

Adsorption for Phenol Removal-A Review

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Abstract: Phenol from the wastewater can be removed by various techniques including biodegradation, photo decomposition and adsorption. This paper presents review on phenol removal by adsorption by using various adsorbents. The present review aims at presenting the research on phenol adsorption, findings and effectiveness of the adsorbents in phenol removal. Effects of various parameters like adsorbent dose, pH, and particle size on rate of adsorption have been studied by various researchers. Also optimum values of these parameters have been reported. The investigation carried out indicates that there is wide scope for use of low cost adsorbents. The isotherm studies carried out by investigators are reported and it was observed that the uptake of phenol follows the Langmuir and/or Freundlich isotherm in most of the cases. Regeneration and reuse of the adsorbent is the key area of research. The development of efficient method for regeneration and recovery will make the adsorption, a more economical and attractive option for phenol removal.

Keywords: adsorption, phenol, isotherms, concentration, adsorbent

1. Introduction

Phenolic pollution of water bodies is a very important area of research, since phenolic wastewater is harmful for aquatic life and human being. The toxicity level for fish is around 9 to 25 mg/l while that for human being ranges 10-24 mg/l. Lethal blood concentration of phenol is around 150-mg/100 ml. As it is highly harmful compound, there is a necessity for its removal in order to preserve the environmental quality. Various treatment processes used for the removal and/or recovery of phenols are hot gas or steam stripping, adsorption, ion exchange solvent extraction, oxidation, phase transfer catalysis and biological treatment processes. Adsorption by using various low cost adsorbents is very widely studied area of research. The present review presents the summary of the research carried out by the researchers by using various low cost adsorbents, their findings and effectiveness.

2. Adsorption

Adsorption is a low cost and important physical process for the treatment and renovation of waste water. 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, baggase pith, rice husk ash, activated coconut shell powder, controlled burnt wood charcoal, fly ash, peat, wood, jute fibers, have been tried by the investigators.

3. Various Adsorbents for Phenol Removal

The removal of phenol by using following adsorbents by investigators, The review presents the summary of this research work. Various adsorbents used for phenol removal includes iron oxide nano-particles, silica gel, activated

alumina, polymeric resins, activated carbon, Rice husk, Tamarind beans, Tea waste, Ground nut shells, Peanut shells, Cashew seed shells, Leaf litter, Fly ash, Coconut shell carbon, hycinthe, Date stone activated carbon, pineapple peels, sawdust etc.

3.1 iron oxide nano-particles

Solid phase extraction of phenol by using iron oxide has been reported by Talvalli and Shiri [1]. The optimization of the parameters like pH, agitation times, and amount of nano-particles was carried out. The highest removal was observed in the pH range of 5 to 7. The lowest removal was observed at the pH value of 12. At these alkaline conditions the OH ions affect the phenol adsorption adversely. The equilibrium time required for the phenol uptake was observed to be 2 hours. The phenol removal was very rapid for first half an hour and attained the equilibrium slowly in 2 hours. 0.3 grams per litre of adsorbent for 98 % phenol removal was an optimum amount. The phenol uptake followed Langmuir isotherm according to these studies.

Montiel-Palacios et. al. have reported the photo catalysis of phenol derivatives with iron oxide nanoparticles [2]. The nanoparticles were dispersed on highly ordered hexagonal (p6mm) mesoporous silica SBA-15. Triblock copolymer, Pluronic P123 was used as direct structuring agent for synthesizing silica mesoporous support, SBA-15. Iron oxide nanoparticles were prepared by calcinations on the surface and in the porous matrix of SBA-15 previously impregnated with an organic, $\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_3$ and two inorganic, FeCl_3 and FeSO_4 , solutions. It was observed that in case of FeSO_4 precursor no greater loading of Fe was introduced after impregnation of SBA-15. FeCl_3 provides the highest amount of Fe loading in mesoporous SBA-15.

A review on degradation of chlorinated phenols by zero valent and bimettals of iron was carried out by Gunawardana et.al [3]. Zero valent iron (ZVI) and iron based bimetallic

systems have the potential to efficiently dechlorinate chlorinated phenols (CPs). Their review was particularly on the research conducted in this area over the past decade, with emphasis on the processes and mechanisms for the removal of CPs, as well as the characterization and role of the iron oxides formed on the zero valent iron surface. This technique is emerging as very effective area of research. Their study also revealed that bimetal prepared by physically mixing ZVI and catalyst or doping of the catalyst onto the ZVI surface can enhance the rate and efficiency of CP dechlorination and decrease the accumulation of less chlorinated intermediate compounds. Also the solution pH and dissolved oxygen are critical parameters that affect the degradation of dissolved CP by ZVI and bimetal.

Babuponnusami and Muthukumar carried out research on removal of phenol by heterogeneous photo electro fenton-like process using nano-zero valent iron (NZVI)[4]. Their study presented the removal of phenol by heterogeneous photo electro Fenton-like (PEF-like) system using nano-zero valent iron. The nano-zero valent iron was characterized using X-ray diffraction (XRD) and Scanning Electron Microscope (SEM) analysis. The research included studies on The effect of initial pH, initial concentration of phenol, NZVI dosage and initial H₂O₂ concentration on phenol removal. It was observed that The removal efficiency was increased with an increase in NZVI dosage and decreased with an increase in initial phenol concentration and initial pH. The analysis of kinetics showed that the removal of phenol by PEF-like process followed pseudo first-order kinetics.

The research on kinetics and isotherms for Adsorption of 4-Chloro-2-Nitrophenol by Zero Valent Iron Nanoparticles and Pd-Doped Zero Valent Iron Nanoparticles Surfaces was carried out by Adami and Fakri[5]. They investigated the removal of The removal of 4-Chloro-2-nitrophenol (4C₂NP) from aqueous solutions using zero valent iron nanoparticles (nZVI) and Pd-doped zero valent iron nanoparticles (Pd-nZVI) in terms of initial pH, adsorbent dosage, contact time and temperature. The optimum values of these parameters were observed to be 5, 0.5 g/l, 10 minutes and 298 °K respectively. Also adsorption decreased with increase in temperature, indicating exothermic process.

Soni et. al carried out batch and column studies on adsorption of o-nitrophenol onto nano iron oxide and alginate microspheres[6]. Nano iron oxide loaded calcium alginate beads were used for removal of o-nitrophenol. They investigated the effect of pH, adsorbent dose, contact time and temperature on adsorption capacity of the magnetic beads. The iron oxide nano particles were prepared by using ferrous chloride, ferric chloride and ammonia solution at 80 degree celcius. The sodium alginate gel was used for preparation of magnetic beads. The maximum removal was obtained at pH value of 6.5, adsorbent dose of 1 gram per 100 ml. With increase of o-nitrophenol concentration, the amount of adsorption also increased. It meant that the adsorption is highly dependent on the initial concentration of

adsorbate. Also it was observed that the adsorption of o-nitrophenol increased with the increase in nano iron oxide concentration up to 0.1 ml and then further increase in iron concentration results a decrease in the adsorption. The reason for decrease at higher doses of nanoparticle may be attributed to the fact that at higher concentration, beads become morphologically compact and consequently the diffusion of o-nitrophenol may be hindered.

3.2 Silica Gel

Laboratory Studies on possible utilization of silica gel sludge for the removal of phenol from aqueous solutions were carried out by Idris and Saed [7]. They studied the kinetics of phenol removal by using silica gel as an adsorbent. It was observed that the adsorption capacity increased as the pH was decreased from 6.5 to 2. The phenol removal was found to follow both, Langmuir and Freundlich isotherms. Roostaei and Tezel have carried out research on adsorption of phenol on silica gel, HiSiv 3000, activated alumina, activated carbon, Filtrasorb-400, and HiSiv 1000. as an adsorbent[8]. The adsorption isotherm model by Langmuir was best fitted for the phenol uptake. It was observed that HiSiv 1000 had the highest rate of adsorption among the adsorbents studied .So they carried out more detailed studies with this adsorbent. It was observed that the adsorption capacity of adsorbent did not change with the particle size but rate of adsorption decreased with increase in particle size. The thermal regeneration of the adsorbent was carried out at 360°C. It was observed that the adsorption capacity was unaffected after 14 regeneration cycles. Silica aerigel was used for synthesizing nanoparticles by Khanahmadzadeh et.al [9]. The effects of initial concentration, contact time, pH and temperature were studied. The studies indicated that that by increasing initial concentration; the adsorption efficiency is reduced, so the mechanism of gel filtration has happened. In this mechanism, the majority of the phenol is trapped. One hour contact time was found to be optimum. The adsorption increased with drop in pH. This may be due to the neutralizing effect of negative charges of the level of activated carbon and the hydrogen ions production. The solubility of phenol in water reduces if pH decreased. If pH is increased from 1 upwards phenol adsorption decreases slowly. For values of pH above 9, the adsorption decreases dramatically. This may be the fact that phenol-ionizing capability in pH is equal to 10.

3.3 Activated Carbon

The research on phenol removal by activated carbon was also carried by Maarof and Hameed [10]. The two adsorbents used in their study were the NORIT Granular Activated Carbon (NAC 1240) and NORIT Granular Activated Carbon D10 (NAC010). These adsorbents were used after proper washing and activation. It is observed that that for NAC 1240 at the initial stage, concentration of phenol drops sharply in less than 3 hours, when almost 85% of the phenol had been removed, then gradually decreases until equilibrium was

attained at around 24 hours. For NAC D 10, however, the concentration drop sharply in less than 3 hours, when almost 96% of the phenol had been removed and equilibrium was attained in less than 24 hours. With increase in the phenol concentration, increase in the adsorption of phenol is observed owing to increase in mass transfer driving force. It was observed that the values of Freundlich constants were greater for NAC D 10 than NAC 1240. Qadir and Rehan have investigated the removal of phenol by using adsorption [11]. The treatment of waste with active carbon is considered to be an effective method for the removal of phenol from waste solution because of its large surface area. Kulkarni et. al. have investigated the phenol removal from the effluent by using activated carbon in batch and fluidized bed experimentation [12]. In batch studies they studied the effects of various parameters like adsorbent dose, pH, and particle size on rate of adsorption. In case of fluidized bed, the effect of various parameters like concentration; fluid flow rate and adsorbent particle size were studied. According to the investigation, the percentage decrease in phenol concentration increases with increase in adsorbent dose. With a reduction in particle size, initially steep increase in percentage removal of phenol is observed and it becomes more significant for finer particles. In case of fluidized beds, increase in fluid flow rate gives better adsorption in case of activated carbon. In this study, particle size of 0.420 mm was found more beneficial

The effect of molecular structure on the adsorption of phenol was studied by Adam and Al-Dujaili [13]. The effect of the introduction of NH_2 , CH_3 , Cl , and NO_2 groups to phenol molecule, the effect of substituted position in cresols and aminophenols, and the effect of the number of substituted NO_2 groups in nitrophenols on adsorption were investigated. Electrostatic interaction and hydrogen bonding between the carbon surface and the solute molecules is postulated to explain the adsorption data. The equilibrium data for the adsorption of individual compounds were found to correlate well with the Langmuir equation for adsorption isotherms in the range of concentration studied.

3.4 Zeolite and polymeric resins

The application of zeolite for phenol removal is also widely discussed research area. The research on phenol removal by using zeolite was carried out by Saravanakumar and Kumar [14]. In case of pH, it was observed that the phenol removal was constant in the pH range of 3 to 6 and it decreased in the pH range of 7 to 9. The optimum pH was observed to be 5. The optimum contact time was 40 minutes. It was observed that the adsorption data fitted Langmuir and Freundlich equations with correlation coefficients value of 0.9988 and 0.9440, respectively. Equilibrium data fitted well in a Langmuir isotherm equation, confirming the monolayer sorption capacity of phenol onto sodium zeolite with a monolayer sorption capacity of 13.051 mg/L. Polymeric resins were used for phenol removal by adsorption and ion exchange by Caetano et. al [15]. A non-functionalized hyper-cross-linked polymer Macronet MN200 and two ion

exchange resins, Dowex XZ (strong anion exchange resin) and AuRIX 100 (weak anion exchange) were used for the studies. The Langmuir isotherm was followed by the adsorption phenomenon. The non-functionalized resin reported the maximum loading under acidic conditions, whereas both ion exchange resins reported the maximum removal under alkaline conditions where the phenolate may be removed by a combined effect of both adsorption and ion exchange mechanisms. The desorption studies indicated that the recovery close to 90 percent was obtained by 50% methanol solution for nonfunctional resins. The desorption processes were controlled by the ion exchange mechanism for Dowex XZ and AuRIX 100 resins. For Dowex XZ and AuRIX 100 resins, the desorption processes were controlled by the ion exchange mechanism. Under alkaline conditions the total recovery increased, especially for Dowex XZ resin, while no significant effect for the addition of Cl^- under acidic conditions was observed.

Studies on Influence of the microporosity and surface chemistry of polymeric resins on adsorptive properties toward phenol were carried out by Wu et. al [16]. The effects of the microporosity and chemical surface of polymeric adsorbents were studied. Textural parameters of four kinds of polymeric resins, namely AB-8, D4006, NKA-II and D16 resin, were separately measured. To obtain the isotherms of phenol on the polymeric resins, static equilibrium adsorption experiments were carried out. Due to its strongest surface polarity and largest micropore volume among four kinds of resins, the isotherm of phenol on NKA-II was much higher than that on the other polymeric resins. It was suggested that the well-developed microporosity and the strong surface polarity would improve the adsorption of phenol on the polymeric resins.

The research on adsorption of phenol, chlorophenols, and dihydroxybenzenes onto unfunctionalized polymeric resins at temperatures ranging from 294.15 K to 318.15 K was reported by Wagner and Schulz [17]. Isotherms of the Redlich-Peterson type with characteristic parameters for different polymers were fitted to the adsorption data (surface excess versus normalized concentration). The investigation on the adsorption of phenolic compounds on aqueous solution was carried out by Li et. al [18]. They used water compatible hyper-cross linked polymeric adsorbents for the purpose. They obtained the equilibrium data for adsorption of various phenolic compounds. The adsorption capacity in hyper-cross linked polymeric adsorbent was observed to be twice of amberlyte XAD-4. The reason may be unusual microporous structure and partial polarity on the network. Adsorption entropy of hyper-cross linked polymeric adsorbents was lower than amberlyte XAD-4, requiring more orderly arranged adsorbate. Same can be said about high values of free energy. Amberlite IRA-420 was tried for phenol removal by Carmona et. al. for adsorption of phenol [19]. They reported combined ion exchange and adsorption studies for the phenol removal. According to their investigation, the higher pH values favored the removal of phenol as an increase of the phenolate ion concentration favors the phenol

removal from the liquid phase. Though the phenol removal occurs primarily because of physical process, the empirical relation based on both the mechanisms, i.e. adsorption and ion exchange was needed. Such model was developed which allowed us determine the concentration of phenolate in solution to as a function of the total concentration of phenol and the pH of the liquid solution. The result depicted that an alkaline pH favors the phenol removal by this type of resin, since phenol is highly dissociated at alkaline pH. It was observed that adsorption capacity does not depend on pH. The amount of phenol removed by molecular adsorption was less than that removed by ion exchange regardless of the liquid phase concentration. The studies on adsorption of phenol from aqueous solution by modified zeolite with FeCl_3 were carried out by Asagiri et.al [20]. They evaluated the phenol removal from a synthetic solution using modified zeolite (clinoptilolite) with FeCl_3 as an adsorbent. The parameters like pH, initial concentration and contact time were optimized. They observed that phenol adsorption equilibrium was achieved within 100 min contact time and the optimum pH for adsorption of phenol using zeolite was found as 3. The adsorption data fitted well in Langmuir isotherm.

3.5 Nano TiO_2

The adsorption of 4-chloro-2-nitrophenol ($4\text{C}_2\text{NP}$) on nano- TiO_2 was studied by Mehrzad et.al [21]. They carried out the work related to the kinetic and thermodynamics of phenol removal. The optimization of the operating conditions was carried out and also kinetic data were evaluated by applying pseudo first order kinetics. The equilibrium time was observed to one hour for the effluent sample of 250 ml and contact time of 3 hours. For studying the effect of adsorbent dosage, the adsorbent in various quantities (0.005, 0.01, 0.05 and 0.1 g) was taken in 250 ml of the effluent. The adsorption capacity increased upto the increase in the adsorbent dose of 0.01 gram. Further increase does not have favorable effect on the adsorption capacity. In fact, beyond maximum adsorption capacity at 0.01 g resulted in a decline in capacity. This reduction in capacity had been explained as due to the overlapping of the adsorption sites as a result of overcrowding of adsorbent particles above 0.01 g dose. The highest amount of $4\text{C}_2\text{NP}$ adsorption was at pH 2 (86.3 mg/g). Adsorption was high for pH value of 6 or less but it decreased for values higher than 6. When the initial $4\text{C}_2\text{NP}$ concentration increased from 2 to 10 mg/L, the amount of $4\text{C}_2\text{NP}$ adsorbed per unit weight of the nano- TiO_2 increased from 6 to 86.3 mg/g. The increase of loading capacity of nano- TiO_2 with increasing initial $4\text{C}_2\text{NP}$ concentration may be due to higher interaction between $4\text{C}_2\text{NP}$ and adsorbent. It was observed that that the adsorption follows pseudo first order kinetics. Negative free energy change of adsorption (ΔG°), positive enthalpy change (ΔH°) and positive entropy change (ΔS°) indicated that the adsorption is a spontaneous and endothermic process. The removal of phenol from nonpolar solvents was tried by Davis et.al. It

was observed that a complete monolayer was formed [22]. An affinity of adsorption, K , is defined in terms of an ideal model of adsorption at the solid/solution interface and it is found that in general K increases with increase in σ , the Hammett p -substituent constant.

3.6 Activated alumina

The adsorption of phenol on activated alumina was carried out by Hassan and Hammad [23]. Five derivatives of phenol, viz. m-nitrophenol, m-aminophenol, m-hydroxyphenol, m-cresol, m-hydroxybenzoic acid and phenol were used. They determined the isotherms at 22 °C, 25 °C, 35 °C. The phenol uptake followed the Langmuir isotherm rather than Freundlich. Increasing temperature led to reduction in adsorbate without change in isotherm patterns. This means that the mechanism is exothermic for all investigated phenols. High voltage electric pulse was applied to the activated alumina bed for phenol removal by Li-nan et.al [24]. With increase in the applied voltage, the phenol removal rate increased, while pH increased. The addition of sodium carbonate reduced the phenol removal rate because it was a radical scavenger. The additive of Fe^{2+} could promote the phenol degradation mainly due to the formation of OH. The activated alumina particles could be polarized in the pulsed high-voltage electric field by applying the pulsed voltage. This induced the formation of local discharge and increased the phenol removal in the thin water film. This method can produce many active species, such as OH, O_3 , H_2O_2 , and so on synchronously, which has high oxidation potential and can oxidize organic pollutions effectively. Though, the method needs energy, it has obvious advantages and hence can be effective for by optimizing it for higher efficiency.

3.7 Rice husk

Experiments were conducted to study the use of rice husk and activated carbon for phenol removal by Kermani et.al [25]. The rice husk ash was prepared at three different temperatures i.e. 300, 400 and 500 °C. The experiments were carried out to examine the effect of various parameters like initial concentration, contact time pH, adsorbent dose on the adsorption capacity. 5 hours contact time was reported for 10 mg/l phenol concentration for maximum removal. Activated carbon followed Freundlich isotherm while rice husk ash followed the Langmuir isotherm. The adsorbent dose of 1 gram per liter, initial concentration of 10 mg/l and pH values of 5, were the optimum parameters for phenol removal.

Rice husk ash (RHA) obtained from a rice mill in Kenya was used as an inexpensive and effective adsorbent (and reagent) for the removal (and detection) of some phenolic compounds in water by Mbui et.al [26]. Its potential in: (i) the removal of phenol, 1, 3-dihydroxybenzene (resorcinol) and 2-chlorophenol from water; and (ii) the detection of 1, 2-dihydroxybenzene (pyrocatechol) and 1, 2, 3-trihydroxybenzene (pyrogallol) present in an aqueous

medium was studied. The rice husk ash exhibited reasonable adsorption capacity. It followed both Freundlich isotherm and Langmuir isotherm. For the detection experiments, pyrocatechol and pyrogallol present in water formed coloured complexes with rice husk ash, with the rate of colour formation increasing with temperature, weight of rice husk ash. Similar experiments were carried out by Bina[27]. The rice husk was washed and then burnt at three different temperatures, 300, 400 and 500 °C. The phenol removal versus time curve was smooth and continuous, indicating monolayer adsorption of phenol. The optimum pH was found to be 5. The equilibrium data for RHA-300 fitted the Langmuir isotherm model best within the concentration range studied whereas equilibrium data for RHA-400, RHA-500 and GAC could be described well by the Freundlich isotherm model. The research on phenol removal by using rice husk and rice husk ash was carried out by Mahvi et.al.[28]. Equilibrium adsorption was higher for rice husk ash compared to rice husk because of higher surface area. The adsorption data for the uptake of phenol versus contact time at 150µg/L initial concentration with 5gram rice husk and 700µg/L initial concentration with 0.12gram rice husk ash were carried out in pH value of 7. Rice husk ash needs only 3 hours for equilibrium whereas rice husk needs 6 hours. Adsorption in both the cases followed first order kinetics. Also Adsorbent dosage was varied from 1g to 7g and 0.1g to 0.5g for rice husk and its ash, respectively. The results showed that for removal of 500 µg/l of phenol in 100 ml of solution, a minimum dosage of 0.3gram of rice husk ash is required for 96% removal of phenol. Under the same circumstances, the removal by using rice husk was only 27 %. Similar experiments were carried out with almost identical results by Daffalla[29]. The surface area of RH increased from 7.1 up to 87.1 m² g⁻¹ after heat treatment.

Kadhim and Al-Seroury have carried out research on characterization the removal of phenol from aqueous solution in fluidized bed column by rice husk adsorbent [30]. They found that the pretreatment of rice husk increases the specific surface area and changes the functional groups, therefore it leads to increase in the capacity of adsorption.

3.8 Sawdust

Jadhav and Vanjara have carried out the research on adsorption of phenol sawdust, polymerized saw dust and sawdust carbon [31]. They studied the influence of the parameters like concentration, agitation speed, and amount of adsorbent and the pH on adsorption capacity. It was concluded that saw dust and modified saw dust can be used effectively as an adsorbent for removal.

3.9. Hycinthe

Hycinthe as adsorbent was used for phenol removal by Uddin et.al [32]. They carried out the batch kinetic and isotherm studies under varying experimental conditions of contact time, phenol concentration, adsorbent dosage and pH. They inferred that the adsorption of phenol decreased with

increasing pH. The results also showed that kinetic data followed closely to the pseudo-second-order model.

3.10 Date stones

Activated carbons prepared from date stones was used for removal of phenolic compounds from aqueous solutions by adsorption by Dhidan [33]. He used activated carbon prepared from date stones by chemical activation with ferric chloride (FAC) as an adsorbent to remove phenolic compounds such as phenol (Ph) and p-nitro phenol (PNPh) from aqueous solutions. He achieved the maximum phenol removal of 98% at pH value of 5 and 90 minutes of contact time.

3.11 Tamarind shell activated carbon

A research on mass transfer coefficients in a packed bed using tamarind nut shell activated carbon to remove phenol was done by Goud et. al. [34]. They reported work on the preparation and characterization of activated carbon from tamarind nutshell, an agricultural waste byproduct, and its use in a packed bed for the removal of phenol. They found that that the sorption of phenol is dependent on both the flow rate and the particle size of the adsorbent, and that the breakpoint time and phenol removal yield decrease with increasing flow rate and particle size. For mass transfer coefficient, experimental values were in excellent agreement with the predicted values from the correlation. The experimentation for examining the application of adsorption packed-bed reactor model for phenol removal was done by Sorour et.al[35]. They conducted the experiments to determine the Langmuir equilibrium coefficients and to determine the bulk sorbate solution concentration for different adsorption column depths and different time as well. They predicted a packed bed model which was in well agreement with the laboratory data.

3.12 Pineapple peels

Pineapple peels immobilized pseudomonas aeruginosa NCIB 950 was used for phenol removal by Agarry and Aremu [36]. The investigation was carried out for batch equilibrium and kinetic studies of simultaneous adsorption and biodegradation of phenol. The effects of initial phenol concentration, pH and adsorbent particle size on the simultaneous adsorption-biodegradation (SAB) of phenol were studied. The synthetic culture was prepared by transferring two loops full of microorganisms from an agar slant culture into 100 ml of feed medium containing 20 ml of mineral salt medium and 80 ml of 50 mg phenol solution in a 250 ml Erlenmeyer conical flask followed by incubation and agitation. 10 ml of this primary culture was transferred to another 100 ml of feed medium and again incubated. This was secondary culture. The pineapple peels were sun dried, washed and activated. The batch study for 150 ml of effluent indicated that 48 hours contact time was sufficient for equilibrium. The optimum pH was reported to 7. With reduction in size, the adsorption increased.

3.13 Tea waste

Bolat et. al. have reported the use of tea waste for the treatment of industrial wastewater[37]. They used black turkish tea and Indian tea for the purpose. They also reused the tea waste for the adsorption. It was noted that metal ions can be efficiently absorbed by tea waste and can see 59 percent of adsorption if the industrial waste water is treated with 4 grams of tea waste. Equilibrium, kinetic, and thermodynamic study on adsorption of phenol from aqueous solution on a low-cost activated carbon produced from tea industry waste was reported by Gundogdu et.al [38]. Their study indicated the maximum adsorption took place in the pH range of 4 to 8. The adsorption followed pseudo second order kinetics. It fitted in Langmuir adsorption model with adsorption capacity of 142.9 mg/g. It was concluded that the removal of phenol from aqueous solution by low-cost activated carbon produced from tea industry waste produced from tea industry wastes with a very low cost took place with an extremely high performance. Similar work on tea waste was also reported by Kazmi et.al [39]. Their results showed that the optimum values for pH, biosorbent dose and contact time were 2.2 g/L and 180 minutes, respectively. Pseudo 2nd order kinetic and the Langmuir's Models best described the kinetic and equilibrium behaviors, respectively.

3.14 Tendu leaves

The application of Tendu leaves, a waste from beady industry, for phenol removal was reported by Nagda et.al [40]. They used raw tendu leaf refuse and chemically carbonized tendu leaf refuse. Adsorption equilibrium of tendu leaf refuse and chemically carbonized tendu leaf refuse was reached within 2 hr for phenol concentration 10-25 mg/l and 1 hr for phenol concentration 20-200 mg/l. It was observed that The maximum adsorption capacity of chemically carbonized tendu leaf refuse as per Langmuir model was 4 times higher than that of raw tendu leaf refuse.

3.15 Flyash

The studies carried out by akerman showed that the fly ash adsorbed 67, 20, and 22 mg/g for phenol, chlorophenol, and 2, 4-dichlorophenol, respectively, for the highest water phase concentrations used[41]. Phenol displayed a much higher affinity for flyash than 3-chlorophenol and 2, 4-dichlorophenol. Flyash from thermal power plants was used for adsorption by Sharan et.al [42]. Their study showed that, at a phenol concentration of 100 mg/l, the percentage removal of phenol was 95.69% at an optimum dosage of 7 g/l fly ash. The usual trend of increase in adsorption with concentration and adsorbent dose were observed. Adsorption equilibrium studies indicated that an equilibrium time of 2 h was necessary for the maximum removal of phenol. The maximum adsorption capacity (q_0) and the Langmuir adsorption constant (K_L) were evaluated and found to be 142.86 mg/g and 0.0199 l/g, respectively. The kinetics was pseudo first order. Kulkarni et.al have reported the use of bagasse flyash as an adsorbent for removal of phenol and

other pollutants. The contact time for phenol was 250 minutes. The optimum pH and adsorbent dose were observed to be 6.5 and 3.5 mg/100 ml respectively [43].

Andini et.al tried Adsorption of chlorophenol, chloroaniline and methylene blue on fuel oil fly ash. The adsorption was highest for 2-chlorophenol, reaching about 70 mg/g, and quite lower in the other two cases[44]. Phenol removal from water with modified carbons prepared from bagasse ash was reported by Basu et.al[45]. They separated unburnt carbon from bagasse ash and modified it to increase its adsorptive capacity. The methods included (i) deashing by HCl and HF (ii) oxidation by H₂O₂ or HNO₃ (iii) deashing followed by oxidation with H₂O₂ or HNO₃. The modified carbons were characterized for composition and surface area. Adsorptive removal was investigated for phenol concentrations between 10 to 2000 mg/l and carbon dosages from 0.1 to 1 gram per 100 ml. The modified carbons showed high removal (80-100%) for low phenol concentrations (10-100 mg per lit.) while a maximum removal of 60% was obtained at higher concentrations (1000-2000 mg /lit.).

3.16 Cassava peels

The removals of phenol from aqueous solution by cassava peel and chemically modified cassava peels were determined under various conditions of contact time, pH and temperature by Allinor and Nwachukwu [46]. The influence of pH on the phenol adsorption by cassava peel was carried out between pH of 4 to 9. The phenol uptake was high for a pH value of 9. The uptake of phenol decreases with temperature increase. The decrease on the uptake of phenol as temperature increases may be explained in terms of the increase in the average kinetic energy of phenolium ions. The increase in average kinetic energy will cause the repulsive forces between the phenolium ions and positively charged cassava peel surface. This electrostatic repulsion may cause desorption or make the phenol to bounce off the surface of the cassava peel instead of colliding and combining with it. At equilibrium 68.0mg/L or 85.0% and 39mg/L or 48.75% of phenol were removed from aqueous solution by modified and unmodified cassava peel, respectively. The result shows that at initial contact time of 20 minutes and concentration 80 mg/L, the amount of phenol adsorbed on modified and unmodified cassava peel were 20mg/L or 25.0% and 3.0mg/L or 3.75%, respectively.

4. Conclusion

Adsorption for removal of heavy metal is widely studied area of research. Various wastes have been effectively used for the phenol by investigators. Most of the adsorbents have shown the phenol removal efficiency above 90 percent except few exceptions. The key to the effectiveness of this method for removal of phenol is the effective method of regeneration of adsorbent or effective disposal of used adsorbent. The research is also carried out for the effective method of regeneration. The regeneration of adsorbent depends on cost of regeneration. Adsorption in fixed bed by

low cost adsorbent is promising alternative for phenol removal from wastewater.

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