



## A review of phenol removal from wastewater by adsorption

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Phenolic compounds are highly toxic to humans, animals and aquatic ecosystems. Industrial effluents contaminated with phenols pollute surface and ground water resources if not managed and treated properly before discharge. Conventional physicochemical treatment processes like adsorption, chemical and electrochemical oxidation, distillation etc. provide high removal efficiencies as compared to advanced treatments like ozonation, UV treatment and Fenton process, which have high energy costs. Thus, over the years physicochemical processes have accentuated various researchers in the field of phenolics treatment. This review summarizes the development of different adsorption techniques developed for phenol removal over the years. Moreover, the chemical modifications of the adsorbent using functionalization, impregnation with nanoparticles or substitution with low cost biosorbents for cost effectiveness has been reassessed and compared. Applicability of micro-carbon and nano-carbon materials (like graphene oxide) and the dependence of the adsorption rate on pH, adsorbent dosage, temperature is also reflected upon.

Keywords: Phenolic compounds, ozonation, graphene oxide nanoparticles, biosorbents, surface modification.

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### Introduction

Phenols are aromatic compounds that have a hydroxyl group directly attached to a carbocyclic nucleus. It's a specific honorific for carboxylic acid or monohydroxy-benzene, being the simplest member of the organic hydroxyl compound family called as phenolics. Phenolic compounds are highly toxic even at trace concentrations to human beings, extremely irritating to skin and eyes upon short term inhalation and dermal exposures, and long-term exposures cause serious harm to liver, kidney and central nervous system. These are problems phenolic compounds share with other simple benzene and pyridine compounds<sup>1</sup>. Thus, industrial effluents with phenolic contaminations need to be carefully addressed so as to prevent pollution of drinking water sources and aquatic ecosystems. Moreover, if a phenol contaminated effluent has to undergo any sort of biological treatment before discharge, phenol removal is necessary as phenol hinders the biological treatment process causing it to become ineffective.

US Environmental Protection Agency (EPA), the European Union (EU), and the National Pollutant Release Inventory (NPRI) of Canada have characterized phenols as crite-

ria pollutants and have set strict benchmarks for discharge into surface and ground water. Surface and ground water can get contaminated from natural, industrial, domestic and agricultural sources. Phenols can naturally be present due to degradation of natural organic matters through discharge of domestic or industrial wastes into water bodies or through runoff from agricultural land containing pesticides<sup>2</sup>. This review paper presents a general review of the removal techniques applied to phenols with particular insistence on adsorption techniques and its types based on adsorbent materials used. Other potential natural sources of carbon like nanomaterials of graphene oxide that can be extracted and used as substitutes to commercial activated carbon to increase cost effectiveness have also been discussed<sup>2,3</sup>.

### Suitable treatment

Phenol is naturally degradable if present water as long as the concentration is not high enough to cause significant interference with microbial activity. Moreover, the rates of degradation of phenol are influenced by the presence of inorganic pollutants or other organic substances along with phenol in water<sup>4</sup>. Though evidence presented by several re-

searchers is suggestive of the fact that phenol can be biodegraded to a certain degree both naturally and in Municipal Wastewater Treatment Plants. But studies on the treated wastewater reveal that even after biological treatment, phenols are still present in the environment and are quite toxic in nature. This leads the researchers to the conclusion that the most suitable condition under which phenol will be degraded naturally might not be prevalent all the time. Else the existing denizens of microorganisms in the system may not be sufficient for total biodegradation of diverse phenols.

Adsorption technologies are very effective in removing phenol and its derivatives present in water from very minute to heavy concentration, in correlation with energy usage, economy, recycling requirement of secondary materials, adsorbent and extractant. Use of commercial activated carbon has proven to be most efficient and effective for treating phenols and other organic aromatic compounds, but it is expensive. Thus, to cut down the cost of reagents, much research work has been carried out for increasing the efficiency of the adsorbent and reducing the cost incurred by replacing the commercial activated carbon by other natural carbon sources. Surface modification of the available adsorbent to increase efficiency has also been tested. Chemical modification of the adsorbent, substitution with biosorbents etc., has also proven to be a better alternative for reducing cost and increasing efficiency for removal of phenolic compounds.

#### *Replacement with alternate carbon source:*

A. M. A. Ameer studied removal of phenolic compounds from tire-char. Char was extracted by pyrolysis of waste tire materials at 400–800°C for 2 h in the anaerobic environment. Modified char was also prepared by treating the char previously obtained with NaOH (5 N) in a shaker for 24 h. The optimum temperature for pyrolysis was observed to be around 600°C. The adsorption capacity was found out to be in the order *p*-chlorophenol > *p*-aminophenol > phenol<sup>12</sup>.

In another study, J. Feng *et al.* produced low cost activated carbon from *Polygonum orientale* Linn. The mass of carbon present in it is nearly about 40–45%. The optimum dosage was 20 mg/L. The average equilibrium time observed was 120 min and adsorbability of phenol was seen increasing and peaking when pH of the solution was nearly 9. Equilibrium data was fitting into Langmuir model<sup>5</sup>. Ionic strength had very nominal effect on adsorption<sup>6</sup>.

P. S. Nayak *et al.* worked with standard low-cost clay for phenol removal by adsorption under varying experimental conditions of pH, temperature and particle size. The clay sample used by her had varying clay particle whose size ranged from 50 µm to 150 µm and was dried at the 110°C for 3 h before use. The results indicated that the adsorption capacity of clay is directly related to temperature and inversely to the system pH and clay particle size<sup>13</sup>.

A. Gladysz-Plaska, used surface modified clay for adsorption of phenol and phosphate(v). He modified sodium bentonite by hexadecyltrimethylammonium-bromide (HDTMA-Br) to obtain a more efficient adsorbent. The process was most effective at pH 7 for phosphate(v) and pH > 7 for phenol. The adsorption follows Dubinin-Radushkevich isotherm model<sup>5</sup>. The maximum adsorption capacity of hexadecyltrimethylammonium-bentonite was 18.8 mg/g for phenol and 38.5 mg/g for phosphate(v) with simultaneous adsorption of both of them from an aqueous solution<sup>14</sup>.

#### *Biosorbents:*

M. Afsharnia *et al.* utilized *Pomegranate* peel carbon for phenol removal. The peels were washed with deionised water and dried at 105°C for 1 h. They were then cut into fine fragments and heated for an hour of 450°C, and then mixed in porcelain mortar. The optimum results showed maximum adsorption of 148.38 mg/g at pH 7 and at a temperature of 23±2°C. The phenol removal rate was found to be increasing with adsorbent dosage and contact time and inversely related to initial phenolic concentration<sup>15</sup>.

In another study, M. Aparecida used chitosan and chitin for phenol removal. Chitin is a natural polymer extracted from crab and shrimp shells, obtained by treatment with sodium hydroxide for deproteinization, followed by treating with dilute HCl for demineralisation. Chitosan is produced by alkaline deacetylation of chitin. Both batch and column adsorption were investigated and maximum 70–80% removal was noted. The adsorption was most efficient in the pH range of 2.0–5.0. Adsorbent dose of 10 mg/mL of was enough to remove 30 mg/L of phenol from the sample used. Use of chitin and chitosan showed reduction in COD and oil and grease of about 52% and 92% respectively<sup>16</sup>.

N. V. Kumar *et al.* studied biosorption of phenol on to *Acacia leucocephala* bark powder (Pine), a lignocellulose-based waste from forestry. Biosorption equilibrium was reached in 5 h of contact time at an optimum pH of 7, which

was found to be decreasing when the pH was raised above neutrality. The maximum adsorption capacities of phenol, 2-chlorophenol and 4-chlorophenol was noted to be 94.33, 147.05 and 181.81 mg/g respectively<sup>17</sup>.

#### Substitution of activated carbon with biosorbents:

L. Khenniche *et al.* utilized commercial activated carbon and coffee residue for adsorptive removal of phenol. The adsorbents were activated using chemical activation with zinc chloride by varying the activating agent ratio (0%, 25%, 50%, 75% and 100%). Consequently, the sample with activating agent ratio equal to 25% showed maximum phenol intake of about 68%<sup>9</sup>.

In another study, R. Huang *et al.* used a composite of chitosan and activated carbon in the ratio of 1:1 for the removal of phenol and chromium, achieving up to 95% removal for both and attaining equilibrium in 40 min<sup>18</sup>.

#### Chemical modifications and impregnations:

K. Gomonsirisuk *et al.* used activated carbon and zeolite composite and coated them with titanium dioxide (TiO<sub>2</sub>) for phenol removal. A composite substrate consisting of activated carbon:zeolite:phenolic resin in the ratio of 1:1:2 was used. Polyethylene glycol was used as organic binder. The dough, after giving it a shape of a hollow cylinder and was coated with 10% titanium dioxide (TiO<sub>2</sub>-P25, Degussa, Germany) and heated at 650°C to make it float in water. Phenolic resins strengthen the activated carbon composites and absorption capacity of zeolite contributed to the phenol removal efficiency<sup>8</sup>.

A. M. Carvajal-Barnal *et al.* developed and supplemented

a chemical modification of activated carbon and impregnated them with phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) or potassium hydroxide (KOH), both of which resulted in increasing the surface area and modifying micropore volume. Results reveal that phosphoric acid transcended more efficient adsorption of 2,4-dinitrophenol whereas potassium hydroxide did not exhibit much enhancing effect on the adsorption process<sup>10</sup>.

#### Other adsorbents developed:

J. Wang *et al.* developed composite hydrogels based on hydroxypropyl cellulose (HPC) and graphene oxide (GO). Single Network Composite Hydrogels (SNCH) and Double Network Composite Hydrogels (DNCH) were prepared by him. His studies indicate DNCH showed better adsorption capacities over SNCH due to large surface area and presence of more functional groups. Even after six adsorption desorption cycles there was no significant loss in initial sorption capacity<sup>19</sup>.

O. A. Adam investigated adsorption of phenol and O-substituted phenols in aqueous solution on petroleum asphaltene. Asphaltenes were isolated from asphalt samples of heavy crude oil. Isolation was procured by solubility based physical method of separation. The adsorption capacity was found to be decreasing in the order of *o*-nitrophenol > *o*-chlorophenol > *o*-aminophenols > phenol. Solution pH had no influence on the adsorption capacity but was found to increase with increase in particle size<sup>20</sup>.

The effect of the presence of natural organic matters (NOM) in the wastewater sample on the adsorption of phenolic derivatives like bisphenol A (BPA) was reported. H. Park

**Table 1.** Adsorbents used in removal of phenols along with removal conditions studied

Sl. no.	Name of adsorbent	Concentration range of phenol (mg/L)	pH of maximum removal	Contact time of equilibrium (min)	Optimal temperature (°C)	Optimal adsorbent dose (g/L)	Adsorption capacity (mg/g)	Ref.
1.	Tire char	50–250	5.5	1440	25	–	30.20	12
2.	<i>Polygonum orientale</i> Linn.	50–150	9	120	25–30	20	–	6
3.	Low cost clay	100–300	2	–	50	2	30.32	13
4.	Modified clay	–	7	360	20–40	4	18.8	14
5.	<i>Pomegranate</i> peel carbon	10–100	7	120	23±2	0.6	148.38	15
6.	Chitosan and chitin	30	6	1440	28±2	–	1.96 and 1.26	16
7.	Pine bark powder	100–400	7	120	25±1	4	143.3	17
8.	Coffee residue	10–170	–	60	20–40	–	67% removal	9
9.	Petroleum asphaltene	0–200	7	–	25	–	127.32	20
10.	Composite hydrogels	100–500	7	120	25	–	213.5	19

*et al.* impregnated different iron oxide nanoparticles (IONPAC) into powdered activated carbon (PAC) to enhance the adsorption of BPA in presence of NOM. The adsorbents used were PAC, ferrihydrite/PAC, magnetite PAC and haematite/PAC. All the adsorbents showed similar adsorption rate for the sample containing BPA only, but when NOMs were present IONPACs shower better results. The equilibrium was reached within 150 min. It was also observed that the concentration of NOM was inversely proportional for BPA adsorption into PAC but for IONPACs, the adsorption rate was more or less same for different concentrations of NOM in the sample which proves better applicability of IONPAC over PAC when there is interference of NOMs in the system<sup>21</sup>. Table 1 shows a consolidated list of adsorbents used in phenol removal.

### Conclusions

Apart from conventional techniques like adsorption on commercial activated carbon, extensive research works are continuously being carried out on removal of phenol from wastewater. Enhancements for overcoming low efficiencies of removal and high operational, maintenance and reagent costs of conventional methods pave the way for enticing alternatives like introduction of nanoparticles, surface modifications, chemical modifications and hybrid systems in order to accomplish total destruction of diverse phenol compounds.

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