APPLICATION OF ADSORPTION PROCESS FOR PHENOLIC COMPOUNDS REMOVAL FROM AQUEOUS ENVIRONMENTS: A SYSTEMATIC REVIEW

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ABSTRACT

Wastewater from various types of industries such as synthetic resins, plywood industries, paper and pulp, gas and coke oven plants, paints, coal gas, tanning, textile, plastic, rubber, pharmaceutical, petroleum and mine discharges, contain different types of phenols. Phenolic compounds are toxic substances and some are known or suspected carcinogens. Therefore it is important to remove phenol and phenolic compounds from contaminated industrial aqueous streams before discharged into any water bodies. Adsorption of phenol and its derivatives from aqueous solution by activated carbon is one of the most investigated of all liquid phase applications of carbon adsorbents. Several adsorbents have been used for treatment of wastewater and removal of phenolic compounds. Literature contains various adsorption processes and adsorbents such as pistachio nut shell ash, Moringa peregrina tree shell ash, agricultural fibers, red mud, low cost clay, olive mill waste, natural zeolites, rubber seed coat, peat, fly ash, bentonite and … which have been used for the removal of phenol and its derivatives. Any of chemical, biological and physical treatment processes has its own advantages and disadvantages. It is worth mentioning that economic aspects of these processes are important, for example biosorption were found to be effective methods with scope for further research in this field in terms of cost effectiveness and regeneration. At present study various adsorbents used by the authors of this article and other researchers for phenol and its derivatives from aqueous environments have been reported and summarized. Additionally, more research is needed to find the practical utility of low-cost adsorbents on commercial scale.

Keywords: Phenol and phenolic compounds, aqueous environments, adsorption

1. Introduction

In recent years, increasing awareness of water pollution and its far reaching effects has prompted concerted efforts towards pollution abatement (Donmez *et al.*, 1999). Contamination of aqueous environments by heavy metals and phenolic compounds is a worldwide environmental problem due to their toxic effects and accumulation through the food chain (Kapoor *et al.*, 1999; Perez-Rama *et al.*, 2002; Sternberg and Dorn, 2002). With regard to increasing effluent discharge standards to the environment, high considerations should be made when selecting proper treatment processes. Any of chemical, biological and physical treatment processes has its own advantages and disadvantages. Application of some waste products that could help in this regard, in addition to reuse of these waste materials, can be

an advantage (Mahvi, 2008). Among the different organic pollutants in wastewater, phenolic compounds are considered as priority pollutants since they are harmful to plants, animals and human, even at low concentrations. The major sources of phenolic compounds are steel mills, petroleum refineries, pharmaceuticals, petrochemical, coke oven plants, paints, coal gas, synthetic resins, plywood industries and mine discharge. The wastewater with the highest concentration of phenol (>1000 mg l^{-1}) is typically generated from coke processing. Phenolic compounds are also emanated from resin plants with a concentration range of 12–300 mg l^{-1}. Environmental Protection Agency (EPA) has set a limit of 0.1 mg l^{-1} of phenol in the treated effluent in order to protect human health from the potential toxic effects caused by exposure to phenol (Balasubramanian and Venkatesan, 2012). The World Health Organization (WHO) is stricter on phenol regulation. It sets a 0.001 mg l^{-1} as the limit of phenol concentration in potable water (Radovic *et al.*, 2001).Therefore, phenol is listed as a toxic substance and is included in the priority list of hazardous substances as well, which demonstrates its serious health and ecological effects (Busca *et al.*, 2008). Phenol ranks in the top 50 in production volumes for chemicals produced in the United States (Ahmaruzzaman, 2008). Biological treatment (Li *et al.*, 2011; Bajaj *et al.*, 2008; Moussavi *et al.*, 2010), coagulation and electrocoagulation (Bazrafshan *et al.*, 2012a; Bazrafshan *et al.*, 2012b), ultrasonic degradation (Mahvi, 2009; Maleki *et al.*, 2007; Pandit *et al.*, 2001), activated carbon adsorption and other adsorbents (Bazrafshan *et al.*, 2012c; Zarei *et al.*, 2013; Mahvi *et al.*, 2004; Mohan and Chander, 2001; El-Naas *et al.*, 2010; Dursun *et al.*, 2005; Gurses and Yalcin, 2005), membrane filtration (Bodalo *et al.*, 2009), enzymatic treatments (Mao *et al.*, 2006), solvent extraction (Juang *et al.*, 2010), photocatalytic degradation (Mahvi *et al.*, 2007; Dianati-tilaki *et al.*, 2014), chemical oxidation and electrochemical methods (Canizares *et al.*, 2002; BelhadjTahara and Savall, 2009; Yavuz and Koparal, 2006), are the most widely used methods for removing phenol and phenolic compounds from wastewaters. Problems such as high expenses, low efficiency, and generation of toxic by-products are associated with the above methods (Nazari *et al.*, 2007). Adsorption is a low cost and important physical process for the treatment and renovation of wastewater. It exploits the ability of certain solids to preferentially concentrate specific substance from solution onto their surfaces. In this manner, the component of either gases or liquid solutions can be separated from each other. Various non-conventional adsorbents like saw dust, bagasse pith, rice husk ash, activated coconut shell powder, controlled burnt wood charcoal, fly ash, peat, wood, jute fibers have been tried by the investigators (Kulkarni and Kaware, 2013). The parameters which have been investigated for optimizing the use of nonconventional adsorbents in wastewater treatment include nature of adsorbate and adsorbent, adsorbate concentration, adsorbent dose, contact time, pH of solution, particle size of adsorbent, thermodynamic parameters, etc. (Singh and Srivastava, 2002). The treatment with activate carbon, silicates and polymer resins are considered to be an effective method for the removal of phenol from wastewater because of its large surface area, micro porous nature, high adsorption capacity, high purity and ease of availability (Radeke *et al.*, 1993). Phenol removal by adsorption process remains the best treatment of choice as it can generally remove all types of phenols in a simple and easy operation. The adsorbent that is used in practice remains activated carbon (Jung *et al.*, 2001). However because of high cost of activated carbon, its usage is sometimes restricted due to economic considerations. As such, attempts have been made by many researchers to develop alternative adsorbents, preferably of low cost. Literature survey shows that a large number of alternative adsorbents have been studied to replace activated carbon. Both, the industrial wastes as well as some natural resource materials such as bentonite (Banat *et al.*, 2000), olive mill waste (Abdelkreem, 2013), pistachio nut shell ash (Bazrafshan *et al.*, 2012c), coconut shell (Kulkarni *et al.*, 2013), rubber seed coat (Rengaraj *et al.*, 2002b), Moringa peregrina seed extract (Bazrafshan *et al.*, 2012a), rice husk and rice husk ash (Mahvi *et al.*, 2004), avocado kernels (Rodrigues *et al.*, 2011) have been utilized for this purpose. Recently interest has turned to using various biomasses and agricultural wastes as biosorbent, which have the advantage of low cost and increased tolerance of environmental conditions. Biosorption can be defined as a process in which solids of natural origin are employed for sequestration or separation of pollutants from an aqueous environment (Muraleedharan *et al.*, 1991). Many natural materials were used as biosorbent for phenol removal, like wheat husk (Jagwani and Joshi, 2014) jute stick (Mustafa *et al.*, 2008), tobacco residues (Kilic *et al.*, 2011) and tamarind nutshell (Goud *et al.*, 2005), presented with low cost viable options. In this article, the use of activated carbon and various low cost natural adsorbents for the

removal of phenolic compounds from contaminated effluents has been reviewed, reported and evaluated. Instead of using commercial activated carbon, researchers have worked on inexpensive adsorbents such as bentonite, biomass, fly ash, zeolites and other natural materials, which have high adsorption capacity and are locally available.

2.   Adsorption of phenol and its derivatives

In recent years literature surveys show that a large number of alternative adsorbents have been studied to replace activated carbon. The review presents the summary of the removal of phenol and its derivatives by using following adsorbents by investigators in research works (Table 1). Also the comparison of adsorption capacities for various phenolic compounds on adsorbents was shown in the Figure 1.
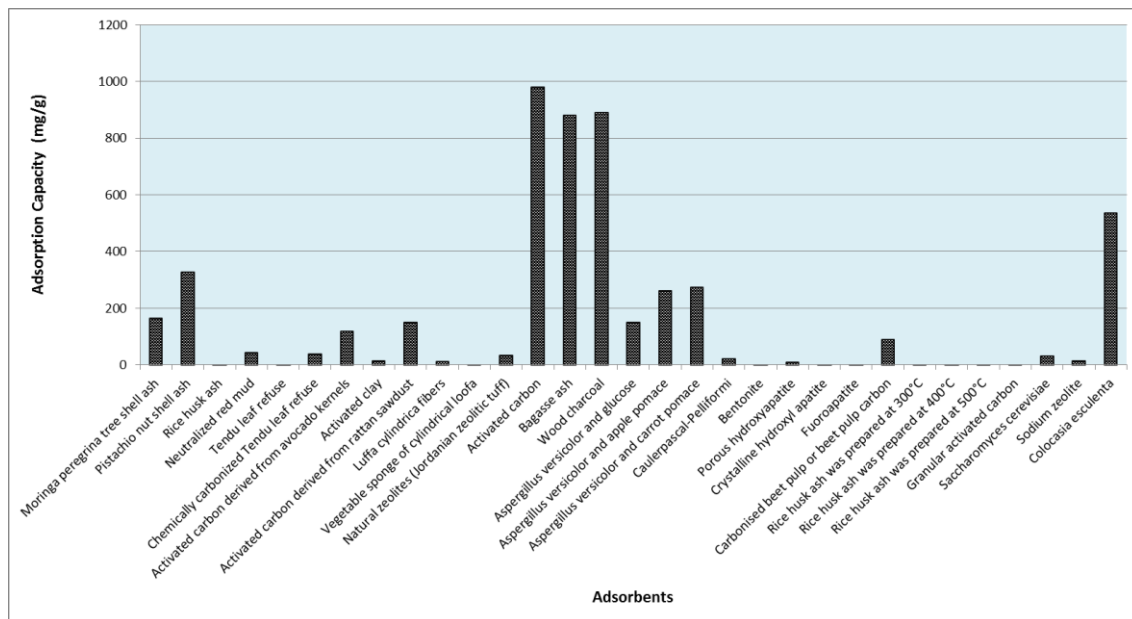

Figure 1. Comparison of adsorption capacities for phenolic compounds on various adsorbents

3.   Various adsorbents used for adsorption of phenol and its derivatives

Zarei *et al.*, (2013), studied the efficiency of Moringa peregrina tree shell ash for the removal of phenol from aqueous solutions; the examination was carried out in a batch system. According to the results of this study, it was found that the Moringa peregrina tree shell ash is not only a low-cost adsorbent but also has a high performance in the removal of phenol from aqueous solutions (Zarei *et al.*, 2013). In another research, the adsorption potential of pistachio-nut shell ash in a batch system was studied by Bazrafshan *et al.* (2012b) for the removal of phenol from aqueous solutions. The possibility of using rice husk and rice husk ash for removal of phenol from aqueous solution was investigated by Mahvi *et al.* (2004). Activated carbon prepared from rubber seed coat (RSCC), an agricultural waste by-product has been used for the adsorption of phenol from aqueous solution by Rengaraj *et al.* (2002b). Rao and Viraraghavan, (2002), have investigated the use of nonviable pretreated cells of Aspergillus niger to remove phenol from an aqueous solution. Five types of non-viable pretreated A. niger biomass powders were used as a biosorbent to remove phenol present in an aqueous solution at a concentration of 1000 g l^{-1}. Sulfuric acid pretreated A. niger biomass was found effective in the removal of phenol present in an aqueous solution at a concentration of 1000 g l^{-1} (Rao and Viraraghavan, 2002). Findings of Tor *et al.* (2006) on the application of neutralized red mud for removal of phenol from aqueous solution showed that the neutralized red mud was an effective adsorbent for the removal of phenol from aqueous solutions. Higher phenol removal by neutralized red mud was possible provided that the initial phenol concentration was low in the solution

(Tor *et al.*, 2006). The potential of tendu (Diospyros melanoxylon) leaf refuse from local bidi industry, which itself is a solid waste disposal menace and its chemically carbonized product to adsorb phenol was investigated by Nagda *et al.* (2007). Activated carbon derived from avocado kernels (AAC) was evaluated for its ability to remove phenol by Rodrigues *et al.* (2011). Adsorption of phenol on natural clay for phenol removal from aqueous solutions have investigated by Djebbar *et al.* (2012). The phenol removal potential of clay, a low cost and abundantly available material has been investigated by Nayak and Singh (2007). Activated carbon derived from rattan sawdust (ACR) was evaluated by Hamid and Rahman (2008) for its ability to remove phenol from an aqueous solution in a batch process. Abdelwahab and Amin (2013) have analyzed the removal of phenol from aqueous solution by Adsorption on to Luffa cylindrical fibers (LC). Adsorption study for phenol removal from aqueous solution on activated palm seed coat carbon (PSCC) were carried out by Rengaraj *et al.* (2002a). A comparative study with a commercial activated carbon showed that PSCC is two times more effective than commercial activated carbon (CAC) (Rengaraj *et al.*, 2002a). The vegetable sponge of cylindrical loofa, a natural product which rows in the north of Algeria, was used by Cherifi *et al.* (2009). Abdelkreem (2013) explored the possibility of using olive mill waste to remove phenol from aqueous effluents. The experimental studies on removal of phenol from waste water in a fluidized bed column using coconut shell activated carbon as an adsorbent have been reported by Kulkarni *et al.* (2013). Arris *et al.* (2012) showed that cereal by-product, an abundant natural material, can be used effectively and efficiently for the removal of phenol from wastewater. Rushdi *et al.* (2011) showed that Jordanian zeolite tuff can be used as a low cost adsorbent for the removal of phenol from water. Another investigation of the use of three carbonaceous materials, activated carbon (AC), bagasse ash (BA) and wood charcoal (WC), as adsorbents was studied by Mukherjee *et al.* (2007). Srivastava *et al.* (2006) research deals with the adsorption of phenol on carbon rich bagasse fly ash (BFA) and activated carbon-commercial grade (ACC) and laboratory grade (ACL). The present study showed that the bagasse fly ash (BFA) is an effective adsorbent for the removal of phenol from aqueous solution (Srivastava *et al.*, 2006). Karatay and Donmez (2014) have carried out the research on an economical phenol bio-removal method using Aspergillus versicolor and agricultural wastes as a carbon source. Viraraghavan and Alfaro (1998) examined the effectiveness of less expensive adsorbents such as peat, fly ash and bentonite in removing phenol from wastewater by adsorption. Batch adsorption research by Kilic *et al.* (2011) for the removal of phenol from aqueous solutions have been carried out by using activated carbon obtained from tobacco residue by chemical activation using K_2CO_3 and KOH as activation agents. A natural bentonite modified with a cationic surfactant, cetyl trimethyl ammonium bromide (CTAB), was used as an adsorbent for removal of phenol from aqueous solutions by Senturk *et al.* (2009). Application of a chemically modified green macro alga as a biosorbent for phenol removal have carried out by Aravindhan *et al.* (2009). The potential of bentonite for phenol adsorption from aqueous solutions was investigated by Banat *et al.* (2000). The removal of phenol (Ph) and 2-chlorophenol (2-CPh) from aqueous solution by native and heat inactivated fungus Funalia trogii pellets investigated by Bayramoglu *et al.* (2009). Batch adsorption experiments were conducted by Bahdod *et al.* (2009) to investigate the removal of phenol from wastewater by addition of three apatites (porous hydroxyapatite (PHAp) and crystalline hydroxyl- (HAp) and fluoroapatite (FAp). The adsorption of phenol from aqueous solutions was investigated using a carbonized beet pulp in the inert nitrogen atmosphere by Dursun *et al.* (2005). Results in comparative studies on adsorptive removal of phenol by three agro-based carbons, which have investigated by Srihari and Das (2008) showed that the black gram husk (BGH) is an effective adsorbent for the removal of phenol from aqueous solution when compared with green gram husk (GGH) and rice husk (RH). Activated carbons prepared from tamarind nutshell, an agricultural waste by-product, have been examined by Goud *et al.* (2005). Another Experiment have been conducted by Kermani *et al.* (2006) to examine the adsorption of phenol from aqueous solutions by rice husk ash and granular activated carbon (GAC). Phenol removal from aqueous system by jute stick has studied by Mustafa *et al.* (2008). In Siboni *et al.* (2013) research activated red mud containing iron and calcium as major components was applied to treat synthetic wastewater in a batch reactor. In another research the adsorption of phenol from wastewater was investigated using sawdust as adsorbent by Dakhil (2013). Moyo *et al.* (2012) investigated the possibility of Saccharomyces cerevisiae as an alternative adsorbent for phenol removal from aqueous solution. Adsorption of phenol from aqueous solution was investigated using sodium zeolite as an adsorbent by

Saravanakumar and kumar (2013). The application of Colocasia esculenta as an alternative adsorbent for the removal of phenol from aqueous solution was investigated by Obi and Woke (2014). The potential of employing wheat husk for phenol adsorption from aqueous solution was studied by Jagwani and Joshi (2014). The potential of activated carbon prepared from Typha orientalis Presl to remove phenol from aqueous solutions was studied by Feng *et al.* (2015).

4.   Results and discussion

4.1. Effect of initial pH on adsorption effectiveness

pH of the solution is one of the most critical parameters that affect the chemical properties of absorbing and adsorbing (Saitoh *et al.* 2011). The solution pH would affect both aqueous chemistry and surface binding sites of the adsorbent (Bazrafshan *et al.*, 2013a). pH also affects the surface properties of the sorbent, i.e., surface charge of the cells used as sorbent (Aksu and Yener, 2001). Nagda *et al.* (2007) observed that the adsorption of phenol decreases by the increase of the pH value of the solution, which can be attributed to the phenol ionization to form phenolate ions and at the same time the presence of hydroxyl ions on the adsorbent prevents the uptake of phenolate ions (Halouli and Drawish, 1995). Similar trend has been reported during the adsorption of phenol onto bentonite (Banat *et al.*, 2000). Hamid and Rahman (2008) defined the phenol removal by Activated carbon derived from rattan sawdust (ACR) was maximum and unaffected when the initial pH of the phenol solution was in the range of 3-8. A similar trend of pH effect was observed for the adsorption of phenol on activated carbon-commercial grade and laboratory grade (Srivastava *et al.*, 2006). Generally, solution pH affects the surface charge of adsorbent and degree of ionization of the adsorbate (Aksu and Kabasakal, 2003). Similar result was given by Liu and Pinto (1997) for granule and spherical activated carbon. They reported that, the decrease in phenol adsorption from pH = 6.3 to 3.07 was due to the increased H^+ adsorption on the carbonyl sites, which suppresses phenol adsorption on these sites (Liu and Pinto, 1997). Similar trend has been reported during the adsorption of phenol onto activated carbon by Ekpete *et al.* (2010), onto rise husk by Mahvi *et al.* (2004) and onto agriculture waste by Tagreed (2010). Jagwani and Joshi (2014) concluded that adsorption amount decreased with increasing pH value, which can be attributed to the phenol ionization to form phenolate ions and at the same time the presence of hydroxyl ions on the adsorbent prevents the uptake of phenolate ions (Halouli and Drawish, 1995). Similar behavior has been reported during the adsorption of phenol onto tendu leaf refuse and modified carbon prepared from tendu leaf refuse by Nagda *et al.* (2007).

4.2. Effect of adsorbent dose on the phenol removal by adsorption process

Because adsorption is mainly a surface phenomenon, the amount of surface available for adsorption process and consequently the mass of adsorbent can considerably affect adsorption efficiency (Bazrafshan *et al.*, 2014). In the investigation which was done by Rengaraj *et al.* (2002b) carbon dosage was varied from 0.5 to 10 g and equilibrated for 24 h. It is evident that for the quantitative removal of 25 mg l^{-1} of phenol in 100 ml, a minimum carbon dosage of 2.5 g RSCC and 3.0 g of CAC is required for 96% removal of phenol. The data clearly showed that the RSCC is more effective than CAC for the removal of phenol. Abdelkreem (2013) indicated that phenol removal increased quickly from 52% to 85% when the olive mill waste dosage increased from 0.25 g to 1 g and reached a maximum for 1 g olive mill waste. This trend is expected because as the adsorbent dose increases, the number of active sites for binding phenol molecules on the adsorbent increases and thus more phenol was attached to their surface. Thus it results in the increment of adsorption efficiency until saturation. These results were agreed with those abstained by Ghaedi *et al.* (2011), and Smithaa *et al.* (2012). The minimum adsorbent dosage required was found by Srihari and Das (2008), they were 0.3, 0.35, and 0.4 g by BGH, GGH, and RH, respectively. Thus, the adsorption trend of these agro based adsorbents was found to be in the following order: BGH>GGH>RH (Srihari and Das, 2008). Findings of Siboni *et al.,* (2013) work indicated that the increase in phenol removal with increase in the activated red mud amount is due to the increase of surface area and adsorption sites available for adsorption (Hameed and Rahman, 2008; Tor *et al.*, 2009a; Lin and Juang, 2009; Shirzad-Siboni

et al., 2011).Similar observations have also been reported from other research groups (Mohd Din *et al.*, 2009; Banat *et al.*, 2000; Tor *et al.*, 2006; Lin and Juang, 2009; Tor *et al.*, 2009b; Nayak and Singh, 2007).

4.3. Effect of contact time on the phenol removal by adsorption process

The contact time between adsorbate and adsorbent is one of the most important design parameters that affect the performance of adsorption processes (Bazrafshan *et al.*, 2013b; Bazrafshan *et al.*, 2015a). The removal efficiency increased with time and attained equilibrium in 3 h for PSCC and 6 h for CAC for initial phenol concentration of 25 mg l^{-1} In investigation on removal of phenol from aqueous solutions by activated red mud which has investigated by Siboni *et al.* (2013), while increasing the phenol concentration from 40 to 80 mg l^{-1}, the removal percentage decreased from 90.3% to 76.6% at initial 30 min of contact time. After that, the removal percentage of phenol slowly increased and ranged from 90.4% to 80.6% at three different phenol concentrations after 60 min. Further increase in the contact time has a negligible effect on the rate of phenol adsorption, and 60 min was determined as a near equilibration time (Siboni *et al.* 2013). The decrease in the removal percentage of phenol by increasing initial phenol concentration can be explained in that the adsorbent had a limited number of active sites, which can be easily saturated at higher adsorbate concentration (Hameed and Rahman, 2008; Al-Asheh *et al.*, 2003; Tor *et al.*, 2006; Tor *et al.*, 2009). The results in Jagwani and Joshi (2014) research showed that equilibrium time required for the adsorption of phenol on wheat husk was almost 5hr. The results also indicated that the sorption process can be considered very fast because of the largest amount of phenol attached to the sorbent within the first 120 min of adsorption as also observed by Mahvi *et al.* (2004), Mustafa *et al.* (2008) and Kermani *et al.* (2006). In addition similar findings were reported by other researchers about the increase of removal efficiency of pollutants with increase of contact time (Bazrafshan *et al.*, 2015b; Bazrafshan *et al.*, 2015c)

4.4. Effect of initial phenol concentration on the effectiveness of adsorption process

The initial concentration of pollutant provides an important driving force to overcome all mass transfer resistance of the adsorbate between the aqueous and solid phases (Anbia and Asl Hariri, 2010). Zarei et al. (2013) observed that phenol adsorption rate by Moringa peregrina tree shell ash will be increased by phenol concentration, so phenol elimination depends on its concentration. The results in Dakhil (2013) research indicated that the percentage of phenol removal increases with increasing the adsorbent dose. The high sorption at the initial concentration (100-500 mg l-1) may be due to an increased number of vacant sites on the adsorbent available at the initial stage. As concentration of initial phenol is increased there is a decrease in percentage removal of phenol. This can be attributed to the accumulation of phenol particles on the surface of adsorbent (Dakhil, 2013). This observation is in a good agreement with the findings of Ekpete et al. (2010) and Mahvi et al. (2004).

4.5. Effect of temperature on phenol removal by adsorption process

Temperature is an indicator for the adsorption nature whether it is an exothermic or endothermic process. Increasing temperature may decrease the adsorptive forces between the phenol species and the active sites on the adsorbent surface as a result of decreasing adsorption efficiency (Ofomaja and Ho, 2007; Jadhav and Vanjara, 2004). Senturk et al. (2009) concluded that the uptake of phenol by organo bentonite decreased from 6.2 mg g-1 (59% removal) to 5.2 mg g-1 (49.5% removal) when increasing the temperature from 0 to 40˚C, which indicating that phenol uptake was favored at lower temperatures. The decrease in adsorption with the rise of temperature may be due to the weakening of adsorptive forces between the active sites of the adsorbent and adsorbate species and also between the vicinal molecules of the adsorbed phase (Panday et al., 1986; Mota and Lyubchik, 2008). Similar results were obtained by Hameed (2007) with adsorption of 2, 4, 6-trichlorophenol by activated clay.

4.6. Adsorption isotherms

Isotherms study can describe how an adsorbate interacts with the adsorbent. The isotherm provides a relationship between the concentration of phenol in solution and the amount of phenol adsorbed on the solid phase when both phases are in equilibrium (Anbia and Asl Hariri, 2010). The Langmuir, Freundlich,

Temkin, BET, Redlich-Peterson and Dubinin–Radushkevich (D-R) isotherm models were used to describe the relationship between the amount of phenol adsorbed and its equilibrium concentration in solutions. Tor *et al.*, (2006) reported the R^2 values for linear form of Langmuir and Freundlich isotherms are 0.988 and 0.992, respectively. According to R^2 values, the Freundlich isotherm best represents the equilibrium adsorption of phenol on neutralized red mud. This result is attributed that various active sites or heterogeneous mixture of several minerals on neutralized red mud has different affinities to phenol molecule (Genç-Fuhrman *et al.*, 2004a; Genç-Fuhrman, 2004b). The well-known Freundlich, Langmuir isotherm equations were applied for the equilibrium adsorption data by Abdelkreem (2013) in the adsorption research of phenol from industrial wastewater using olive mill waste. The best-fitted adsorption isotherm models by Rushdi *et al.* (2011) were found to be in the order: Freundlich>Redlich–eterson>Langmiur>Temkin for temperature range 25-45°C.

4.7. Thermodynamic parameters in the adsorption process

Thermodynamic parameters are the actual indicators to determine where a process proceeds spontaneously and to ascertain if the process has any practical use (Nayak and Singh, 2007). The thermodynamic parameters that must be considered to determine the adsorption processes are the changes in standard enthalpy (ΔH^0), standard entropy (ΔS^0), and standard free energy (ΔG^0) due to transfer of unit mole of solute from solution onto the solid–liquid interface (Rushdi *et al.*, 2011). Adsorption process can be classified as physical adsorption and chemisorption by the magnitude of the enthalpy change. It is accepted that if magnitude of enthalpy change is lesser than 84 kJ mol^{-1}, then the adsorption is physical. However chemisorption takes place in the range of 84-420 kJ mol^{-1} (Bazrafshan *et al.*, 2015d; Bazrafshan *et al.*, 2015e). Also If the process is endothermic ($\Delta H >0$), the equilibrium constant increases with temperature and If the process is exothermic ($\Delta H <0$), the equilibrium constant decreases as temperature is raised (Cherifi *et al.*, 2009). The thermodynamic parameters are presented in Table 2.

Abdelwahab and Amin (2013) reported that the standard Gibbs free energies (ΔG^0) of adsorption were negative at all investigated temperatures. The negative values of ΔG^0 of the adsorption confirmed that the adsorption of phenol onto LC was feasible and spontaneous (Fu *et al.*, 2009; Su *et al.*, 2011). Similar results were reported in the literature for the adsorption of phenol by organomontmorillonit (Fu *et al.*, 2009) and adsorption of phenol onto chemically modified activated carbon (Canizares *et al.*, 2006) and adsorption of phenol onto solid waste products from olive oil industry (Bhatnagar *et al.*, 2014). Rushdi *et al.* (2011) reported that the Negative ΔG^0 values are obtained at all temperatures revealing the spontaneous nature of these adsorptions. Generally, the values are close to each other indicating that such spontaneity is independent on the temperature where the adsorption occurs (Okolo *et al.*, 2000). It is also supposed that the change of ΔS^0 value is related to the displacement of the adsorbed water molecules by the adsorbate (Li *et al.*, 2005). In this study, the negative ΔS^0 value may reveal that zeolite surface does not prefer phenol molecules over adsorbed water molecules. Thus, the adsorption of phenol onto zeolite under employed conditions is considered as an enthalpy driven process (Bhatnagar and Sillanpaa, 2010).

5.   Conclusions

Chemical contamination of water from a wide range of toxic pollutants, especially aromatic molecules, is a serious environmental problem due to potential human and environmental toxicity. Phenol and its derivatives appear to be the major organic pollutants globally in this century. They derived from many chemical plants and pesticide and dye manufacturing industries and cause serious threat to human health and to natural water. Adsorption is relatively new practice for the removal of phenol and its derivatives. In this article the role of activated carbon for the removal of phenol and its derivatives from water and wastewater was discussed. It is only able to remove few milligrams of phenol and its derivatives per gram of activated carbon and there are still some problems encountered in the regeneration process. This makes activated carbon an expensive adsorbent for this aim. Therefore, low-cost materials are needed

that are comparable to activated carbon or synthetic resins in terms of adsorption capacity and should be locally available. The present review shows that several adsorbents (pistachio nut shell ash, Moringa peregrina tree shell ash, agricultural fibers, red mud, low cost clay and etc.) have equivalent or even more adsorption capacity to activated carbon and synthetic resins. It should be kept in mind that economic aspects are important. As an example, biosorption were found to be effective methods with scope for further research in this field in terms of cost effectiveness and regeneration. The alternative adsorbents mentioned in this article are found to be highly efficient for the removal of phenol and its derivatives. This is highly valuable for, not only the industries but the living organisms and the surrounding environment since they would be benefited from the potential toxicity. Thus the use of low-cost adsorbents may contribute to the sustainability of the surrounding environment. However, despite the number of published laboratory data, non-conventional low-cost adsorbents have not been applied at an industrial scale. Undoubtedly low-cost adsorbents offer a lot of promising benefits for commercial purpose in the future and the development of the adsorption process requires further investigation in the direction of testing low cost adsorbents with real industrial effluents. So there is a particular need for future studies to verify the performance of the promising low-cost adsorbents at the pilot plant scale.

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Table 1. Application of adsorption process by using various adsorbents for phenol and phenolic compounds removal from aqueous environments

Adsorbent	C_0 (mg l⁻¹)	pH	Contact time (min)	Adsorbent dose (g l⁻¹)	Optimum pH	Optimum dose (g l⁻¹)	Temperature (°C)	Equilibrium time (min)	Removal efficiency (%)	Adsorption capacity (q_e) (mg g⁻¹)	Isotherms Freundlich	Langmuir	References
Moringa peregrina tree shell ash	10-100	2-12	15- 210	0.1-0.7	6	0.4	23±2	45	97.82	164.23	R^2=0.94	R^2=0.96	(Zarei et al., 2013)
Pistachio nut shell ash	1- 100	2-13	15- 120	0.1-0.6	5	0.3	25±2	45	98.28	327.6	R^2= 0.94	R^2= 0.83	(Bazrafshan et al., 2012c)
Rice husk	0.15-0.5	5-11	10-180	1- 7	5	0.3	23±2	360	27	-	R^2= 0.96	R^2=0.87	(Mahvi et al., 2004a)
Rice husk ash	0.5-1.3	5-11	10-180	0.1-0.5	7	0.3	23±2	180	96	0.886	R^2=0.98	R^2=0.97	
Rubber seed coat (RSCC)	10-30	1-14	15-1440	0.5-10	6.2	2.5	27 ± 1	180	96	-	R^2=0.3	-	(Rengaraj et al., 2002b)
CAC (commercial activated carbon)	10-30	1-14	15-1440	0.5- 10	6.2	3.0	27 ± 1	360	96	-	R^2 =0.9	-	
Aspergillus niger	1.0	2-10	1800	0.05- 0.45	5.1	0.2	21±1	1440	66	-	R^2=0.73	R^2=0.72	(Rao and Viraraghavan, 2002)
Neutralized red mud	5 – 200	1-12	10-840	1-10	6	10	25±1	600	48	42	R^2=0.99	R^2=0.98	(Tor et al., 2006)
Tendu leaf refuse (TLR)	10-200	4.2-12	60-480	0.1-100 mg ml⁻¹	8.5	3 mg ml⁻¹	25±1	120	48	1.9	R^2=0.97	R^2=0.95	(Nagda et al., 2007)
Tendu leaf refuse (TLR-CM)	10-200	4.2-12	10-240	0.1-50 mg ml⁻¹	8.5	0.5 mg ml⁻¹	25±1	60	98	39	R^2=0.98	R^2=0.96	
Activated carbon derived from avocado kernels (AAC)	100-600 mg dm⁻³	2-8	0-250	0.02-0.20	4-8.5	0.1	25	15	69	117	R^2=0.94	R^2=0.99	(Rodrigues et al., 2011)
Natural clay	100 ml of 5 mg l⁻¹	4-8	0-3000	1–5 mg	5	5 mg	23	300	60	-	R^2=0.94	R^2=0.92	(Djebbar et al., 2012)
Activated clay	5	4-8		1–5 mg	5	5 mg	23	300	70	15	R^2=0.97	R^2=0.98	
Low cost clay	500 mg dm⁻³	2-10	-	-	6.5	-	30	-	37.56	-	-	-	(Nayak and Singh, 2007)
(ACR)	25–200	3-10	1440	0.20	4	0.20	30	240		149.25	R^2=0.86	R^2=0.98	(Hamid and Rahman, 2008)
Luffa cylindrica fibers (LC)	5-40	2-12	0-150	1-5	7	3	20	120	85	10.37	R^2=0.94	R^2=0.99	(Abdelwahab and Amin, 2013)

(PSCC)	10-60	1-13	1440	0.5-10	4-9	2	27±1	120	96	-	-	-	(Rengaraj et al.,
(CAC)	10-60	1-13	1440	0.5-10	4-9	3	27±1	360	96	-	-	-	2002a)
cylindrical loofa	0- 50	8.5	120	0.1	8.5	0.1	23	50	-	4.70	R^2 =0.86	R^2 =0.94	(Cherifi et al., 2009)
Olive Mill Waste	100 – 600	-	120	0.25-1	-	1	20	120	85	-	R^2 =0.90	R^2 =0.96	(Abdelkreem, 2013)
Coconut Shell Activated Carbon	100-300	-	10- 60	5	-	5	25 ±1	15-20	46	-	R^2=0.98	-	(Kulkarni et al., 2013)
Cereal by-products	20	2-10	0-350	10	3	10	20	120	70	-	R^2=0.72	R^2=0.58	(Arris et al., 2012)
Natural zeolites (Jordanian zeolitic tuff)	10-90	4	0-1440	-	4	-	25	120	96	32.6	R^2=0.99	R^2=0.97	(Rushdi et al., 2011)
Activated carbon (AC)	20-100	2-10	0-6 h	30 and 50 mg l^{-1}	6.8	10	24±1	60	98	0.98 mg mg^{-1}	R^2=0.90	-	(Mukherjee et al., 2007)
Bagasse ash (BA)	20-100	2-10	0-360	30 and 50 mg l^{-1}	6.8	15	24±1	60	90	0.88 mg mg^{-1}	R^2=0.92	-	
Wood charcoal (WC)	20-100	2-10	0-360	30 and 50 mg l^{-1}	6.8	60	24±1	60	90	0.89 mg mg^{-1}	R^2=0.90	-	
46346Carbon rich bagasse fly ash (BFA)	75-300	3-10	0-1440	1-10	6.5	10	30	300	-	-	R^2=0.99	R^2=0.98	
Activated carbon-commercial grade (ACC)	75-300	3-10	0-1440	1-10	6.5	12	30	300	-	-	R^2=0.97	R^2=0.99	(Srivastava et al., 2006)
Laboratory grade (ACL)	75-300	3-10	0-1440	1-10	6.5	10	30	300	-	-	R^2=0.99	R^2=0.95	
MSG	100-600	4-7	4320	1	6	1	30	60	61.5	149.64	-	-	
MSA	100-600	4-7	4320	1	6	1	30	60	98.7	261.88	-	-	(Karatay and Dönmez, 2014)
MSC	100-600	4-7	4320	1 and 5	6	1	30	60	100	274.29	-		
Peat	1	2-8	1440	-	4-5	-	21±1	960	46.1	-	R^2=0.86	-	
Fly ash	1	2-8	1440	-	4-5	-	21±1	300	41.6	-	-	R^2=0.97	(Viraraghavan and Alfaro, 1998)
Bentonite	1	2-8	1440	-	4-5	-	21±1	960	42.5	-	R^2=0.86		
Tobacco residues (ACK1)	1–12	5-9	10-240	0.5–8	7	2	20	120	90.5	-	R^2 =0.99	R^2 = 0.99	
Tobacco residues (ACK2)	1–12	5-9	10-240	0.5–8	8	4	20	120	87.6	-	R^2 =0.99	R^2 =0.92	(Kilic et al., 2011)

Adsorbent													Reference
Organomodified Tirebolu bentonite	100–1000	1-11	0-500	1–25	9	10	20	60	58.5	-	R^2 =0.99	R^2 =0.99	(Senturk et al., 2009)
Caulerpascal-Pelliformi	10–150	2-10	360	6	6	6	30±1	240	93.58	20	R^2 =0.97	R^2 =0.98	(Aravindhan et al., 2009)
Bentonite	25-500 mg ml^{-1}	5-11	0-3000	2.5	5	2.5	20	360	73	0.18	R^2 = 0.90	R^2 = 0.98	(Banat et al., 2000)
Funaliatrogii pellets	30-600	2-11	3000	0.25 and 2.0	8	2	25	360	80	-	R^2 =0.97	R^2 =0.99	(Bayramoglu et al., 2009)
porous hydroxyapatite (PHAp)	0-100	2-12	180	20	6	20	25	60	-	8.2± 0.4	R^2> 0.99	-	(Bahdod et al., 2009)
crystalline hydroxyl apatite(HAp)	0-100	2-12	180	20	6	20	25	120	-	3.9 ± 0.2	R^2> 0.99	-	
fluoroapatite (FAp)	0-100	2-12	3h	20	6	20	25	120	-	3.1 ±0.2	R^2> 0.99	-	
(BPC)	25–500 mg dm^{-3}	2-12	120	0.5 g dm^{-3}	6	-	60	120	70	89.5	R^2=0.99	R^2= 0.98	(Dursun et al., 2005)
Black gram husk (BGH)	100	2–12	1440	More than 0.3	5.1	0.5	25 ± 2	360	more than 95	-	R^2=0.94	R^2=0.95	(Srihari and Das, 2008)
Green gram husk (GGH),	100	2–12	1440	More than 0.35	5.1	0.5	25 ± 2	360	more than 95	-	R^2=0.88	R^2=0.95	
Rice husk (RH)	100	2–12	1440	More than 0.4	5.1	0.5	25 ± 2	360	more than 95	-	R^2=0.95	R^2=0.95	
(TNSAC)	25-200	2-10	0-80	2, 5 ,10	4	5	25 ± 2	-	78	-	R^2 =0.99	R^2 =0.99	(Goud et al., 2005)
(RHA-300)	10 – 300	1-13	0-480	1-10	5	1 gr/100 ml	21 ± 2	300	-	0.951	R^2=0.97	R^2=0.98	(Kermani et al., 2006)
(RHA-400)	10 – 300	1-13	0-480	1-10	5	1 gr/100 ml	21 ± 2	300	-	1	R^2=0.98	R^2=0.97	
(RHA-500)	10 – 300	1-13	0-480	1-10	5	1 gr/100 ml	21 ± 2	300	-	0.989	R^2=0.97	R^2=0.96	
(GAC)	10 – 300	1-13	0-480	1-10	5	1 gr/100 ml	21 ± 2	300	-	1	R^2=0.99	R^2=0.88	
Jute Stick	10-60	6-12	50-400	0.5- 4	10	3	25-40	300	68	-	-	-	(Mustafa et al., 2008)
Activated Red Mud	40 to 80	3-11	5-60	2-10	7	6	25 ± 2	60	90.4	-	R^2 =0.99	R^2 = 0.87	(Siboni et al., 2013)
Sawdust	100-500	3-9	20-180	0.1-1	6.7	0.82	30 ± 1	120	91.6	-	R^2 =0.99	R^2 =0.99	(Dakhil, 2013)
Saccharomyces cerevisiae	10-160	1-12	1-360	0.3-10	1	0.3	27 ± 2	240	-	30	R^2 = 0.99	R^2 =0.99	(Moyo et al., 2012)

Sodium zeolite	100-500	3-9	10- 60	0.8 -5.2	5	1	25 ± 2	40	100	13.051	$R^2 = 0.94$	$R^2 = 0.99$	(Saravanakumar and kumar, 2013)
Colocasia esculenta	10- 60	2-12	120	1	2	1	25	40	-	536.14	$R^2 = 0.90$	$R^2 = 0.99$	(Obi and Woke, 2014)
Wheat husk	0.1-0.9	3-11	30-180	1-9	3-5	3	25 ± 2	300	91.7	-	$R^2 = 0.92$	$R^2 = 0.90$	(Jagwani and Joshi, 2014)
Typha orientalis Presl	50-150	2-11	0-200	0.1-8	5	14.30	20-30	135	-	-	$R^2 = 0.96$	$R^2 = 0.62$	(Feng *et al.*, 2015)

Table 2. Thermodynamic parameters in the adsorption process of phenol and phenolic compounds from aqueous environments

Temperature (°K)	ΔG⁰ (kJ mol⁻¹)	ΔH⁰ (kJ mol⁻¹)	ΔS⁰ (J mol⁻¹ K⁻¹)	Spontaneous	Non Spontaneous	Endothermic	Exothermic	Physical/chemical	References
298	-20.36	-16.4	13.31						
308	-20.54			•	-	-	•	Physical	(Rodrigues *et al.*, 2011)
318	-20.57								
328	-20.80								
296	3.293	-1.666	5.510 (J K⁻¹ mole⁻¹)						
301	-3.311			-	-	-	•	Physical	(Djebbar *et al.*, 2012)
306	-3.340								
303	-2.316	2.4112 (kcal mol⁻¹)	15.60 (cal mol⁻¹)						
313	-2.472			•	-	•		Physical	(Nayak and Singh, 2007)
323	-2.670 (kcal mol⁻¹)								
293	-1.866	-32.749	-126.47 (J mol⁻¹)						
303	-0.666			•	-	-	•	Physical	(Abdelwahab and Amin, 2013)
313	-0.515								
323	-0.102								
313	20.87	31.785	190.0						
296	24.43			•	-	•	-	-	(Cherifi *et al.*, 2009)
303	25.82								
298	-8.58	-10.16	-5.3						
308	-8.53			•	-	-	•	Physical	(Rushdi *et al.*, 2011)
318	-8.48								
328	-8.42								
273	-0.83	-6.70	-21.96						
283	-0.59								
293	-0.37			•	-	-	•	-	(Senturk *et al.*, 2009)
303	-0.19								
313	0.05								
303	-5.535	-26.442	-69.0						
313	-4.845			•	-	-	•	-	(Aravindhan *et al.*, 2009)
323	-4.155								