Removal of Phenol from Wastewater by Adsorption: A Review

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Abstract— Phenol is the priority pollutant since it is toxic & harmful to organisms even at low concentrations. The importance of the study related to phenol degradation is to ensure and provide a safe place for next generation i9n future especially water sources. In this study, phenol removal from wastewater by adsorption method has been reviewed. The adsorptive removal of phenol, adsorption isotherms, kinetics, various factors that affect the rate of adsorption and regeneration and disposal of adsorbents has been discussed in this study. However, there is a strong need to study more on cost effective and efficient methods for regeneration & disposal of adsorbents.

Key words: Adsorption, phenol, isotherms, kinetics, regeneration

I. INTRODUCTION

Environmental pollution is a worldwide problem that is faced by developing and developed countries over the period. Phenol is a common industrial substance involve in especially the production of chemicals such as oils, plastics, aspirins, antiseptics, pharmaceutical, oil refining, explosives, dyes, reagents in chemical analysis and leather and food preservatives. Industrial usage of phenols has been widespread since it can be used as an intermediate chemical in a wide range of applications, especially in the production of dyes, pesticides and drugs.

Phenol itself exists as a crystalline substance colorless in room temperature, and has hydroscopic properties in water and slightly in organic solvents that make them easily spilled or leaked into the surface water and or inside the groundwater source. Undergoing a variety of chemical reaction either at benzene ring or its hydroxyl group had made phenol to become very reactive compound. [2]

Phenol is considered as the main concern pollutant because of its harmful and toxic effects, and can be accumulated in living organism. Due to this concern, the level of phenol in drinking water and effluent has been also limited by international act and each country has proposed many profit and non-profit agencies such as EPA, and WHO. Phenol exposure cause by either directly or accidently exposure can disrupt the metabolic system in microorganism, human or animals [2]

Conventional methods for the removal of phenolic pollutants in aqueous solutions can be divided into three main categories: physical, chemical and biological treatment. Among them, physical adsorption method is generally considered to be the best, effective, low-cost and most frequently used method for the removal of phenolic pollutions. Therefore, the search for low cost and easily available adsorbents has led many researchers to search more economic and efficient techniques of using the natural and synthetic materials as adsorbents. [6]

II. ADSORPTIVE REMOVAL OF PHENOL

Adsorption is a separation process in which certain components of the fluid phase are transferred to the surface of the solid adsorbents. When a solid surface is exposed to a fluid phase, the molecules from the bulk of the fluid phase have tendency to accumulate or concentrate at the surface of a solid. The phenomenon of the enrichment of chemical substances at the surface of a solid is called 'adsorption'. All adsorption performance processes are depends on solid-liquid equilibrium and on mass transfer rates. If the mass transfer is in opposite direction then it is called as 'Desorption'. Most adsorbents are highly porous materials, and adsorption takes place primarily on the walls of the pores or at the specific sites inside the particle. [13]

The process of adsorption has an edge due to its sludge-free clean operation and complete removal of phenols from aqueous solutions having dilute or moderate considerations. Activated carbon is most widely used adsorbent. [4, 5, 7] in spite of good capacity it suffers from several disadvantages. The cost of activated carbon is higher. Chemical as well as thermal regeneration is expensive, impractical and produces additional effluent. This led many workers to search for economic, practical and efficient adsorbents. [5]

Some of the important adsorbents used in adsorption of phenol and its derivatives are:

1) Activated carbon
2) Naturally Occurring materials like clay, fly ash, coal, soil, etc.
3) Synthesized materials [7]

The adsorption capacity data reveal that non-conventional adsorbents possesses remarkable capacity for the removal of phenols from aqueous solutions.[5] Some review documents for removal of phenol from wastewater using various adsorbents are as follows:

Ahmed Ismail Mustafa, Md. Saiful Alam et al. (2008) has studied that the jute stick is an effective adsorbent for the removal of phenol from aqueous solutions. Jute stick can be used as an adsorbent for phenol removal in a wide pH range of 6-12. The extent of removal was dependent on concentration of phenol, contact time, pH, and quantity of adsorbent. With an initial concentration of 40 ppm phenol in 100 mL and pH 10.0, the maximum removal was found to be about 68% with 3.0 g jute stick. [3]

Laila Mandi et al (2009) has studied that Banana peel is a promising material for the removal of contaminants from olive mill wastewater. The results showed that the increase in the banana peel dosage from 10 to 30 g/L significantly increased the phenolic compound adsorption rates from 60 to 88%. [8]

Meghzili Bachir, Medjram Mohamed Salah et al (2014) and S. M. Mousavi et al (2006) have investigated that the raw (gross) and modified bentonite have the potential to adsorb of phenol pollutants respectively.[9,14

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Tries were performed on water contaminated by known concentration of phenol. The results (profits) of the tries (essays) led in laboratory show the 64 % and 80-88% elimination of the concentrations by raw and modified bentonite respectively. [9]

III. ADSORPTION ISOTHERMS AND KINETICS

A. Adsorption Isotherms:

An adsorption isotherm is the presentation of the amount of solute adsorbed per unit weight of adsorbent as a function of the equilibrium concentration in the bulk solution at constant temperature. Langmuir and Freundlich adsorption isotherms are commonly used for the description of adsorption data.

Langmuir isotherm assumes monolayer sorption onto a surface containing a finite number of identical sorption site is occupied, no further can takes place at that site. The linear form of the Langmuir isotherm is

$$Ce/qe = Ce/qm + 1/ qm$$

Where,

Ce is the equilibrium concentration of solute (mmolL−1).

qe is the amount of solute adsorbed per unit weight of adsorbent (mmol g−1 of clay).

Xm is the adsorption capacity (mmol g−1) or monolayer capacity, and b is a constant (L mmol−1).

The Freundlich isotherm describes heterogeneous surface adsorption. The energy distribution for adsorptive sites (in Freundlich isotherm) follows an exponential type function which is close to the real situation. The rate of adsorption/desorption varies with the strength of the energy at the adsorptive sites. The Freundlich equation is expressed as:

$$\log qe = \log KF + 1/n \log Ce$$

Where, k (mmol g−1)
1/n are the constant characteristics of the system.

B. Adsorption kinetics:

Two kinetic models; Lagergreen (pseudo-first-order) and pseudo-second-order reaction can be used to test experimental data to predict to the adsorption kinetic.

1) Pseudo-first-order reaction kinetic:

The adsorption rate constant proposed by Lagergreen using first order reaction kinetic is shown below:

$$dqt/dt= k1(qe − qt)$$

Where, k1 is the adsorption rate constant (min−1) for the first order adsorption, qt is the amount of phenol adsorbed at time t (mg g−1) and qe is the amount of phenol adsorbed at equilibrium (mg g−1).

2) Pseudo-second-order reaction kinetic:

Adsorption data was also evaluated according the pseudo second-order reaction kinetic proposed by Ho and McKay:

$$dqt/dt= k2(qe − qt)2$$

Where, k2 is the second order reaction constant (gmg−1 min−1) [15]

IV. FACTORS THAT INFLUENCE RATE OF ADSORPTION

A. Nature of Adsorbate:

The characteristics of ions, molecules (size, shape, charge, etc.) present in wastewater and their concentration have profound influence on the extent of adsorption. Phenols are dissociated in aqueous medium to form anionic species at pH > 6. These anionic species adsorbs at positively charged surface centers on adsorbent. [5]

B. Nature of Adsorbent:

Though every solid is an adsorbent, the physicochemical nature of adsorbent can have profound effect on both, the rate and capacity for adsorption. [5]

Sameer al-Asheh et al (2002) has reported that different types of activated bentonite have shown better efficiency of phenol rmoval than natural bentonite. They found that the amount of phenol removal was seriated in the following order: CTAB/ Al-Bentonite > Al-Bentonite >CTAB bentonite > thermal-treated bentonite > cyclohexane bentonite > natural bentonite. [12]

C. Effect of Adsorbate Concentration:

The increase in concentration of the adsorbate results in increase in the magnitude of adsorption at a given temperature. This parameter has been studied by several investigators and the results are generally expressed by linear form of Frendluich and Langmuir isotherms. [5]

Zohra Dali- Youcef et al (2011) have investigated that when the initial phenol concentration was 400 mg/L, the adsorbed amount at equilibrium was maximized. Fixing the phenol thus became more heavily favoured as the initial concentration increased. The increase in concentration enhances mass transfer, thereby exerting a force on the surface of adsorbent and leading to an increase in phenol adsorption speed on the activated mud. [16]

D. Adsorbate dose:

It is important to determine the dose of adsorbent required to achieve a desired level of treatment. [5] Muhammad et al. (2012) have reported that the amount of lignosulfonate compound adsorbed increased from 78.83% to 92.16% with an increase in adsorbent dosage from 5 g to 30 g at pH = 7.

As the dosage of eggshell is increased, the solution becomes more basic and the surface area negative charge increases; thus, adsorption of ligno¢sulfonate is increased. A maximum removal of 92.16% was observed at an adsorbent dosage of 30 g per 100 mL of lignosulfonate solution. [10]

E. Effect of Contact Time:

Adsorption of adsorbate species is faster in the initial stages of contact period and becomes slow near equilibrium. Contact time required to attain equilibrium is a function of particle size, pH, rate of agitation, temperature, etc. Pretreatment of adsorbent also influence the rate of equilibrium time. [5]

M.T. Uddim et al. (2007) have reported that equilibrium time required for the adsorption of phenol on water hyacinth ash was almost 120 minutes (2h). However, for subsequent experiments, the samples were left for 5h to ensure equilibrium. These results also indicated that up to 90-95% of the total amount of phenol uptake was found to occur in the first rapid phase (30min) and thereafter the sorption rate was found to decrease. The higher sorption rate at the initial period (first 30min) may be due to an increased number of vacant sites on the adsorbent available at the initial stage, as a result there exist increased concentration

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gradients between adsorbate in solution and adsorbate on adsorbent surface. [11]

F. Effect of pH:

The removal of phenol from water by adsorption is highly dependent on pH of the solution; which affects the surface charge of the adsorbent, degree of ionization, and speciation of phenol. It is reported that per cent adsorption of phenol on activated carbon increases upto pH6 and then decreases with further increase in pH. [5]

Ihsan Habib Dakhil (2013) have reported that the removal of phenol increases slightly with increasing the pH value from 3 to 6, then, fast decreases at pH 7-9. In general, the phenol uptake decreases at low and high pH values. At low pH values, the uptake of phenol is less due to the presence of H+ ions suppressing the ionization of phenol and hence its uptake on polar adsorbent is reduced. In the high pH range, phenol forms salts which are readily ionized leaving negative charge on the phenolic group. At the same time the presence OH- ions on the adsorbent prevents the uptake of phenolate ions. [16]

G. Effect of Particle Size:

Adsorption is a surface phenomenon such that the extent of adsorption is proportional to the specific surface area (micropores). Thus, the adsorption is greater small particle size. [5] Muhammad et al. (2012) have determined the effect of particle size on sorption was conducted using samples of three different average particle sizes: 50, 100 and 150 µm at pH 7 and temperature of 25°C for 90 minutes. the effect of particle size on sorption was conducted using samples of three different average particle sizes: 50, 100 and 150 µm at pH 7 and temperature of 25°C for 90 minutes. The result is shown at Figure 6. As seen from Figure 6, variation of the particle size of powdered eggshells statistically has no significant effect on the adsorption of lignosulfonate compounds as indicated by 89 – 92%. Variation of the particle size of powdered eggshells statistically has no significant effect on the adsorption of lignosulfonate compounds as indicated by 89 – 92%. [10] The difference in adsorption capacity with particle size is small but significant. [5]

H. Effect of Temperature:

Temperature affects the adsorption rate by altering the molecular interactions and solubility of the phenol solution thereby increasing active sites on the carbon surface; Aditi Gupta et al (2013) observed that an increase in temperature resulted in an increase in the percentage of phenol removed from the solution. [1]

V. Regeneration and Disposal of Adsorbent

The common technique in regeneration is thermal volatilization in which adsorbed organics are desorbed at high temperature. This process is uneconomical due to loss of carbon (5-10%) and the cost of energy in heating the carbon around 800-850ºC. An alternative technique is that of chemical regeneration in which chemical reagents are applied to exhaust adsorbent. Efforts have been made to regenerate and recover the adsorbed phenols. Almost complete removal of adsorbed phenolic compounds on iron hydroxide loaded marble could be achieved with 1M NaOH solution. This is probably due to ligand-exchange reaction and thus the sodium salts of phenolic compounds were easily eluted. Sodium hydroxide has been used as a reactive chemical in regeneration of granular activated carbon. The phenol reacts with caustic soda to form sodium phenate which is readily desorbed and carried out of the carbon-bed in the regeneration stream. Ethanolic-NaOH has also been reported for the desorption of phenols.

Since, tyhermal regeneration of adsorbent is likely to cause air pollution problems and chemical regeneration will lead to increased water pollution, it is not desirable to regenerate non-conventional adsorbents in view of their low-cost and ease of availability provided their disposal after use is easier and safe. [5]

VI. Conclusion

In this study, the adsorption of phenol, parameters that influence on adsorption, regeneration & disposal of adsorbents has been reviewed. From this study, it can be said that natural materials shows a good replacement for commercial activated carbon on the adsorption of phenol, but there is a strong need to investigate on the following points: (a) to improve the effectiveness of natural adsorbents for removal of pphenol from wastewater (b) to increase the studies on various adsorbents to ascertain cost reduction, (c) to study on effective methods for regeneration and disposal of natural adsorbents efficiently.

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