Recycling Phenolic Wastewater from Phenol-Formaldehyde Resin Production

I G Pervova¹, I A Klepalova¹, I N Lipunov¹

¹Department of physical and chemical technologies in environmental engineering of Ural State Forest Engineering University, Yekaterinburg, Russia

E-mail: pervovaig@m.usfeu.ru

Abstract. The sorption Phenolic wastewater is a kind of hazardous waste due to the presence of free phenol which is a highly toxic organic compound. Described in the literature and implemented, technology solutions for dephenolization are commonly based on thermal destruction. However, thermal treatment technologies have a range of disadvantages and the main ones of them are the losing of phenol and formaldehyde, which are valuable chemical raw materials and changing the balance of atmospheric oxygen and carbon dioxide. At the same time, owing to bonding properties, phenol and formaldehyde are used as polymer binders for manufacturing composite materials gradually replacing commercial synthetic resins. The paper presents results of the investigation related to developing a resource-saving technology for the recovery of phenol and formaldehyde from industrial phenolic wastewater by obtaining composite construction material and sodium phenolate. Sawdust and wastes from textolite manufacturing and processing were used as fillers and modifiers in a composite mixture. The presented technological process has been developed on the base of recycling using combined technologies through inter-industrial collaboration. This approach makes it possible to obtain high-quality recycled products from technogenic raw materials (degree of phenol conversion was 0.995) and to carry out complete dephenolization of the wastewater (residual phenol concentration was $2 \cdot 10^{-2}$ mg/l), which can be used in the wastewater reuse system for the main chemical manufacturing.

1. Introduction
Phenolic wastewater from chemical, coke-chemical, oil refining, electrical, and woodworking industries is considered as absolute hazardous since it contains free phenol, which is a highly toxic organic compound. The highest volume of the waste is created by Chemical industries including production of phenolic and phenol-formaldehyde resins (PR) which are widely applied as binders and adhesives in manufacturing wood-based panels, paints and varnishes, abrasive, refractory, heat and electrical insulating materials. The growing consumer demand for phenolic and phenol-formaldehyde resins drives the PR market. For example, over the last 10 years, the PR production for the woodworking industries in the Russian Federation increased by 55%. And this, in turn, has led to increasing in the volume of wastewater, which is characterized by phenol and formaldehyde concentrations, reaching values hundreds of times higher than the MACs. Since the MACs for phenol and formaldehyde in the water used for drinking, household, recreation, and fishing in the Russian Federation are limited to values ranged from $1 \cdot 10^{-3}$ to $5 \cdot 10^{-3}$ mg/l, phenolic wastewater has to be completely neutralized before the effluent is discharged to the natural water reservoirs. Otherwise, it...
has a negative impact on the environment, followed by the death of biota and deterioration of the hydrochemical regime of a reservoir.

The development of effective methods and technical solutions for neutralization of phenolic wastewater has gained increasing attention in the literature in the past number of years [1-8]. Phenolic wastewater has been attracting considerable interest from researchers due to high toxicity of phenolic compounds and the fact that up to now, there are not environmental friendly and economically viable technologies for dephenolization, that allow recovery of phenol and formaldehyde from a phenolic resin plant effluent and use recovered phenol as the valuable chemical raw material. Having implemented treatment technologies are commonly based on thermal destruction [9-11], the main disadvantage of such destruction is the losing of phenol and formaldehyde. Regenerative methods for treatment of the ammonia-tar liquor, for example, sorption or secondary polycondensation, cannot be recognized as satisfied technologies to be widely used in industries due to their low economic profitability or the low-quality resulting product [12-14]. Today, the ammonia-tar liquor is most often burned in cyclone-type installations, the process is power-intensive by nature so it is a high carbon source contributing greatly to changing the balance of atmospheric oxygen and carbon dioxide. The complete neutralization of phenolic wastewater from phenol-formaldehyde resin production remains one of the most urgent environmental challenges.

One of the promising solutions for dephenolization of phenolic wastewater to the environmentally safe standard value for phenol and almost complete conversion of it into chemically pure products is recycling, when industrial wastes are treated so that they can be used again as semi-finished products, products or secondary raw materials. Recycling of industrial wastes is a rapidly developing dynamic area in resource conservation in the countries of the EU and Asia (Japan, China) and it is considered as a priority sign of the scientific and technological development of any country, which is based on involving waste in further technological reusing as a technogenic raw material. Modern scientific and industrial development requires increasing use of not only natural, but also technological resources. In the future, chemical industries may come to zero-waste technologies; since it is almost always possible to develop such a recycling technology where waste from the main production can be continuously recycled, turning into raw material [15].

The purpose of this study was to develop a resource-saving technology for the recovery of phenol and formaldehyde from industrial phenolic wastewater by obtaining composite construction material and sodium phenolate. When developing technological solutions for the treatment of wastewater from PR production, we used the main provisions of the scientific [17, 18] and conceptual [16] foundations for industrial waste recycling through inter-industrial collaboration.

2. Objects and research methods
Phenol-formaldehyde resins are used as a polymer binder for wood-polymer composite production. Pressed wood pulp made of short chopped wood raw material and phenol-formaldehyde resin has been used for the electrical equipment manufacturing, as well as various products, including those for machines and mechanisms, made by the hot pressing method since the end of the 20th century [19]. Composite materials are composed of at least two base materials; one material is the reinforcement, the second is the binder, and the others are modifiers or plasticizers that affect the properties of the finished part.

The main task solved in this study is incorporating technogenic raw materials into manufacturing of wood-polymer composite which has physical, mechanical and operational properties similar to those for pressed wood pulp. The objects of the research are the following industrial wastes: phenolic wastewater from phenol-formaldehyde resin production; short chopped wood raw material; and shredded waste from the production and processing of laminated plastics. Phenol and formaldehyde containing in the wastewater serve as the polymer binder. Coniferous sawdust modified with a 25% solution of NH$_2$OH, a grain size distribution of 0.5–5.0 mm, was used as an effective sorbent and polymer reinforcement of natural origin, and shredded waste from the production and processing of textolite, dispersion of 0.15–3.0 mm, was used as a modifier. The content of phenol in the wastewater...
was in the range of 12.4–13.8 wt. %; such resins are used in the electrical industry to obtain sheet and wound electrical insulating materials.

Methods used for preliminary preparation of solid industrial wastes; chemical modification of wood waste; sorption extraction of phenol from sewage and condensate waters; analytical determination of phenol and formaldehyde; and mathematical description of isotherms and calculation of kinetic parameters for the sorption process were described in papers [20, 21]. The determination of the optimal technological parameters of the sorption and conversion of phenol into a wood-polymer composite was carried out by conducting a fractional factorial experiment; the design and interpreting of the results of which was carried out according to the method described in [22]. The parameter of dephenolization optimization is the residual concentration of phenol in condensate water, and the main factors are: the molar ratio in the reaction mixture of formaldehyde and phenol (\(\text{CH}_2\text{O}:\text{C}_6\text{H}_5\text{OH}\)), the mass ratio of the liquid to solid phases (L:S) and the process temperature.

The studies were carried out on a pilot laboratory setup in a static mode, the temperature in the reaction zone of a chemical reactor at the corresponding stages of the process was maintained in an automatic mode in the range of 60÷98 °C, the mass ratio L:S = 3÷5, and the molar ratio (\(\text{CH}_2\text{O})/(\text{C}_6\text{H}_5\text{OH})=(1.4÷2.9):(1)\). The degree of conversion of phenol (\(X_P\)) was calculated by the formula [23]:

\[
X_P = \frac{m_{P0} - m_P}{m_{P0}},
\]

where \(m_{P0}\) is the initial amount of phenol in waste water, g/l; \(m_P\) is the residual amount of phenol in condensate water, g/l.

The toxicity of aqueous extracts of the wood-polymer composite and products obtained on its base was carried out by the biotesting method using a synchronized model of *Daphnia magna Straus* and a day-aged culture of *Chlorella vulgaris beijer* [24].

3. Results and discussion

When developing a technological module for recycling phenolic wastewater, we used the results of earlier studies by the authors to study the physicochemical regularities of sorption extraction of phenol from aqueous solutions with both synthetic sorbents [20] and wood waste-based sorbents [21], as well as the polycondensation of phenol immobilized on the surface of a solid-phase filler with formaldehyde [25]. Based on the values of the static exchange capacity and the degree of affinity for phenol, calculated using sorption isotherms as well as kinetic and dynamic characteristics of sorption, the characteristic features of phenol extraction from waste and condensate waters were revealed. They were used for choosing the most effective sorbent for the developed technology.

The degree of phenol extraction (\(\eta\)) for all studied values of its concentration in aqueous solutions and optimal parameters of temperature and time of sorption is 2–2.5 times higher for the modified wood sorbent compared to the initial sorbent (Figure 1).

![Figure 1](image-url)  
**Figure 1.** Degree of sorption extraction of phenol by the initial (1) and modified (2) wood sorbent (\(t= 60 \degree\text{C}\); particle size distribution 0.5-5.0 mm; \(\tau = 15 \text{ min}\)).
The sorption efficiency of the modified wood sorbent is confirmed by the kinetic characteristics of phenol sorption from a solution containing 124 g/l of free phenol. For the modified sorbent, the rate constant of the phenol extraction process \( k = 1.19 \times 10^{-3} \text{ c}^{-1} \) at 60 °C is two times higher than for the initial sorbent \( k = 0.68 \times 10^{-3} \text{ c}^{-1} \). The value of the activation energy (14.3 kJ/mol) indicates that the phenol extraction by the wood sorbent occurs according to the external diffusion mechanism, and the calculated value of the diffusion coefficient \( 0.94 \times 10^{-6} \text{ cm/s} \) is characteristic of the adsorption of organic molecules [21].

These data have revealed what is the sorption advantage of the modified wood sorbent. It is known that the adsorption capacity of short chopped wood pulp to phenol, due to the reducing properties of its surface, depends on the value of its specific surface. The swelling capacity of sawdust in 25% NH₄OH solution increases by 1.5 times compared to the swelling capacity in water, which contributes to increasing in the specific surface area of the modified sorbent and, as a consequence, its adsorption activity. This is directly confirmed by the results of the experimental studies, showing the higher degree of phenol extraction by the modified sorbent (96 wt.%) compared to the original one (55 wt.) [21]. The immobilization of phenol molecules onto the surface of the wood sorbent results to the producing an intermediate product – wood phenolic oligomer, which has high chemical activity and is able to participate in the polycondensation reaction with formaldehyde containing in wastewater and additionally introduced into the reaction mixture as formalin solution.

The study of polycondensation characteristics of the wood phenolic oligomer with formaldehyde, which was additionally introduced into the reaction mixture in the form of a formalin solution, resulted to establishing the optimal values of the main factors influencing the degree of phenol conversion into wood polymer composite: the content of resin-forming components in phenolic water – 11÷15 wt. %; t = 98÷80 °C; νC₅H₅O : νС₆H₅OH = 2:1; mL: mT (hydromodule) – 3, modifier mass – 20 wt. % by weight of solid-phase filler. The process of polycondensation starts at temperature from 60 to 98 °C in the reaction zone, when chemical interaction of the wood-phenolic oligomer with formaldehyde molecules from the wastewater occurs. The introduction of a modifier into the reaction mixture contributes to the better kinetics of polycondensation and increases the composite performance indicator – its fluidity.

While drying the wood polymer composite, condensate water was formed; it contained residual phenol from 500 to 700 mg/l. In order to minimalize residual phenol content, the condensate water was subjected to sorption purification using synthetic ion-exchange materials as neutralized wastewater can be used in a recirculation water system in the main chemical production when residual phenol content is not higher than an environmentally acceptable standard value. Anion exchangers AV-17, AN-251 and the cation exchanger KU-36 have shown the highest sorption affinities towards phenol among the large number of studied ion exchangers. Established physicochemical characteristics of phenol sorption onto these ion exchangers under static and dynamic conditions are described in detail in [20]. The choice of KU-36 cation exchanger for dephenolization of phenolic water is justified by its higher dynamic characteristics of phenol sorption from condensate water in comparison with anion exchangers. All other things being equal (the rate of the solution filtration, the ratio of the diameter to the height of the ion exchanger layer, temperature), the value of the dynamic exchange capacity of the cation exchanger, the time of the protective action of its filter is 2.5 and 7 times, respectively, higher than that of the anion exchangers. The degree of regeneration of the spent cation exchanger with 2 N. solution of NaOH is 100%, and further processing of the resulting eluates allows to obtain the second target product of the utilization of phenolic waters - sodium phenolate.

Thus, the results of the experiments carried out have shown the real possibility for involving waste in further technological reusing industrial wastes from various industries through inter-industrial collaboration. Moreover, each specific waste, being a kind of a material object in the process of waste recycling, is characterized by its own chemical composition, life cycle and ability to regenerate [16]. The cycle-forming stage of recycling is the processes of genesis and transformation of waste [18], which are carried out in regeneration systems with the formation of a secondary resource (solid-phase
waste) and recuperation ones with the extraction of valuable components from wastewater with their subsequent utilization into target products.

The processes of successive transformation and change in the status of waste in the technological chain of wastewater recycling from the production of phenol-formaldehyde resins are schematically shown in Figure 2. Pre-regenerated and modified sorbent based on wood waste and free phenol from wastewater at the adsorption stage are transformed into wood-phenolic oligomer, which participates as reactive filler at the next stage of the technological cycle. In the presence of the alkaline catalyst (NaOH) and a regenerated modifier (textolite crumb), wood-phenolic oligomer (WPO) is transformed into a wood-polymer composite (WPC) for structural purposes at the stage of polycondensation. The degree of conversion of phenol from wastewater into a wood-polymer composite, due to the processes of adsorption and polycondensation, is 99.5%. An additional product of the transformation of free phenol from the condensate water is sodium phenolate, which is formed at the stage of elution of a saturated ion exchanger with a NaOH solution.

Developing both a formulation and a method for producing WPC from technogenic raw materials forms the basis for the development of a technological module for recycling phenolic wastewater using combined technologies, the flow chart of which is shown in Figure 3. To recover solid-phase industrial wastes up to the state of a secondary raw material resource with the definite granulometric composition, regenerative recycling technologies, based on physical and mechanical processes of grinding and fractionation, are used. Regenerative technologies based on physicochemical processes make it possible to improve the textural characteristics of the sorbent based on wood waste and, as a consequence, its adsorption activity towards phenol. Recycling conversion technologies (conversion of a recycled component) based on physicochemical (sorption, ion exchange) and chemical (polycondensation) processes successfully solve the problem of phenol extraction from wastewater and its subsequent utilization into target products.

![Figure 2](image2.png)

**Figure 2.** Main transformation processes and changes in the status of industrial waste in the technological chain of recycling phenol-containing wastewater.

![Figure 3](image3.png)

**Figure 3.** Flow chart of waste water recycling of phenol-formaldehyde resin production and the utilization of valuable components into target products: 1 – main production; 2 – storage tank for
phenolic wastewater; 3 – dosing pump; 4 – unit for regeneration of textolite waste; 5 – unit for regeneration of wood waste; 6, 7 and 8 – dosing tanks for NH₄OH, NaOH and CH₂OH solutions, respectively; 9 – reactor-mixer; 10 – condenser refrigerator; 11 – vacuum pump; 12 – collection of phenolic condensate; 13 – sorption column; 14 – collection of eluate; 15 – tank 2 N. NaOH solution; 16 – collection of treated waste water.

The inclusion of basic and satellite technologies, which are classified according to genetic characteristics and indicate the reason and place of implementation of the developed technology, makes it possible to use the capacities and engineering infrastructure of the main chemical production. At the same time, the technological module for recycling phenolic wastewater is easily integrated into the technological process for the production of phenol-formaldehyde resins, being its logical continuation. The main advantage of the integration of recycling technologies lies in the developing a technological process for treatment of industrial wastes with a high degree of closeness of the production cycle.

The technological module for recycling phenolic waters includes 3 technological units. The first unit for the regeneration of solid-phase wastes is equipped with devices for their crushing and fractionation and is designed to recover wood waste and waste from the production and processing of textolite to the state of technogenic raw material resources and use them at the next stages of the technological process for their direct purpose. The second unit for the recovery of resin-forming components in phenolic water includes a reactor-mixer, a refrigerator-condenser combined with a vacuum pump, in which there is a sequential conversion of wastewater, in the presence of solid-phase fillers, into wood-polymer composite using adsorption and polycondensation processes. The third unit of sorption post-treatment of phenolic condensate water is the final stage of the technological process, which allows the treated wastewater to be used in the recirculating water system, and the eluate, which is sodium phenolate, is returned as a raw material to the main production.

A distinctive feature of this technological module is the implementation of all stages of the technological process (loading of components, chemical modification of wood sorbent, adsorption of phenol, polycondensation, drying of the composite) in one highly efficient apparatus - a mixing reactor. The developed design of such an apparatus makes it possible to successfully solve the problem of intensifying mass transfer and reaction processes in heterogeneous systems and, as a consequence, obtaining a composite with a high degree of homogenization, which results to its advanced physical, mechanical and operational parameters [26]. This is confirmed by the results of studies of the main physical and mechanical parameters of the wood polymer composite, which are not inferior to the similar indicators of the pressed wood mass, obtained from technical raw materials (Table 1).

| Parameter                        | Wood polymer composite | Pressed wood mass (GOST 11368-89 regulations, Russian Federation) |
|----------------------------------|------------------------|---------------------------------------------------------------|
| Density, kg/m³                   | 1320                   | 1300-1380                                                     |
| Water absorption, mg             | 333                    | not more > 480                                                |
| Breaking stress, MPa             | 56,8                   | not less < 50                                                  |
| under static bending             | 124,9                  | not less < 100                                                 |
| in compression                   |                        |                                                               |
| Fluidity by reduced diameter, mm| 129                    | not less < 105                                                 |

The results of biotesting of aqueous extracts from the composite and products made on its base showed the absence of acute toxic effects, and the product itself, obtained on the base of the technogenic raw materials, is safe to use.
4. Conclusion
The research has resulted to developing a resource-saving technology based on the processes of sorption and polycondensation of resin-forming components from phenolic waters from the production of phenol-formaldehyde resins in the presence of technogenic raw materials (dispersed waste from wood raw material processing and glass-fiber reinforced plastics) to obtain technical products – wood polymer composite and sodium phenolate as well as treated recirculating water. Recycling of 1000 m³ of phenolic wastewater using this technology makes it possible to obtain 608 tons of wood polymer composite and sodium phenolate as well as treated condensate water. The residual concentration of free phenol in treated condensate water is 2·10⁻² mg/l. Thus, an important environmental problem is being solved, associated with complete neutralization of highly toxic phenolic wastewater.

5. References
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