a quartz pipe where samples of supports are placed. Impregnation of supports with nanoiron continues for 60 min. During this process, partial pyrolysis of supports and decomposition of iron (0) pentacarbonyl take place.

6. **Pressure treatment of $Fe(CO)_5$:** Wood samples were placed into flask and 5ml of iron (0) pentacarbonyl was added. The mixture was stirred on a magnetic stirrer for 12 h at room temperature in the area of argon. Samples without drying were transferred to 0.5 L high-pressure reactor (autoclave, the inner surface is covered with Teflon) in the area of argon. Operative conditions were: pressure 5 atm, temperature 200°C, time 2 h. Obtained Fe_3O_4 was deposited on wood and reactor walls.

7.3 RESULTS AND DISCUSSIONS

As a research object was used samples of *Alnus incana* wood (Georgia, Gonio). After drying at 105°C, samples were treated with 0.2 M $FeCl_3 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ at ambient temperature during 48 h. Impregnated samples were dried at room temperature. The deepness of vertically impregnated with salts wood capillaries was 3–5 mm, while horizontal migration of iron ions was just 0.5–1mm. Results are visible on a slice of wood sample. Limit of impregnation is more contrast when the surface of the wood slice is treated with a dilute solution of KSCN or NH_4SCN. SNC^- ions are used for qualitative analysis of Fe^{+3} ions. Reduction of wood samples size or mechanical destruction of structure leads to complete impregnation. XRD and SEM analysis show that wood retains structure, but iron content varies in a large range. When Iron (III) nitrate was used, the content of iron was 6.5–13.6% m/m, in average 9.47% (Figures 7.1–7.4).

It should be noted that the atomic ratio of N:Fe and Cl:Fe is more than 1, quite different from stoichiometry ratio in salts (3:1). We can conclude, that impregnation causes interaction between salts and supports. EDX analysis shows that iron content and ratio (Fe:N and Fe:Cl) is different in different part of the wood. XRD analysis shows–that there are no separate phases of salts–products of hydrolysis or products obtained by the interaction of functional groups (hydroxyl, phenolic OH, carboxyl, amide) presented in wood. The same results were obtained in case of iron (III) chloride. The content of iron varies 13.8–22.2%, average–17.44%, which is obviously more than in case of impregnation by using iron (III) nitrate.

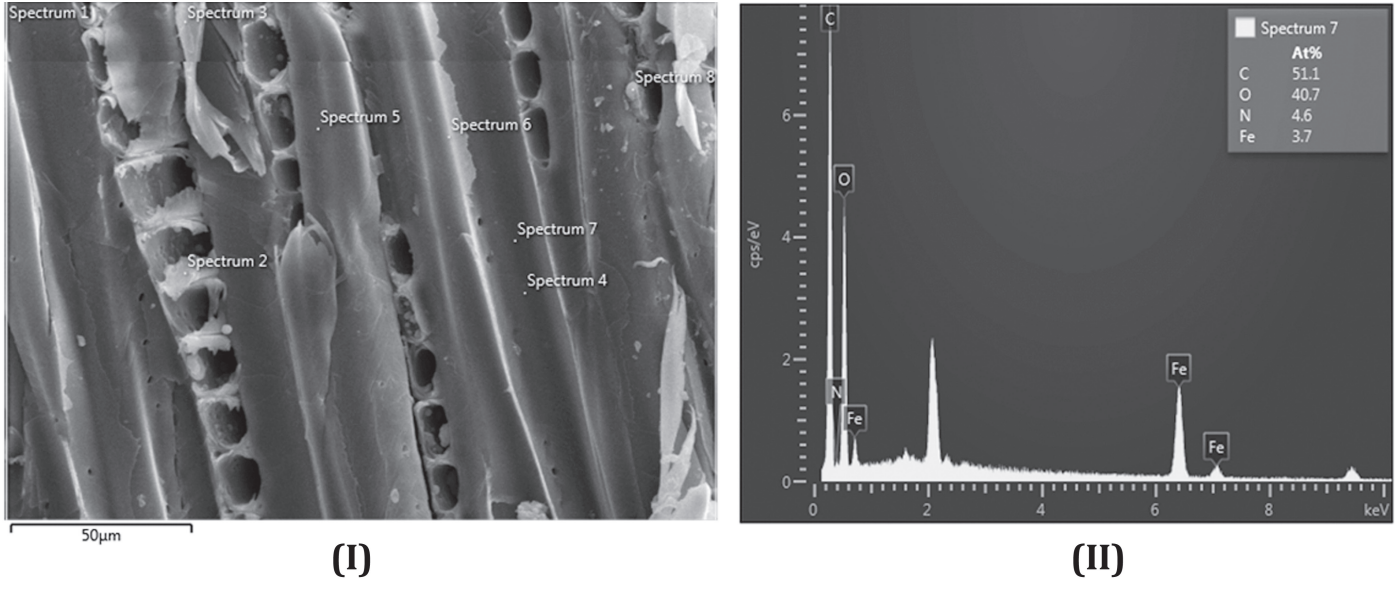

FIGURE 7.1 SEM micrograph (I) and EDX spectrum (II) of $Fe(NO_3)_3$-Wood systems.

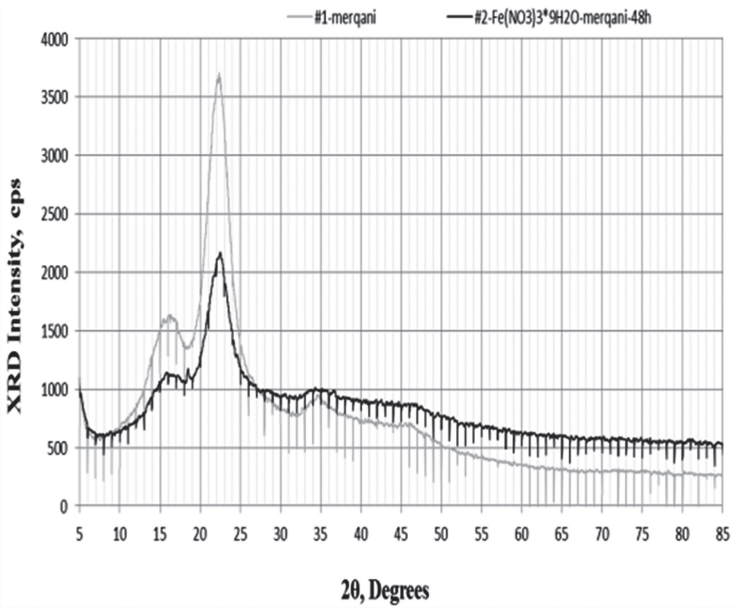

FIGURE 7.2 XRD patterns of Wood (yellow) and $Fe(NO_3)_3$-Wood (red) systems (I).

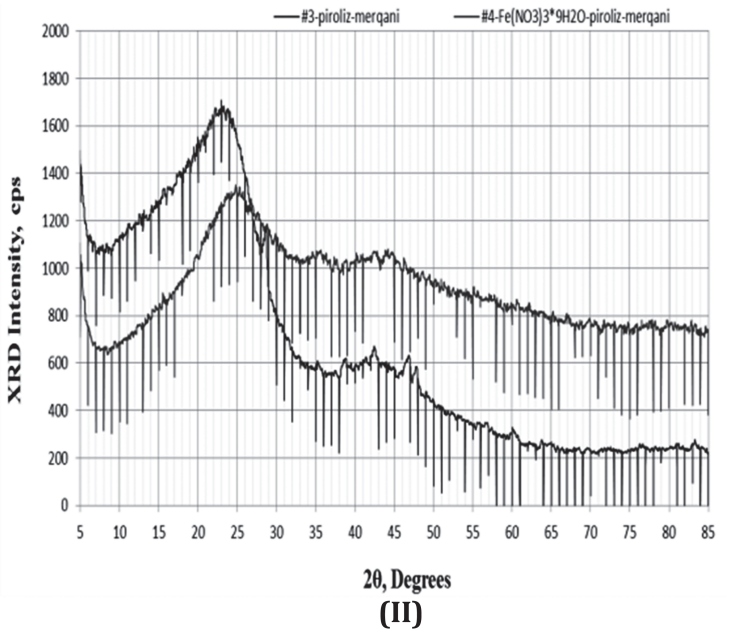

FIGURE 7.3 XRD patterns of partial pyrolyzed wood (blue) and $Fe(NO_3)_3$-partial pyrolyzed wood systems (450°C, 30 min.),(II, red).

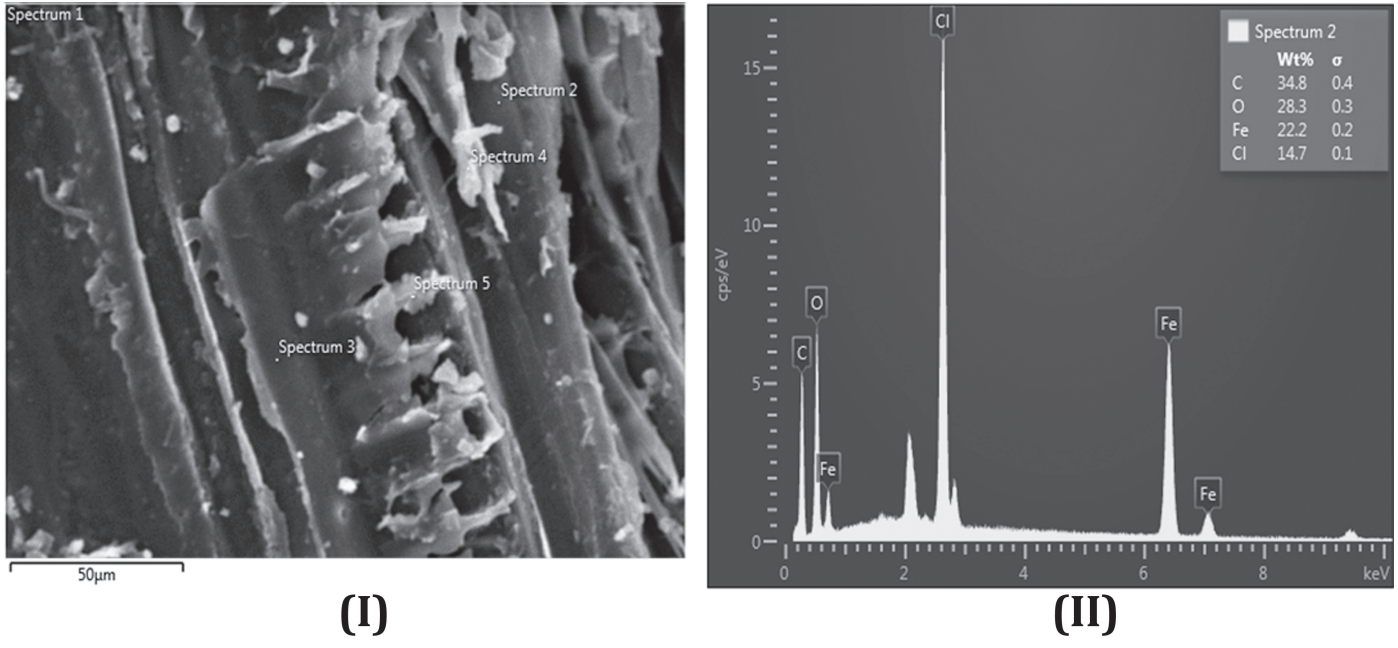

FIGURE 7.4 SEM micrograph (I) and EDX spectrum (II) of $FeCl_3$-wood systems.

Certain changes in structure and chemical composition take place during partial flame pyrolysis or pyrolysis in the inert area. At the same time, the morphology of the charcoal layer is similar to initial wood (Figure 7.5). During rapid flame pyrolysis (10–30 sec) the only surface forms charcoal, the lower surface remains unchanged, the formation of charcoal on the lateral surface is not significant. Fe^{+3} ions migrate in sample volume from any side during impregnation. Reduction of these ions leads to obtaining nanoiron impregnated sorbents. One part of this surface is Fe^0/wood, but another part –Fe^0/C. In common, Fe^0/wood surface adsorbs heavy metals, Fe^0/C adsorbs heavy metals and organic pollutants, but they easily degraded by nanoiron. Thus, polyfunctional sorbent for inorganic (radionuclides) and organic pollutants are obtained, by using this method.

In inert area, partial pyrolysis occurs on the surface, and charcoal layers are obtained. Its impregnation with $Fe^{+3}$and further reduction with $NaBH_4$ gives adsorbents with surfaces Fe^0/C.

Thus, partial pyrolysis makes it possible to receive polyfunctional sorbents. It was established that rapidly pyrolyzed wood sample (700°C, 30 sec) adsorbs 12.26% (mass) of iron from $FeCl_3$ solution. These results are less than for unpyrolyzed samples (17.44%). It may be explained by the hydrophobicity of the charcoal layer. Pyrolysis of wood-$Fe(NO_3)_3$ samples gives sorbents impregnated with iron oxides. Such sorbents are perspective for removing different pollutants from wastewaters.

Iron (0) pentacarbonyl was used for low-temperature nanoiron impregnation of supports. Ultrasonic decomposition of iron (0) pentacarbonyl is one of the easiest methods for deposition of iron on the supports [25]. Iron was deposited on the surface of wood samples by passing iron (0) pentacarbonyl through a quartz pipe (Figure 7.6). 6.3% of iron was deposited when pentacarbonyl/Ar mixture was used (200°C). Composite Fe^0/wood particles are paramagnetic and were easily moved through the water by the effect of the magnetic field. The same process was used when cotton fiber was impregnated with iron (0.3%).

Iron pentacarbonyl was easily decomposed, and iron, iron oxides, and carbides were formed. In a closed system in the presence of wood samples iron (0) pentacarbonyl gives iron (II, III) oxide (magnetite), because it undergoes oxidation by organic compounds and water released from the wood (Figure 7.6). Partial pyrolysis of organic components of the wood takes place, so magnetite powder contains carbon (7% m/m). Magnetite is formed in the whole volume of the autoclave. Just 8% iron is impregnated in wood. Most part of Fe_3O_4 has fiber structure and contains spherical grains (2–4 μm); in turn, it contains nanosize (50–200 nm) primary crystallites (Figures 7.7 and 7.8).

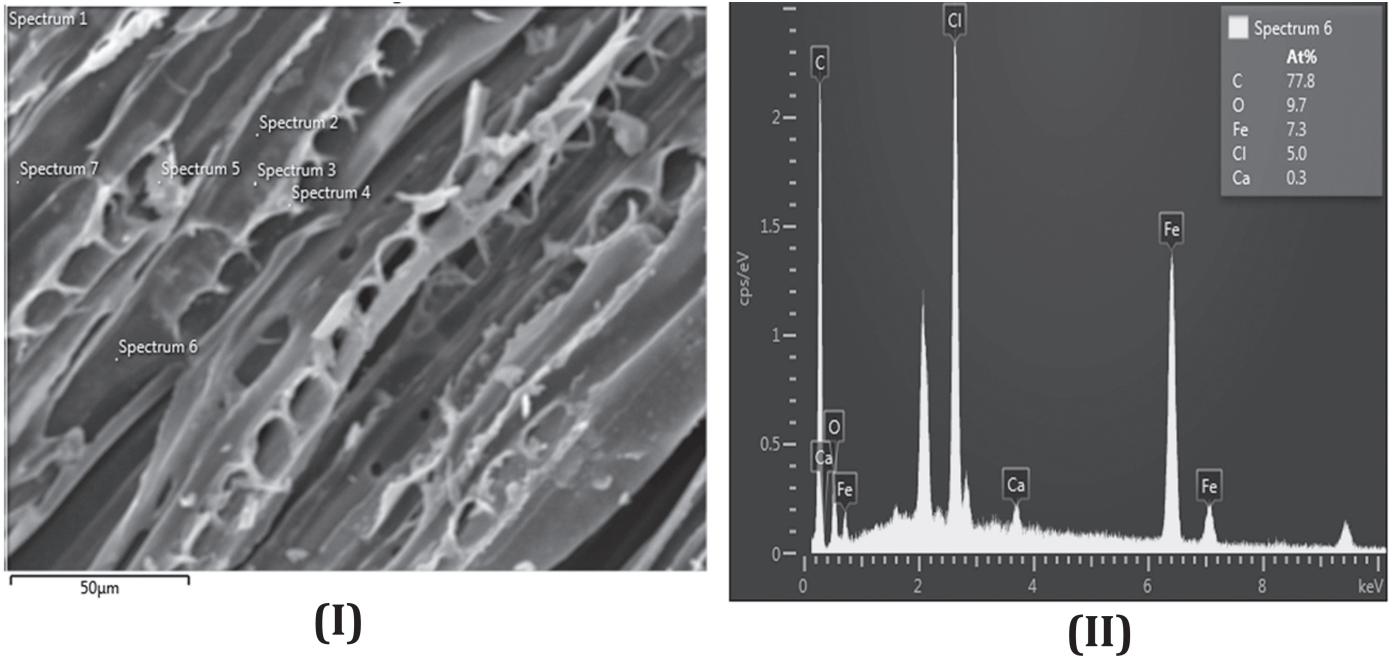

FIGURE 7.5 SEM micrograph (I) and EDX spectrum (II) of $FeCl_3$- partial pyrolyzed wood (450°C, 30 min) systems.

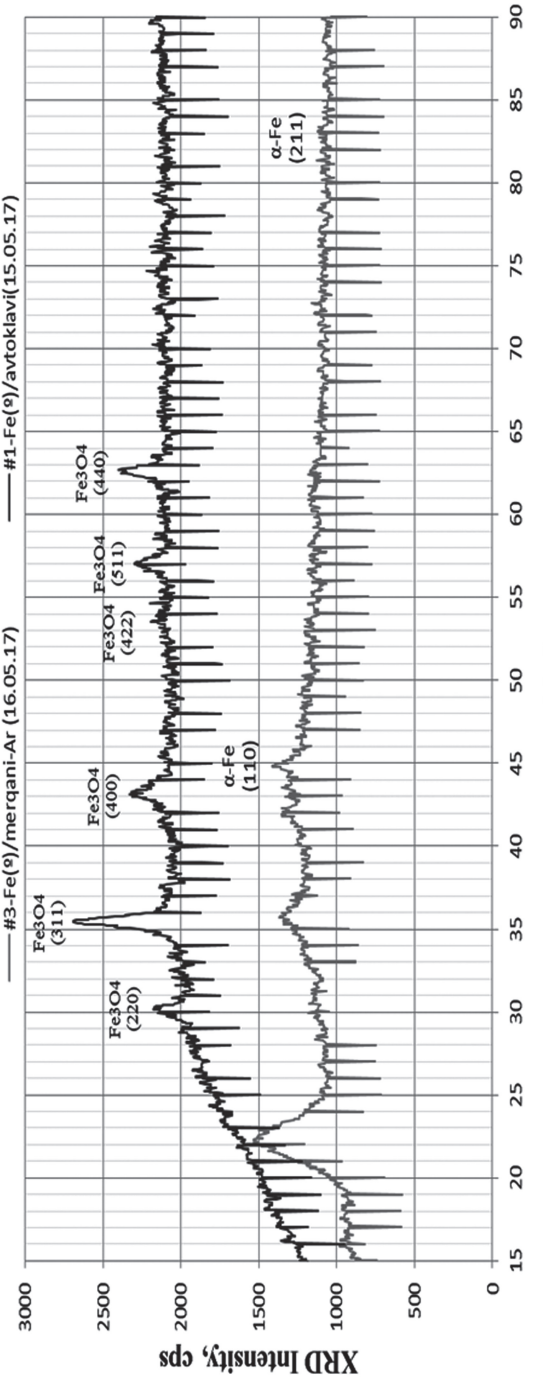

FIGURE 7.6 XRD patterns of Fe_3O_4 obtained from $Fe(CO)_5$ in an autoclave (200°C, 2 hr, red) and deposited ultra-dispersive iron (green) on wood with $Fe(CO)_5$ vapor flows into the quartz pipe.

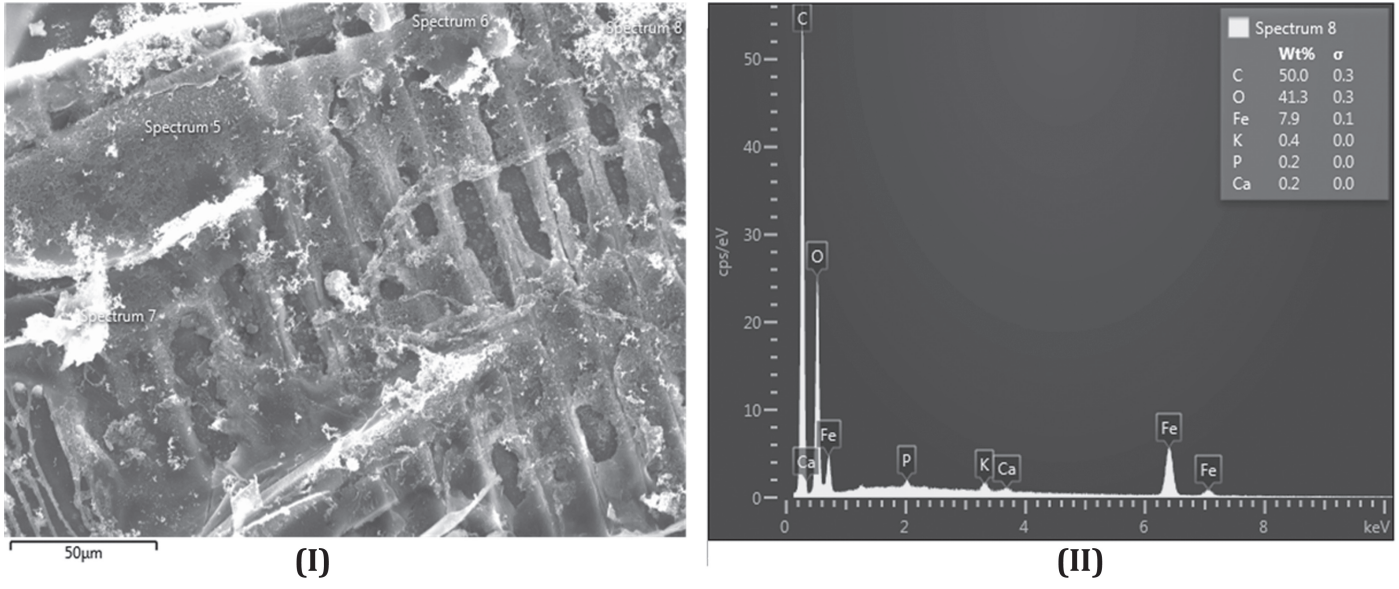

FIGURE 7.7 SEM micrograph (I) and EDX spectrum (II) of Fe_3O_4-wood systems (autoclave, 200°C, 2 hr).

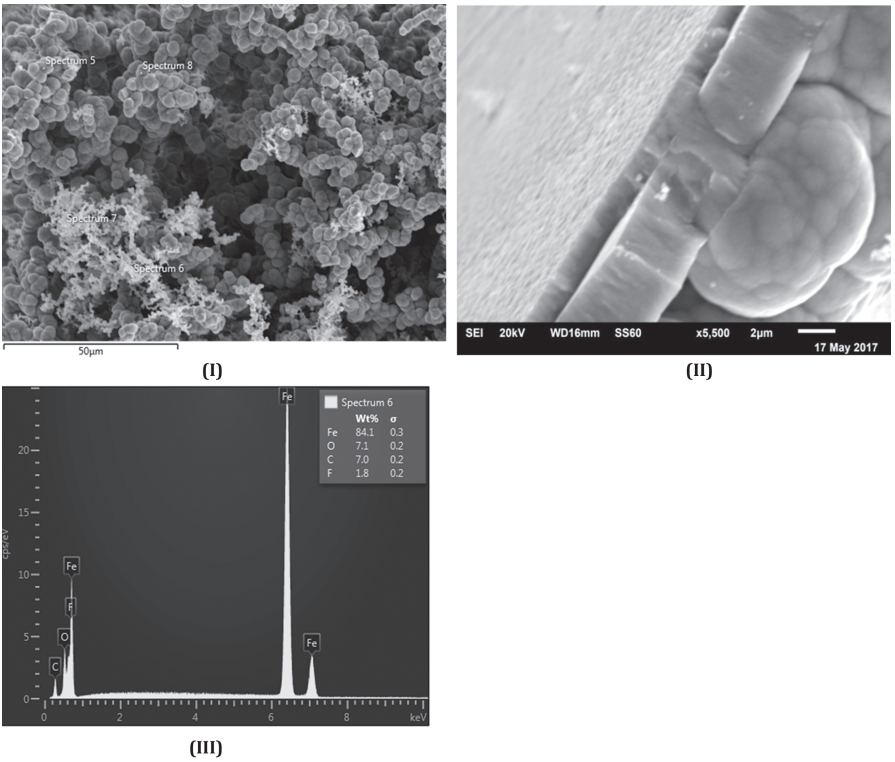

FIGURE 7.8 SEM micrograph (I, II) and EDX spectrum (III) of Fe_3O_4 obtained from $Fe(CO)_5$ in an autoclave (200°C, 2 hr).

The density of magnetite powders is 22–26 mg/ml. Iron content in powders attained to 81.55% m/m, but the content of iron in Fe_3O_4 is less (73%). XRD analysis shows that the formation of crystalline carbides from carbonyl is not noticeable. It is possible that magnetite powder contains an amorphous iron or other iron-containing phases. The obtained sorbents easily cause degradation of halogenated organic pollutants (1,4 dichlorbenzol and 4-bromanaline) and completely remove Cu^{+2} ion from model solutions.

7.4 CONCLUSIONS

Iron (III) nitrate and chloride are impregnated into the wood, and it's partially pyrolyzed samples. XRD and SEM analysis show that wood retains its structure, but iron content varies in wide ranges. When iron (III) nitrate

has used the content of Fe was 6.5–13.6% (average 9.47%). In the case of iron (III) chloride the content of Fe varies from 13.8 to 22.2% (average 17.44%). It was established that rapidly pyrolyzed wood sample (700°C, 30 sec) adsorbs 12.26% % of Fe^{+3} from $FeCl_3$ solution. These results are lower than for unpyrolyzed samples. This can be explained by the hydrophobicity of the charcoal layer. Pyrolysis of wood–$Fe(NO_3)_3$ samples gives sorbents impregnated with iron oxides. Iron was deposited on the surface of wood samples by passing iron (0) pentacarbonyl vapor through a quartz pipe. 6.3% of nanoiron was deposited when pentacarbonyl/Ar mixture was used (200°C). In the closed system and in the presence of wood samples $Fe(CO)_5$ gives iron (II, III) oxide (magnetite). Most of Fe_3O_4 has fiber structure and contains spherical grains (2–4 μm); moreover, it contains nano-size (50–200 nm) primary crystallites.

KEYWORDS

- **biosorbents**
- **impregnation**
- **iron**
- **iron oxides**
- **multifunctional sorbents**
- **organic and inorganic pollutants**
- **partial pyrolysis**
- **wood**

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