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Regeneration strategies for spent solid matrices used in adsorption of organic pollutants from surface water: a critical review

Martins O. Omorogie[a], Jonathan O. Babalola[b], Emmanuel I. Unuabonah[a,c,*]

[a]*Environmental and Chemical Processes Research Laboratory, Department of Chemical Sciences, Redeemer's University, P.M.B. 3005, 110115, Mowe, Ogun, Nigeria, Tel. +234 8026827920; emails: omorogiemoon@yahoo.com (M.O. Omorogie), iyaemma@yahoo.com, unuabonahe@run.edu.ng (E.I. Unuabonah)*
[b]*Department of Chemistry, University of Ibadan, Ibadan, Nigeria, Tel. +234 803454 0881; email: bamijibabalola@yahoo.co.uk (J.O. Babalola)*
[c]*Dalian Institute of Chemical Physics (DICP), Chinese Academy of Sciences, 116023, Dalian, Liaoning, P.R. China*

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ABSTRACT

Adsorption is a very important physicochemical process used for several purposes including separation and purification of proteins and in water treatment. This article reviews the various strategies that have been employed in the regeneration of spent adsorbents used in the adsorption of organic pollutants from aqueous solutions. The principles, advantages, disadvantages, and factors influencing each of these techniques are discussed. Future perspectives on the use of these techniques in regeneration process are provided for further studies with the view to make the regeneration process of spent solids more efficient and sustainable.

Keywords: Regeneration; Degradation; Organic pollutants; Sustainable; Activated carbon; Adsorbents; Water treatment

1. Introduction

Adsorption has become a widely used technique in many industries on a large scale for purification, separation, and compliance purposes. The main types of adsorbents used to adsorb a range of pollutants with varying concentrations in aqueous solutions are activated carbon, polymeric adsorbents, and zeolites. Adsorption is widely preferred over other techniques for pollutant recovery from aqueous solution because of its high efficiency, low-cost, and friendly operations. It has been estimated recently that global production of activated carbon is expected to hit 2.3 million metric tons by 2017 [1]. The per capita consumption of active carbon per year is 0.5 kg in Japan, 0.4 kg in the United States, 0.2 kg in the Europe, and 0.03 kg in the rest of the world [2]. These conventional adsorbents (activated carbon and zeolites) were thought to be initially expensive which was why there was serious effort in the last decade, especially from scientist in the developing world, to search for low-cost adsorbents. Today, there is a huge database of low-cost adsorbents already prepared and used for the recovery of several adsorbates/pollutants from water, which do have the potentials of replacing these conventional adsorbents.

While adsorption technique in the liquid phase is advancing at different industrial and commercial levels, there is the serious challenge of maximizing and exploiting an adsorbent continuously with minimal

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*Corresponding author.

loss of efficiency. Economical application of an adsorbent depends on an efficient means of regenerating and recycling after its adsorptive capacity has been reached [3]. On a large scale, it is economically viable to regenerate adsorbents especially when the adsorbents are not naturally abundant. One approach which has been investigated by many workers is the development of low-cost adsorbents based on carbonaceous waste products that are used on a once through basis, hence eliminating the need for regeneration [4,5]. A major concern with this approach is the danger of adsorbates (the adsorbed pollutants) being leached into the environment when spent adsorbents are dumped into the environment without proper desorption of pollutants from them. This makes regeneration of spent adsorbents of such economic and environmental importance.

The second approach is the use of various regeneration techniques for regenerating spent adsorbents for continuous reuse. While the former approach suffers from fear of huge deposits of spent adsorbents within a short time and the financial cost of pre-treating the solid waste before disposal, the latter approach is popular among researchers and industries for several reasons discussed in detail in the latter part of this article. In both approaches, there is the crucial need for desorption of pollutants from the adsorbent. Fig. 1 shows the various basic regeneration techniques used in the recovery of pollutant-loaded adsorbents.

There is so much in the literature about efficient adsorbents for adsorption processes but very little information on how these adsorbents could be regenerated for possible reuse or final disposal. In our recent search of the ISI Web of Science using the words “adsorption pollution”, 5,592 related articles were found between 1962 and 2013 of which 603 related articles were published in 2013. Using the words “regeneration adsorbents” 1,715 related articles were found between 1950 and 2013 of which 225 related articles were published in 2013. These data suggest the current low attention paid to this process, which should be given as much attention as the adsorption process itself.

This review is therefore focused on the different techniques currently employed in the regeneration of adsorbents from research perspective, including microbial [7], microwave [8], thermal [9], chemical [1,2], photo-assisted [10,11], electrochemical [12], supercritical fluid (SCF) [13], ultrasound [14,15], and dielectric barrier discharge plasma (DBDP) [16] regeneration techniques, their principles, advantages, disadvantages, and future perspectives in the regeneration of adsorbents which will be of benefit to future research in adsorption and its industrial application. Except for the thermal regeneration technique, these techniques are not currently used in the industry. However, some of them do have the potentials of being employed on a large scale in the nearest future which is why this review seeks to highlight these potentials to stimulate interest in their use.

2. Microbial regeneration technique

Microbial regeneration of an adsorbent involves renewing the adsorbent by microbial activities. Microbial regeneration is a synergistic combination of adsorption and biodegradation processes in which the microbes with nutrients and dissolved oxygen are mixed with the pollutant-loaded adsorbent and there is subsequent desorption and biodegradation of the adsorbate(s) on the adsorbent. This is referred to as “offline microbial regeneration” [17,18]. It is believed that the adsorbent protects the microorganisms from shock loadings of toxic and inhibitory materials [19].

Two mechanisms have been proposed for microbial regeneration: the concentration gradient and exoenzyme mechanisms. In the concentration gradient mechanism, adsorbed organics are desorbed from solid surfaces as a consequence of the microbial degradation that lower its concentration in the liquid phase which leads to a concentration gradient between the adsorbent and the bulk liquid [20]. Furthermore, the difference in the Gibbs free energy between adsorbate molecules in solution ($-\Delta G^o_{\text{ads}}$) and the modified adsorbed molecules inside the porous structure of the adsorbent ($-\Delta G^o_{\text{mod}}$) plays a role in this mechanism and is suggested to be the driving force for the regeneration process [21]. In the exoenzyme mechanism, it is believed that the adsorbate on the solid matrix may sometimes not be available for degradation by the microorganism, in which case exoenzymes excreted by the microorganism diffuses into the pores of the adsorbent and reacts with the adsorbate with a resultant hydrolytic decay or desorption of enzyme metabolite which is a combination of the adsorbate and the exoenzyme that have weak adsorption ability [20,22–24].

Some studies have shown that the regeneration efficiency of a microbe strongly depends on several factors such as presence of mineral components (nitrogen, phosphorus, sulfur, etc.) for metabolism of adsorbate, optimum conditions for microorganism activity [18], reversibility of adsorbate from the adsorbent’s surface which is largely controlled by the bonding mechanism, biodegradability of adsorbate, adsorbent

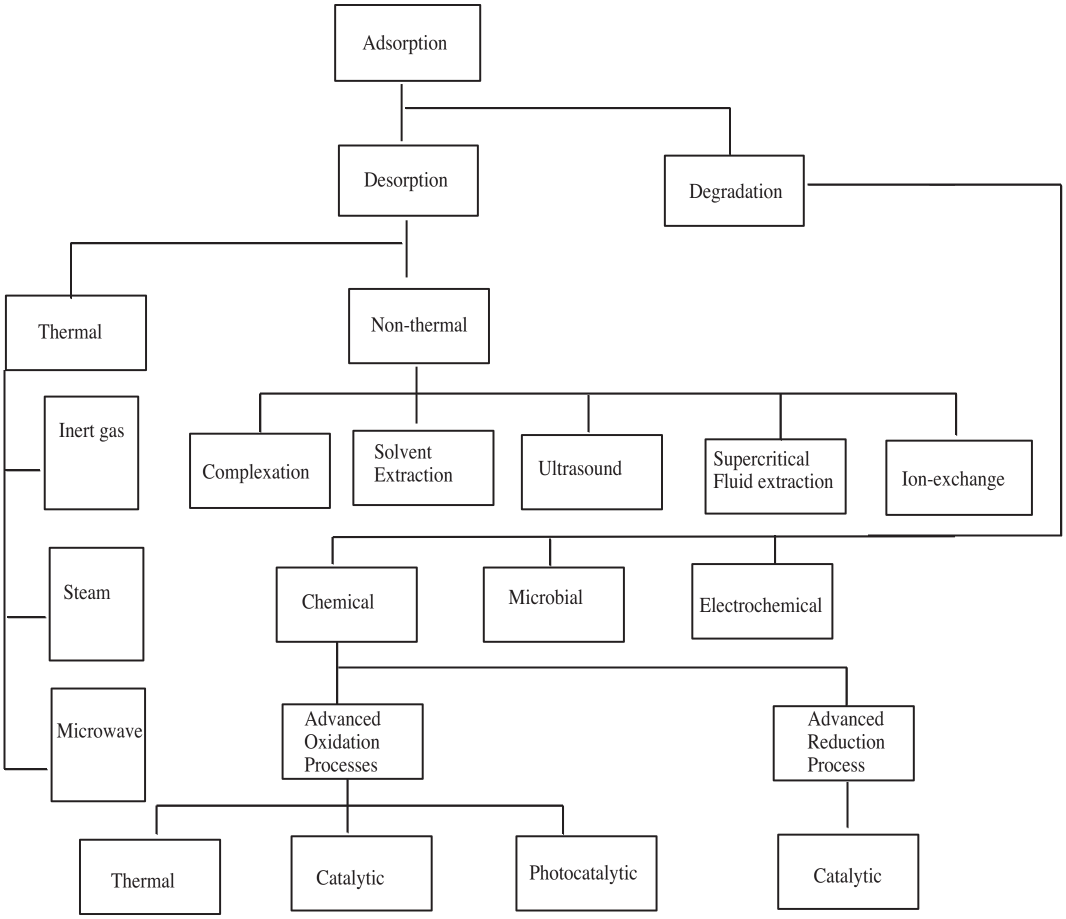


Fig. 1. Basic regeneration techniques for recovery of spent adsorbents (Modified from [6]).

particle size, adsorbent porosity, nature of adsorbent, desorption kinetics, concentration gradient of adsorbate and adsorbent saturation, biomass concentration, dissolved oxygen, type of microorganism, molecular structure of organic pollutants, and structural characteristics of the adsorbent [25–29]. A clear case of the effect of structural characteristics of an adsorbent on microbial regeneration was reported by Coelho et al. [30] who showed that microbial regeneration of molinate (a herbicide)-loaded activated carbon by a mixed culture of bacteria was favored in the macro- and mesopores of the activated carbon but not in the micropores where it was strongly adsorbed.

In the case of the influence of molecular structure of an adsorbate, powdered activated carbon (PAC) loaded with a non-phenolic compound (3-chlorobenzoic acid) was more readily bioregenerated by a bacteria (*Pseudomonas* B13) compared with o-cresol-loaded PAC [24]. In the case of nature of adsorbent, chemically prepared PAC was found more efficiently bioregenerated compared with thermally prepared PAC [24]. The nature of chemical substitution on an adsorbed organic pollutant could also influence microbial degradation of such organic pollutant adsorbed on an adsorbent. For instance, phenol-loaded PAC was more efficiently regenerated by microbes in a laboratory scale sequencing batch reactor compared with p-methylphenol, p-ethylphenol, and p-isopropyl phenol-loaded PAC. Increasing the alkyl chain length of the substituted phenols decreased the microbial regeneration efficiency [31–34]. Substituted aromatic adsorbates with electron-donating substituents like the hydroxyl group (e.g. Phenol) exhibited higher irreversible adsorption unlike substituted aromatic adsorbates with electron-attracting chemical substituents like the nitro- and chloro- groups [35–38]. Unsaturated groups (e.g. carboxyl and nitro groups) on an aromatic compound have been reported to decrease its susceptibility to oxidation (which is the mechanism of biodegradation) whereas saturated groups (e.g. methyl groups) increase its probability of oxidation [24,39].

Microbial regeneration also occurs with organic compounds that are not easily degraded from an adsorbent if given sufficient contact time with the adsorbent [40]. Hence, microbial regeneration of adsorbents loaded with slowly degradable organic compounds increase with time [41,42].

Some reported investigations on microbial regeneration of adsorbents include the microbial regeneration of: activated carbon saturated with benzene, tetrachloromethane, tetrachloroethylene and toluene using *Pseudomonas* spp. and *Rhodococcus rhodochrous* [43], activated carbon saturated with 4-chlorophenol using a bacteria consortium [44], activated carbon saturated with tectilon red using *Flavobacterium sp.* [45], sulfur-loaded π-complexation zeolite adsorbent using *Pseudomonas delsfieldii* R-8 [46], PAC loaded with substituted phenols using a cocktail of microbes in a sequencing batch reactor [32], azo dye loaded bone char using a consortia of bacteria including *Flavobacterium sp.* [47], phenol-loaded activated carbon using a mixed culture of phenol-degrading bacteria [48], azo dye-loaded bone char, commercial activated carbon (F400) and activated carbon from bamboo using *Aeromonas sp.* [49], Coal char loaded with p-nitrophenol using *Pseudomonas putida sp.* and A*rthrobacter sp.* [50], phenol-loaded natural zeolite, activated carbon, pyrolized rice husk loaded with phenol and p-nitrophenol and chloroform and chlorinated benzene-loaded activated carbon [41] using *Pseudomonas putida sp.* [41,51,52]. However, it has been suggested that yeast has some advantage over bacteria in the degradation of organic pollutants because of its strong tolerance to high-solute concentration and easy recovery from water [26].

A first-order desorption and biodegradation kinetic model was developed by Ng et al. [52]. It was suggested through the model that bioregeneration was in two steps: desorption of adsorbate from adsorbent and biodegradation of adsorbate in bulk solution. Both steps were assumed to follow the first-order kinetics with the overall rate of microbial regeneration being

$$\frac{dC}{dt} + kC = mk_d q_o e^{-k_d t} \tag{1}$$

Further solution to Eq. (1) gives

$$C = C_i e^{-kt} + \frac{mk_d q_o}{k - k_d}\left(e^{-k_d t} - e^{-kt}\right) \tag{2}$$

where q_o is the amount of adsorbate adsorbed per unit weight of the adsorbent (mg/g), t is the time of desorption, C is the amount of adsorbate in equilibrium solution (mg/L), C_i is the observed initial adsorbate concentration in the bulk equilibrium solution (mg/L), k_d is the first-order desorption rate constant for the microbial regeneration process, and k is the first-order biodegradation rate constant.

Some major drawbacks with microbial regeneration are its low rate of regeneration [53], which on a large scale is not attractive. Furthermore, not all adsorbents are suitable for microbial regeneration. Some reagents used in modifying the surfaces of adsorbents like cationic surfactants at loadings above the cation exchange capacity of the adsorbent, are toxic to microbes [54].

Complete regeneration of spent adsorbents is difficult to accomplish using microbial technique because effluent concentrations lower than the growth threshold concentration of the microorganism may deactivate the microorganism or there could be fouling of the adsorbent pores from by-products of microbial biodegradation [42]. It is suggested that the use of alternative organism or a mixed culture could reduce or eliminate the threshold concentration effect present during regeneration. The exponential decay of the rate of desorbed adsorbate due largely to intraparticle mass transfer resistance which prevents complete recovery of adsorptive capacity of the adsorbent, is another drawback suffered by this technique.

However, microbial regeneration has the merit of converting toxic adsorbed organic pollutants to small molecules and/or organic molecules/moieties that are non-toxic.

Although microbial regeneration has been well studied and understood in single solute systems, the same cannot be said for bisolute or multisolute systems given that most aqueous systems (e.g. wastewater) do contain a cocktail of these solutes. While in some cases microbial regeneration favors an adsorbate in a bisolute or multisolute system the reverse may be the case in a single system. For example, microbial regeneration was more favorable for 2, 4-dichlorophenol in a bisolute system than in a single solute system [34] probably due to the co-metabolic removal of the less biodegradable compound; phenol was suppressed in this bisolute system, probably due to competition for adsorption sites. The study of microbial regeneration in multisolute systems will be very important.

3. Microwave-assisted regeneration technique

Microwaves are electromagnetic energy form whose applied energy is converted into heat by mutual interaction between the electric field component of the wave with charged particles [55, 56]. These microwaves have energy, which are electromagnetic radiation in the microwave frequency or wavelength region of 300 MHz–300 GHz or $\lambda = 0.1$–100 cm [57,58] found between the infrared and radio wave regions of the electromagnetic spectrum [59]. Microwave technology has found application among several other applications, in the regeneration of adsorbents. Desorption using microwave irradiation is a complicated process which involves electromagnetic energy conversion into heat energy that is strongly linked to other phenomena like thermodynamic equilibrium, heat transfer, as well as mass transfer [60]. In recent times, the microwave technology has attracted the attention of chemists, chemical engineers, and material scientists due to its unique molecular level heating ability that leads to quick and homogeneous thermal reactions [61–63]. It has found relevance in the regeneration of carbonaceous materials. This is especially so because it does not damage the carbonaceous material, rather it increases the pore and surface area of the material thereby creating active sites for the adsorption of more recalcitrant pollutants [64].

A clear distinction between microwave devices and conventional heating systems is the mode of heat generation [65]. Thermal regeneration is performed conventionally in rotary kilns or vertical furnaces. Hence, the source of heat is situated outside the adsorbent bed heated via heat transfer through convection or/and conduction, creating a temperature gradient in the adsorbent until steady state conditions are reached [66]. In contrast, the microwave device supplies microwave irradiation directly to the adsorbent bed [67] with the transfer of heat energy being readily transformed into heat inside the adsorbent particles by dipole rotation and ionic conduction [68]. Fluidized beds are more practicable in the industries for microwave regeneration technology because of its short penetration depth. For fixed bed application, annular bed geometry may help to overcome the penetration problem usually experienced [69]. The application of high voltages to an adsorbent results in molecular response with a permanent dipole moment or induced dipole, which changes the high-voltage orientation in the direction opposite to that of the applied field [70]. This leads to synchronized agitation of molecules that generates heat energy.

Unlike with thermal regeneration, the pore width of the adsorbent is not significantly altered in microwave regeneration [65,71]. Besides, microwave regeneration offers the possibilities of rapid and precise control of the adsorbent bed temperature, shorter regeneration time, a more compact furnace, and an energy saving process [72]. Some authors have argued in favor of the microwave regeneration technique because of its positive impact on the adsorption capacity and improved rate of adsorbate uptake of the adsorbent. This is unlike conventional thermal regeneration technique where the adsorbent capacity decreases gradually with subsequent regeneration cycles due to pore blockage of the adsorbent and weight loss due to attrition [65,73,74].

A strong motive for promoting microwave regeneration of adsorbents is its potential for selective desorption of multicomponent adsorbate-loaded adsorbent [75]. The selective heating of the adsorbates with respect to their dielectric properties permits the separation of the adsorbates in a sequential order and thus simplifies the post-regeneration processing [76].

The effectiveness of microwave regeneration depends on the nature of the adsorbate [60] as well as the adsorbent. Polar molecules (e.g. water, ethanol) absorb microwave energy and are desorbed with ease while non-polar molecules (e.g. toluene, cyclohexane) need intense heating and higher temperature to be desorbed from the surface of an adsorbent. Similarly, transparent adsorbents do not absorb microwave energy making them poor materials for microwave regeneration but colored or high-silica adsorbents do [77].

Microwave regeneration technique has been used by various researchers in regenerating adsorbents (most especially activated carbon) loaded with acid orange [78], methyl ether ketone [79], benzene [80], phenol [81], 2,4,5-trichlorobiphenyl [82], ethanol and acetone [83], and spent activated carbon for decolorizing xylose [84].

Although the microwave regeneration technique has been taunted as the most viable option for regenerating pollutant-laden adsorbents [85,86], it however suffers from some disadvantages. Chlorinated products and nitrogenous organic compounds held on adsorbents, produces HCl, CO_2, and N_2 gases when these adsorbents are regenerated by microwaves. These are undesirable by-products, which require a secondary treatment process to remove them [87]. This does add to the cost of the regeneration process. It is suggested that improvement of regeneration efficiency via microwave is expected if the regeneration is carried out under an oxidizing atmosphere (steam, CO_2, air), which could promote the decoking of the coke deposits formed due to thermal cracking of the adsorbate thereby counteracting the pore plugging effect [88].

4. Thermal regeneration technique

Thermal regeneration is a technique that requires high temperatures to regenerate exhausted adsorbents. This process is energy driven and hence commercially expensive compared with other regeneration techniques. This technique is currently used for the regeneration of activated carbon by industries and plants [89,90]. Thermal regeneration technique is commonly employed in various industrial processes in columns and generally follows three steps, namely, adsorbent drying at approximately ~105℃, high-temperature desorption and decomposition (500–900℃) under an inert atmosphere, and residual organic gasification by an oxidizing gas (CO_2 or steam) at elevated temperature of 800℃. The second stage involves partial cracking and polymerization of the adsorbed organics. The last stage aims to remove charred organic residue formed in the porous structure of the adsorbent in the previous stage and the re-exposure of porous structure of the adsorbent. After treatment, the adsorption column can be reutilized. For every adsorption–thermal regeneration cycle around 5–15 wt% of the carbon bed is burnt off with consequent loss of adsorptive capacity. An important point that has to be noted in thermal regeneration is that the thermal stability and thermal history of an adsorbent has to be properly understood. Exposure of adsorbents to very high temperatures above their thermal stabilities will destroy them [91–94].

In real life, two modes of thermal regeneration of spent adsorbents is onsite and offsite thermal regeneration. The offsite technique is applied when there is a large amount of spent adsorbent to be regenerated. In this case, the adsorbent is transported to a special site where it is regenerated by either a kiln or a furnace. This technique suffers from the disadvantage of being less efficient compared with the onsite mode and the process becomes more complicated, when adsorbents laden with different pollutants from different sources are mixed together for regeneration.

The onsite regeneration technique is considered to be very expensive and not useful for small facilities. The onsite technique is used when the adsorbate concentration is high and if the adsorbent is considered as hazardous waste. The onsite regeneration is not cost-effective unless the regeneration rate is above 910 kg/d, while the offsite regeneration is considered if spent adsorbent generation rate is between 225 and 700 kg/d.

Wei et al. [95] reported the thermal regeneration in air of diclofenac sodium and carbamazepine-loaded granular carbon nanotube/alumina hybrid adsorbent at temperature below the ignition temperature of carbon nanotube and below the boiling points of the two organic adsorbates which enabled the oxidation of the adsorbates. Only recently, Sekret and Koldej [96] proposed the use of a regeneration chamber with a retort burner for thermal regeneration of non-organic mineral-based adsorbents.

Other workers have reported thermal regeneration of adsorbents loaded with toluene [97], nitrogen, 1,2-dichloroethane [98], phenol [99], 2-methylisoborneol [100], substituted phenols [101], and p-nitrophenol [102], trinitrotoluene, nitrobenzene, chlorobenzene [103], and chlorophenols [104].

Current concerns with the high-energy cost, increase in global carbon foot print, and nature of thermal regeneration of adsorbents have spurred the interest of several workers to look into other alternative regeneration techniques, in order to minimize the cost and environmental impact of regenerative processes of adsorbents [105–107]. Increase in cost arises from the need for a steam generator/inert gas supply to operate at very high temperature, which leads to 5–15% of adsorbent weight loss at every regeneration cycle. However, Mingzhu et al. [108] have proposed an energy saving thermal regenerative compressed air technique, which uses the residual heat of compressed air from an air compressor to preheat regeneration air flow from an electric heater.

5. Chemical regeneration technique

Several researchers [109–111] have investigated the chemical regeneration of adsorbents, as a cost-effective alternative to the traditional steam regeneration technique. Chemical regeneration of adsorbents is quite different from the thermal or microwave regeneration techniques because desorption of adsorbates is achieved using specific solvents and/or chemical species in solutions or by the decomposition of adsorbed species using chemicals that are oxidants under either supercritical or subcritical conditions [112]. Although, on a laboratory scale, chemical regeneration method has been generally, successfully, used for a large library of adsorbates, large investment cost is often involved. The regeneration efficiency is highly dependent on the solubility of adsorbates in the solvents and the process sometimes alters the chemical structure of adsorbent [113,114]. If the solubility of an adsorbate in a given solvent is low, the regeneration efficiency of the solvent will be minimal. Chemical regeneration is based on three principles: change in solution pH, degradation via oxidation, and complexation (useful for adsorbed inorganic pollutants). In the context of this manuscript, the initial two principles will be further discussed.

5.1. Change in pH principle

Reagents like NaOH, HCl, H_2SO_4, and HNO_3 have been used for the regeneration of adsorbents (especially those with ionic functionalities) via the change in solution pH, which reverses the charged state of either adsorbents or adsorbates. The cations or anions in these reagents are then able to exchange with already adsorbed pollutants on an adsorbent especially when there is a large concentration gradient between the adsorbate and these ions. This kind of system could be regarded as an ion-exchange regenerative system. Some workers have successfully used these reagents in regenerating pollutant-laden adsorbents. For example, sodium hydroxide solution was used to, effectively, desorb tannin [115] and phenol [116] from organoclays, 0.001, 0.01, 0.1 M HNO_3 for desorption of methylene blue dye from a clay-papaya seed composite adsorbent [117]. Organic solvents could be used to also regenerate an adsorbent. Acetone has high-extraction efficiency for basic dye (safranine) from anionic surfactant (Sodium dodecyl sulfate or sodium dodecyl benzene sulfonate) modified hydrotalcite without any change in the structure of the adsorbent [118]. Furthermore, methanol has been used to regenerate carbonaceous materials [119]. Liu et al. [120] have shown that to regenerate activated carbon saturated with red and yellow dyes requires 60% acetone in water or 40% isopropanol in water. Depending on the concentration, some of these chemical reagents could change the chemical structure of some adsorbents (especially the aluminosilicates such as clay, zeolites, etc.) by interacting with some constituents of the adsorbent. This sometimes leads to loss in adsorption capacity of the adsorbent as these reagents could "kill off" some active sites in the adsorbents via leaching of some amount of silica and/or alumina into the desorbing solution [121] with each desorbing cycle.

5.2. Degradation principle

The degradation principle for regeneration of adsorbents is restricted to adsorbents loaded with degradable or oxidizable organics. The advanced oxidation processes (AOPs) which includes Fenton, photo-Fenton, and other oxidation processes are often employed under this principle.

5.2.1. Fenton oxidation

Fenton oxidation process involves the use of H_2O_2 and an iron catalyst to oxidize degradable organic contaminants such as trichloroethylene, 1,2-dichloropropane [3,122], methyl tert-butyl ether [123], and tetrachloroethylene [124]. Essentially, in this process, Iron(II) is oxidised by H_2O_2 to iron(III), $^{\cdot}OH$ radical, and OH^-. Thereafter, Iron(III) is then reduced back to iron(II), a superoxide radical, and a proton by the same hydrogen peroxide. The free radicals generated by this process undergo secondary reaction, which lead to the release of powerful super hydroxyl radicals that degrade organic compounds rapidly and exothermically [124]. A reaction scheme for the formation of radicals and ions in the fenton process are:

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + HO^{\cdot} + H_2O \qquad (3)$$

This catalytic reaction is propagated by the Fe(III) reduction, which leads to the Fe(II) regeneration:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + Fe - OOH \qquad (4)$$

$$Fe^{2+} + Fe\ - OOH\ \rightarrow Fe^{2+} + H_2O \qquad (5)$$

Once hydroxyl radicals have been created, the degradation can be either due to hydrogen abstraction (reaction (6)) or due to hydroxyl addition (reaction (7)) [125]:

$$ROH\ + {}^{\cdot}OH \rightarrow {}^{\cdot}R + H_2O \qquad (6)$$

$$R + {}^{\cdot}OH \rightarrow {}^{\cdot}ROH \qquad (7)$$

The Fenton process has some advantages. It can be done at room temperature and atmospheric pressure. In addition, required reagents are readily available, easy to store and handle, and are safe [124]. However, two main drawbacks have been identified with the process. The first is the wastage of oxidants due to the radical scavenging effect of hydrogen peroxide and its self-decomposition. The second is the continuous loss of iron ions and the formation of solid sludge. Several economic and environmental drawbacks have been reported to occur with Fenton sludge [125].

5.2.2. Modified Fenton systems

In the modified Fenton system, the radical formation is enhanced by the addition of chemicals and/or by high-peroxide concentrations. When high-oxidant concentrations are used, many complex reactions are involved in the Fenton's system, and numerous reacting species can be generated in addition to hydroxyl radical, including hydroperoxide radicals ($HO_2^{\cdot}$), superoxide anions (O_2^-), and hydroperoxide anions (HO^{2-}) [126–128]:

$$H_2O_2 + {}^{\cdot}OH \rightarrow H_2O + HO_2^{\cdot} \quad (8)$$

$$HO_2^{\cdot} \rightarrow O_2^{\cdot} + H^+ \quad (9)$$

$$HO_2^{\cdot} + Fe^{2+} \rightarrow HO_2^- + Fe^{3+} \quad (10)$$

These radicals are highly reactive and are able to degrade even recalcitrant compounds or contaminants in the adsorbed form [125–127]. Therefore, strong oxidation conditions will improve regeneration efficiency even with the most refractory compounds. On the other hand, too high-peroxide concentrations should be avoided, because they can enhance the oxidant's self-consumption [125,128], leading to poorer oxidant efficiency. The Fenton oxidation reactions are traditionally quick and appear to be concluded within few hours or less, especially in the case of modified Fenton's reagent [125,128].

For photo-Fenton process, photo-radiation from a lighting source under certain wavelength is employed. Its effectiveness is attributed to the photolysis of Fe (III) cations in acidic media which yields Fe(II) cations, in addition to the reaction between Fe(III) and H_2O_2 that yields hydroxyl radicals [129,130]. The reaction scheme below shows the formation of hydroxyl radicals under photo-Fenton process:

$$Fe(OH)^{2+} + hv \rightarrow Fe^{2+} + OH^{\cdot} \quad (11)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe(OH)^{2+} + OH^{\cdot} \quad (12)$$

The photo-Fenton process is more efficient than the Fenton process [131]. Pollutants such as azure-B [132], herbicides [133], ethylene glycol [134], 2-nitrophenol (2-NP), 4-nitrophenol (4-NP), 2,4-dinitrophenol (DNP), and 2,4,6-trinitrophenol (TNP) [135] were degraded effectively by photo-Fenton process. Possible chemical reaction schemes for the decomposition of nitrophenol via Fenton and photo-Fenton processes are shown in Fig. 2.

Other variants of the Fenton process include: sono-photo-Fenton process which has been used in the treatment of water containing azure B dye [132] and acid orange 7 dye [136]; sono-electro-Fenton process used in the treatment of hydrophilic chlorophenols [137] and cationic red X-GRL dye [106] pollutants in water; photo-electro-Fenton process used in the treatment of reactive black 5 [111], sunlight-assisted electro-Fenton for mineralizing aromatics in water [124], and microwave-enhanced Fenton-like system in the presence of magnetic nanoscaled Fe_3O_4 catalyst for the degradation of methyl orange dye in [138]. Recently, a Fenton-like catalyst, Schwertmannite, was developed for the oxidation of phenol [139]. A possible mechanism of phenol by H_2O_2 in the presence of the Schwertmannite catalyst is shown in Fig. 3. Although, some of these variants have been used for water treatment, they could find use in the regeneration of organic-laden adsorbents.

5.2.3. Ozonation

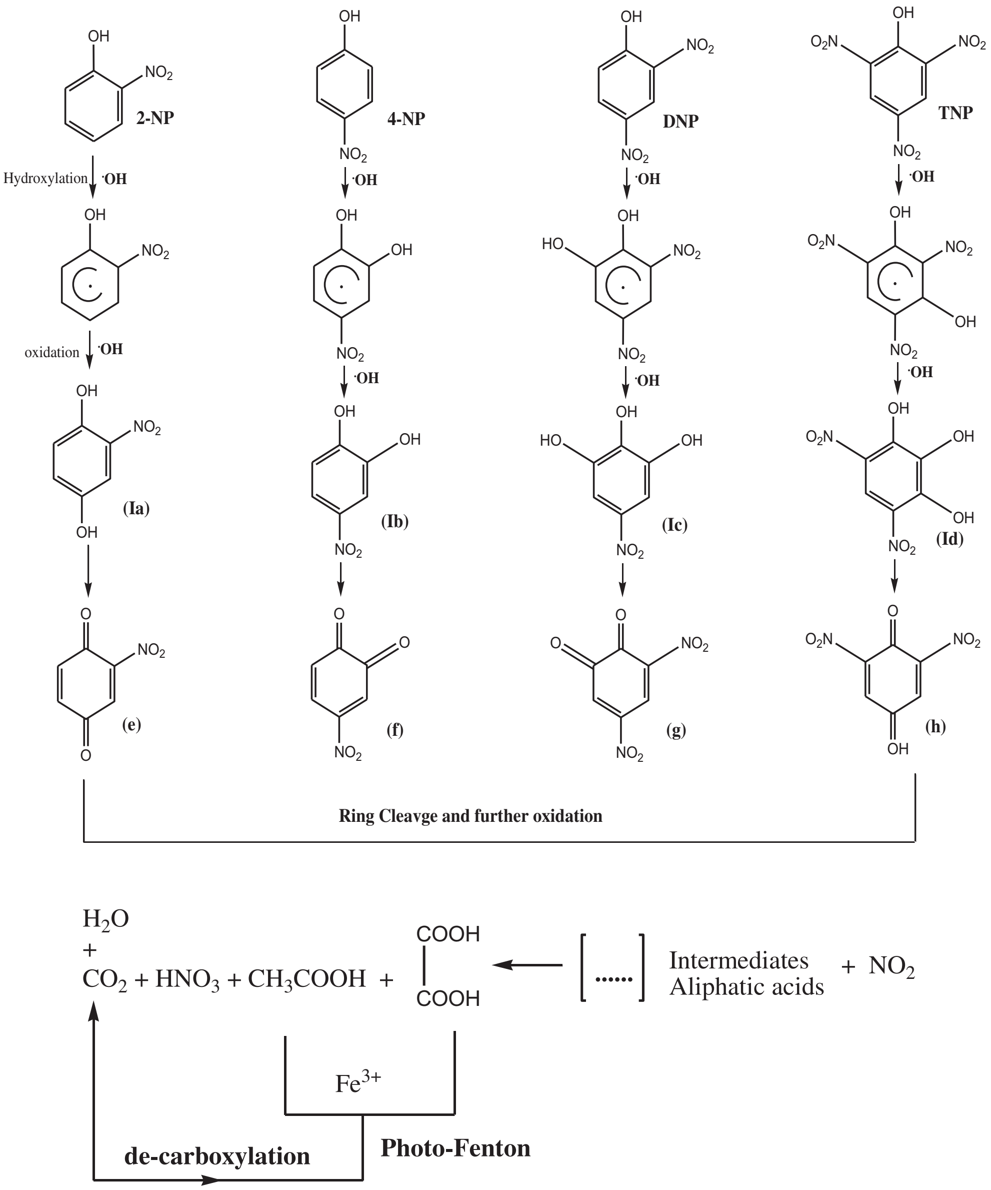
Another very useful technique under the degradation principle is the ozonation process. Ozone can be used to degrade organic compounds through the process of *ozonation* which can proceed either by direct oxidation in the presence of molecular ozone or by indirect oxidation with ·OH radicals that are formed from the decomposition of ozone in alkaline conditions. With respect to the molecular mechanism, ozone molecule is a rather selective oxidant that does not react with some molecules or do so slowly. This is the case with nitrobenzene [140], a highly refractory pollutant. Furthermore, it has been observed that some adsorbents with high-Si/Al ratio could degenerate the ozone molecule to its radical specie such that it is able to effectively degrade organic pollutants even refractory organics like nitrobenzene with improved adsorption capacities of the adsorbents and higher selectivity for polar compounds [141,142]. This was attributed to a surface modification of the adsorbent, by highly reactive species generated during molecular ozone decomposition in the course of regeneration. However, excessive application of ozone could lead to the formation of acidic surface which will decrease the adsorbent's efficiency to hold anionic pollutants [143].

Previously, ozone generators were maintenance intensive and required a lot of energy. Today, there are more energy efficient ozone generators. However, there is need for further studies to optimize the ozonation regeneration process and analyze their by-products to ascertain its potentials for future use in regeneration. However, this technique has one disadvantage. It requires the calcination of the adsorbent before reuse, which increases the cost of the process.

5.2.4. Permanganate oxidation

Since potassium permanganate has been successfully used to degrade organics in soils, surface water and ground water, [143,144], it is therefore possible to employ its potentials in the regeneration of organic-laden adsorbents. The general equation for the oxidation of organics by potassium permanganate is:

$$R + MnO_4^- \rightarrow MnO_2 + CO_2 \; or \; (ROX + MnO_2) \quad (13)$$



Where (Ia) nitrodihydroxy benzene (Ib) nitro catechol (Ic) dinitro catechol (Id) trinitro dihydroxy benzene (e) nitro p-benzoquinone (f) nitro o-benzoquinone (g) dinitro o-benzoquinone (h) dinitro p-benzoquinone

Fig. 2. Possible reaction scheme for degradation of Nitrophenols during Fenton and photo-Fenton processes [150].

where ROX label stands for intermediate organic compounds.

Oxidation of organic compounds by permanganate ion produces manganese dioxide (MnO_2) plus CO_2 or organic intermediates [145]:

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O \quad (14)$$

Polyaromatic Hydrocarbon (PAH) oxidation could be written as:

$$C_nH_m + (n + m/4)O_2 \rightarrow nCO_2 + (m/2)H_2O \quad (15)$$

with

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (16)$$

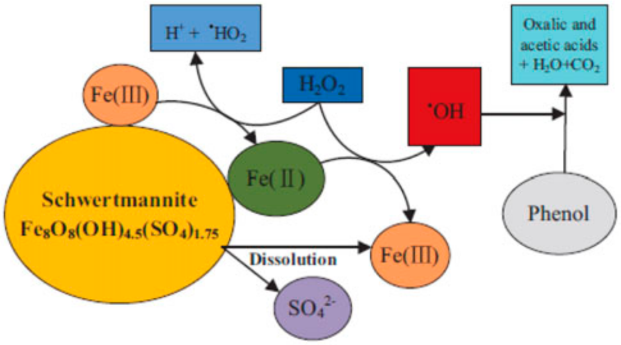


Fig. 3. A possible mechanism in the oxidation of phenol by H_2O_2 in the presence of schwertmannite [139].

Thus, $(4n + m)e^-$ involved in the total reaction permanganate has been widely used to break down organic compounds, such as taste and odour producing compounds, alkenes, organic chlorates, phenols, pesticides, PAHs, organic acids, and methyl-tertiary-butyl ether in effluents, groundwater, and soils as already reported [145–150].

However, one drawback the use of permanganate as regenerating agent will likely face is that modified adsorbent surfaces with functionalities reactive to it will be unsuitable for permanganate regeneration e.g. adsorbents with cyanide and sulfide functionalities.

6. Photo-assisted oxidation method

Photo-assisted oxidation is also an advanced process technique, which involves photocatalytic and photosensitized oxidation that are able to generate very reactive free radicals for the degradation of organic pollutants [151,152] without the use of chemicals.

Photo-assisted degradation technique thus degrades the organic pollutants to very low concentrations at a fast rate. In the application of this technique, the photocatalyst or photosensitizer is added to the suspension containing the adsorbent such that the adsorbed organic pollutants are first desorbed into the solution and subsequently degraded by photo-irradiation. This process continues until the adsorbent is fully regenerated. However, for adsorbents with layers (clays and their modified forms), the photocatalysts and photosensitizers could be incorporated into the interlayers of the adsorbent displacing organic pollutants already lodged in such layers and further degrading them [153,154]. Xiong et al. [153] showed that there is enhanced photodegradation of 2,4,6-trichlorophenol over palladium phthalocyaninesulfonate-modified organobentonite under ultraviolet (UV) light.

The most widely used photocatalyst is TiO_2 [155–157]. It has been used in the regeneration of spent organoclays (hexadecylpyridinium montmorillonite). At shorter wavelength (>254 nm) of UV irradiation, about 99% of adsorbed 2-chlorophenol was degraded from TiO_2/hexadecylpyridinium chloride-modified montmorillonite within 160 min with destruction of the organoclay. At longer wavelength (>310 nm) of UV irradiation, degradation of the organic pollutant took much longer time (7 h) to reach 99% degradation with no observed destruction of the organoclay [157].

A widely used photosensitizer for the regeneration of spent adsorbents is the metal phthalocyanine [152,153,158]. Photosensitized oxidation has the advantage of the metal phthalocyanine being activated under visible light (e.g. > 450 nm) as against using UV light required by photocatalysts like TiO_2. This cuts down on the overall cost of regeneration. The incorporated metal phthalocyanine in the layers of ionic surfactant modified clay minerals enhances the organoclay's regenerability even for the removal of phenols and organic sulfides [152,153,158–160] from aqueous solution. Direct degradation of organic pollutants on the adsorbents is achieved by the singlet oxygen generated *in situ*. Recently, Chen and Bai [161] regenerated a methylene blue dye loaded-TiO_2@yeast microspheres using UV light. The mechanism of this regeneration is shown in Fig. 4.

Although photo-assisted techniques for regeneration has been widely used (though on a laboratory scale), yet there are no concrete evidences to show that by-products from the process are not toxic to human especially from chlorinated pollutants where chlorides are produced as one of the by-products [150,160]:

$$6OH^{\cdot} + Cl_2C = CHCl \rightarrow 2CO_2 + 2H_2O + 3Cl^- + 3H^+ \tag{17}$$

Besides, the CO_2 gas generated need to be trapped for other useful purposes else they add to the growing problem of climate change.

7. Electrochemical regeneration

Electrochemical regeneration refers to the regeneration of loaded adsorbent inside an electrolytic cell. The regeneration involves desorption and/or degradation of the adsorbed pollutant, restoring the adsorptive capacity of the adsorbent [162–164]. The first report on electrochemical regeneration of activated carbon was by Owen and Barry [163] who achieved regeneration efficiencies of up to 61% and suggested further studies on the process.

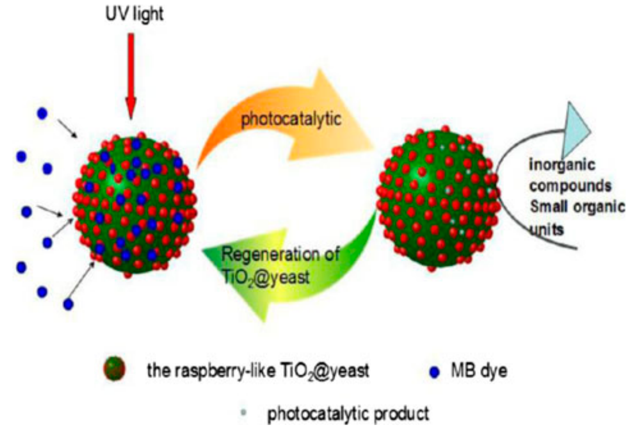


Fig. 4. Mechanism for the regeneration of Methylene blue dye loaded-TiO_2@yeast microspheres [161].

The principle of electrochemical regeneration is based on passing current through an electrochemical cell which generates ions that can change the local pH conditions in the cells and thus promote desorption/degradation of pollutants [165,166]. It is expected that the with the generation of OH^- at the cathode, local pH of solution changes, and desorbed pollutants is held on the anode in the case of inorganic pollutants or degraded by oxidative destruction at the anode in the case of organic pollutants. However, because of mass transfer limitations between both electrodes, there is often residual pollutant left at the cathode except when large currents or long regeneration times that are employed. At the anode (oxidizing electrode) direct anodic oxidation occurs where the pollutants are adsorbed on the anode surface and degraded by the anodic electron transfer reaction or from hydroxyl radicals via water electrolysis [167].

Electrochemical oxidation over anodes made of graphite, Pt, TiO_2, IrO_2, PbO_2, various Ti-based alloys and more recently, boron-doped diamond electrodes in the presence of suitable electrolyte (usually NaCl) could be employed for the regeneration of adsorbents [168]. Degradation at the anode is less efficient than at the cathode with no observable residual pollutant due to the strong oxidizing nature of the anode [169]. However, coating the surface of the anode with a catalytic material could enhance its efficiency. For example, it was observed that phenol could be readily mineralized at the Ti/SnO_2-Sb anode but its rate of degradation was found to be considerably decreased at Ti/RuO_2 and Pt anodes [170]. The coating of the Ti-anode surface with SnO_2-Sb material ensured that the anode is able to further degrade rapidly, intermediate products formed from the electrochemical regeneration process including benzoquinone and organic acids which was a difficult step (ring breakage) for the Ti/RuO_2 and Pt anodes [170]. The regenerative efficiency of an electrochemical system depends on (i) the type of electrode: active or non-active electrode with non-active electrodes such as PbO_2 showing enhanced degradation of organic pollutants than active electrodes like Pt [171] (leaching of Pb into the solution [170] however, makes it currently unattractive for use), (ii) electrolyte concentration, (iii) current intensity, (iv) time [172], and (v) adsorbent bed thickness [162]. Other factors could include the effluent pH and the initial concentration of the pollutant on the adsorbent [165]. Mechanisms of electrochemical regeneration include reactions between the ions generated and adsorbed pollutants resulting in the formation of species with lower adsorptive affinity for the adsorbent and subsequently desorbed, or the oxidative destruction of the organic pollutant on the adsorbent surface [168]. An electrochemical degradation pathway for phenol is shown in Fig. 5.

Electrochemical regeneration has been used for regeneration of adsorbents loaded with toluene, phenol, crystal violet dye, and p-nitrophenol [162,173–176]. Narbaitz and McEwen [177] and Zhang et al. [169] carried out detailed investigations into the use of electrochemical regeneration of granular activated carbon (GAC) loaded with phenol, achieving regeneration efficiencies up to 95%. A schematic diagram of a simultaneous adsorption–desorption process via an electrochemical reactor is shown in Fig. 6 [178]. The theoretical charge (TC) required for decomposition of pollutant materials in an electrochemical cell was estimated to be [179,180],

$$\mathrm{TC} = \frac{n(C_o - C_e)VF}{M_w} \tag{18}$$

where n is the number of electrons required per molecule of pollutant oxidized, F is the Faraday's constant (96,487 C mol^{-1}), V is the volume of solution (L), and M_w is the molecular weight of the pollutant molecule.

The current efficiency, η, is the ratio of the TC to the actual charge used:

$$\eta = \frac{n(C_o - C_e)VF}{M_w It} \tag{19}$$

where I is the DC current supplied (A) and t is the electrochemical regeneration time,

The regeneration efficiency, η_r, for electrochemical regeneration is [181]:

$$\eta_r = \frac{q_r}{q_i} \times 100\% \tag{20}$$

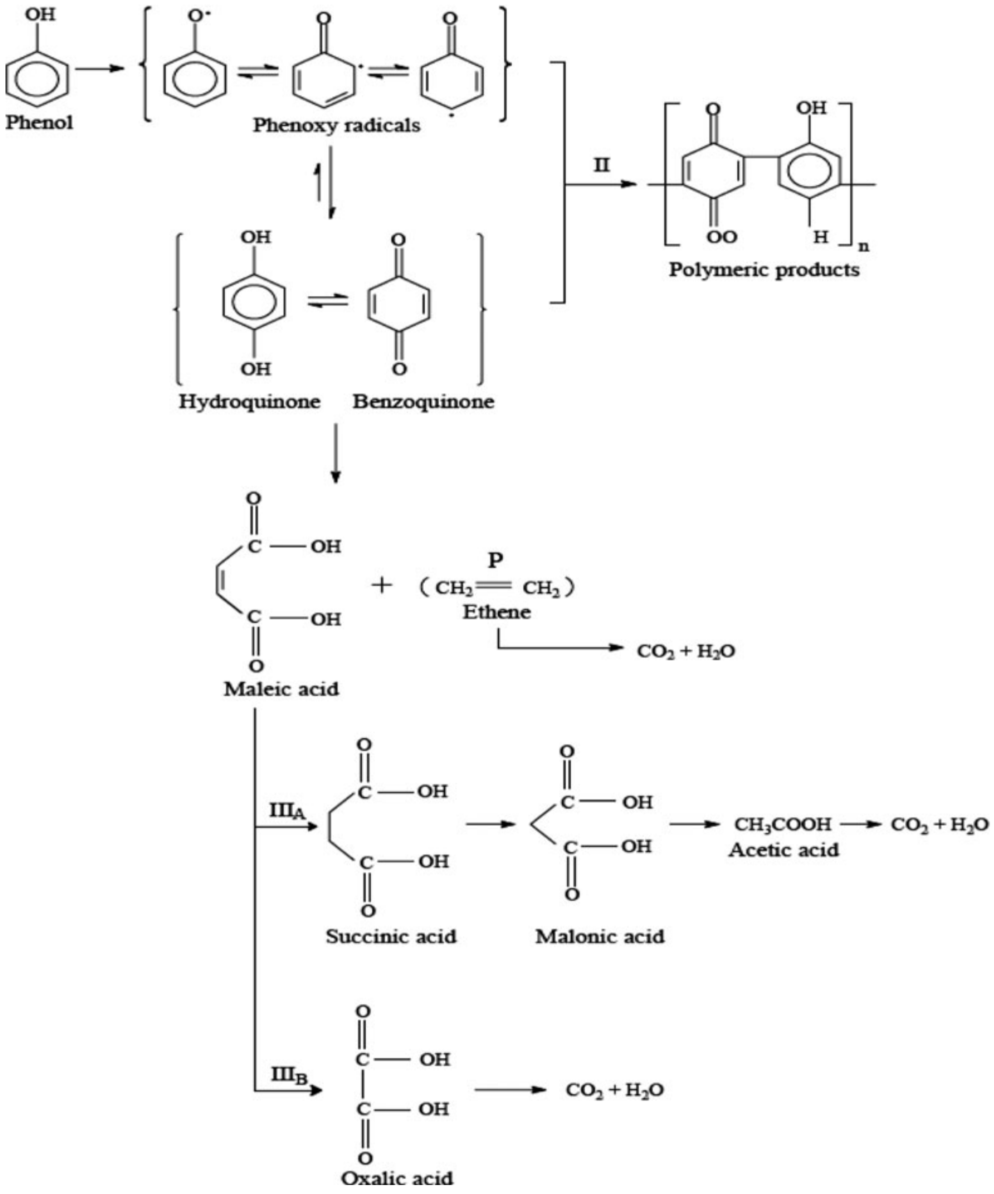


Fig. 5. Reaction pathway of electrochemical phenol degradation [170].

where q_i is the adsorption capacity of fresh adsorbent and q_r is the adsorption capacity of the adsorbent after regeneration.

A draw back with the use of this regeneration technique is the fact that salts formed and other by-products with change in solution pH do negatively affect the efficiency of the electrodes with a 2% decrease in desorption efficiency per regeneration cycle [182]. Another disadvantage of this technique is the long time required to reach high-regeneration efficiency which does influence the economics of the process and thus limits its application [177]. The reasons for this long process time is because of the type of electrode used and mass transfer effect [171]. Although Zhou and Lei [176] have produced a novel non-active modified PbO_2 electrode, it is not presently clear if it is specific for certain organic pollutants just as Narbaitz and McEwen [182] observed that their platinum wire mesh electrode failed to regenerate efficiently, a natural organic matter loaded-granular activated carbon (NOM-GAC). Narbaitz and McEwen [182] therefore suggested the use of Zhou and Lei [176] electrochemical system (which is an adsorbate-oxidation controlled system) or the Brown et al. [183] electrochemical system which is

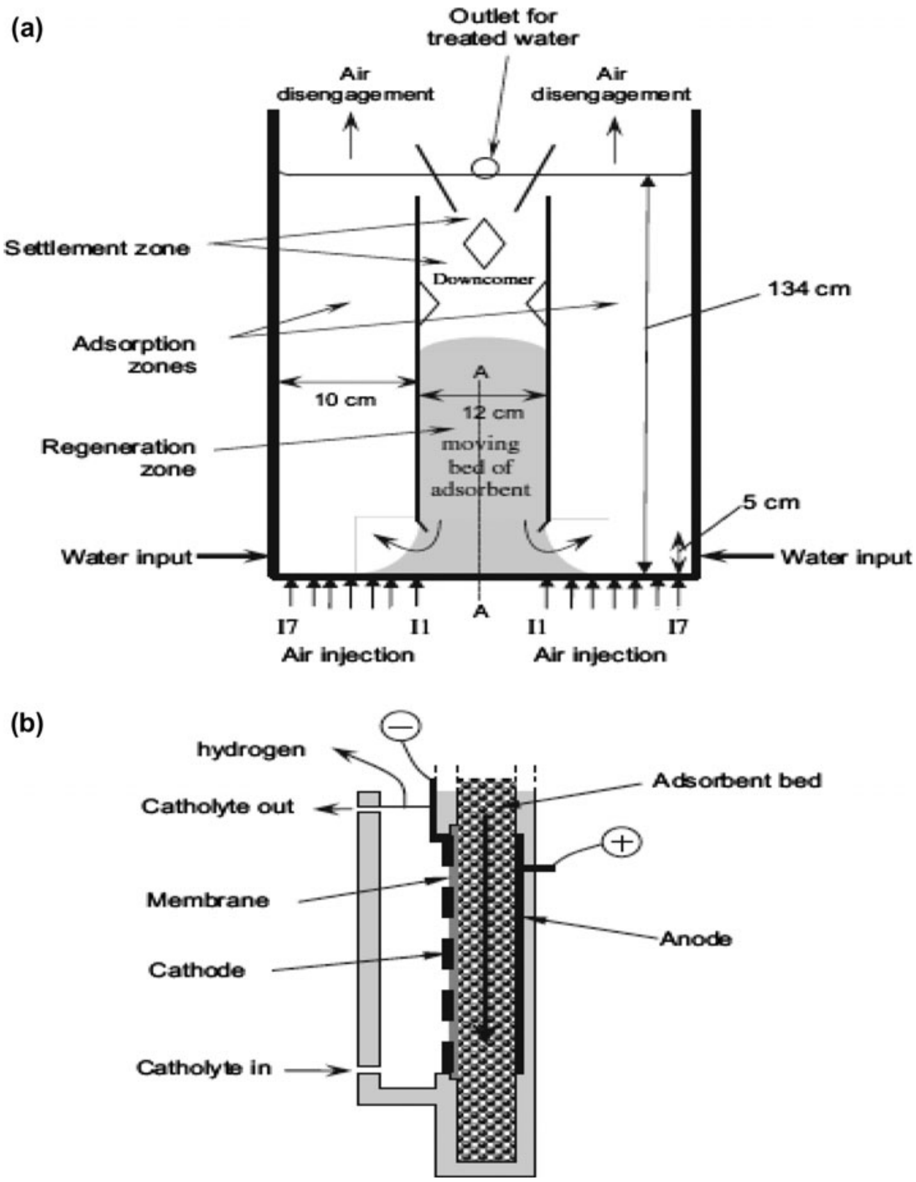


Fig. 6. (a) Schematic diagram of the continuous air-lift adsorption/electrochemical regeneration reactor. (b) Schematic diagram of the electrochemical regeneration zone showing a cross section through line A–A in (a). [178]

perceived to work well with low-porosity high-conductivity carbonaceous adsorbents. Regeneration efficiency in electrochemical regeneration may decrease over subsequent cycles as a result of pore blockages from by products and active site damage by the applied current [183, 184]. However, Brown et al. [183] and Weng et al. [185] showed that the adsorbents used in their studies (Nyex 100 and GAC) had better adsorptive capacity after electrochemical regeneration, and Asghar et al. [186] recently demonstrated the successful electrochemical regeneration of humic acid-loaded Nyex 2000 adsorbent. These discrepancies in the various reports suggest that the electrochemical regeneration technique may be quite efficient but still requires some more studies to provide concrete results that will aid its application on a large scale. The cost of some of the accessories for electrochemical regeneration still poses a great challenge for its large-scale application. Besides, in some developing countries where the generation of power is still a huge challenge, this technique will presently not be cost-effective.

8. SCFs regeneration

SCFs are defined as fluids at certain temperature and pressure, which are above their critical values.

SCF has been used to remove various kinds of pollutants from distinct types of adsorbents for over 30 years. It has the advantage of being flexible in terms of adjusting its dissolving power and inherent elimination of organic solvent which implies time and cost reduction. Several factors influence the efficiency of this type of regeneration process: temperature, pressure, and solute solubility in SCF. The impact of these factors on SCF efficiency and the various matrices in which SCF technique have found relevance has been discussed by Salvin et al. [187] and Cavalcante et al. [188]. The most employed supercritical solvent is CO_2 because it is non-toxic, non-flammable, relatively inexpensive, has higher mass transfer rate and adjustable extraction power for organic compounds depending on the density [189–191] and has low regeneration pressure and temperature [192]. Despite these advantages, supercritical CO_2 is known to incompletely regenerate adsorbents loaded with phenol because of the strong intensity of phenol adsorption on adsorbents especially activated carbon. To overcome this, Salvador et al. [192] used supercritical water (rather than supercritical gas) to desorb phenol and achieved 100% efficiency. However, Ledesma et al. [193] showed that the use of supercritical water for regeneration of para-nitrophenol-loaded activated carbons increased their adsorption efficiency up to 80% but desorption efficiency was between 21% and 49%. This may suggest the possibility of SCF regeneration creating new adsorption sites on the organic-laden adsorbent.

The extraction of solutes from solid matrices using SCFs takes place via four different mechanisms [189]:

(1) If there are no interactions between the solute and the solid phase (an individual or a simple mixture), the process is simple dissolution of the solute in a suitable solvent which does not dissolve the solid matrix.
(2) If there are interactions between the solid and the solute, then the extraction process is desorption in the presence of the solvent and the adsorption isotherm of the solute on the solid in the presence of the solvent determines the equilibrium. Most solid extraction processes, e.g. soil remediation, desorption of analytes from adsorbents, and activated carbon regeneration, fall into this category.
(3) The third mechanism involves swelling of the solid phase or the destruction of the solid texture by the solvent accompanied by extraction of the entrapped solute through the first two mechanism mentioned above, such as occurs in the extraction of essential oils [194].
(4) The fourth mechanism is reactive extraction, where the insoluble solute reacts with the solvent and the reaction products are soluble and hence extractable, e.g. the extraction of lignin from wood [195].

SCF regeneration technique provides an efficient means of extracting organic compounds from solid matrices, [187,188]. The supercritical extraction technique has been applied in the extraction of organic pollutants, such as phenols [189], ethyl acetate [190,191], and salicylic acid [187], from the spent adsorbents. Studies using SCF regeneration shows that factors such as density and viscosity of the SCF are more important factors for the extraction of adsorbed organic pollutants [189]. Under optimal conditions, Park and Yeo [189] reported that the extraction efficiencies of phenols from spent organoclays can be up to 90%, and Cavalcante et al. [188] also reported 84% extraction efficiency for ethyl acetate. The extraction efficiency of organic adsorbate from an adsorbent may be further improved in the presence of co-solvent depending on the type of organic adsorbate [196,197]. Salgın et al. [187] showed that the maximum extraction percentage of salicylic acid from organoclays is about 76% using CO_2 SCF without the addition of a co-solvent. However, with the addition of 10 vol% of ethanol as co-solvent, the extraction efficiency could reach 98%, and the spent organoclays can be well regenerated [187]. In a separate study by Bensebia et al. [198], they concluded that the particle size of the adsorbent do play a big role in determining the time of desorption in SCF regeneration while resistance due to external transfer and axial dispersion were negligible in the desorption of m-xylene from GAC using same technique.

De Filippi et al. [199] investigated the adsorption and desorption of different pesticides [trifluralin, i.e. α,α,α-trifluoro 2,6-dinitro-N,N-dipropyl-p-toluidine; diazinon, i.e. *O*,*O*-diethyl-*O*-2-isopropyl-6-methylopyrimidin-4-yl phosphorothioate; alachlor, i.e. 2-chloro-2´,6´-diethyl-*N*-methoxymethylacetanilide; atrazine, i.e. 6-chloro-N^2-ethyl-N^4-isopropyl-1,3,5-triazine-2,4-diamine; carbaryl, i.e. 1-naphthylomethylcarbamate; and pentachlorophenol [200], phenol and acetic acid from different activated carbons, and carbonaceous resinous adsorbent, Ambersorb XE-348 in supercritical CO_2 [201].

From the supercritical regeneration of ethyl acetate-laden organoclays, the activity of ionic surfactant can remain intact during the extraction of adsorbates, and the organoclays exhibit undiminished adsorption capacity toward phenols after several regeneration cycles [200,201]. In addition, it is possible to recycle the extracted organic compounds.

However, Grajek [201] suggested that the key in designing large-scale supercritical desorption processes depends on the understanding of how the desorption process is influenced by variables such as pressure, temperature, and extraction solvent flow rate. Grajek [201] further showed that density of the SCF rather than pressure of the system plays a more important role in SCR regeneration while liquid CO_2 rather than supercritical CO_2 is preferred in the process since regeneration processes carried out with liquid, sub- and super-critical CO_2 behave similarly. The cost of regenerating 1 kg of spent activated carbon using supercritical CO_2 according to Grajek [201] is ca. $0.23 under continuous process conditions. The properties of the adsorbate (contaminant) influence the economics of SCF regeneration more strongly than the adsorbent properties [201].

SCF regeneration could be as fast as 4.17 min [196], 10 min (with 100% efficiency), and as slow as 350 min [192]. Although both supercritical water regeneration mode and thermal regeneration mode require high temperatures, supercritical water has the advantage of very short process time, which is in minutes and this could significantly lower the cost of regeneration. While SCF regeneration technique seems to be much favored over the conventional thermal regeneration technique, there is still very little information that will aid its application on a large scale. The cost of pressure vessels could limit its large-scale application as a regeneration technique.

9. Ultrasound regeneration

Ultrasonic regeneration of solid matrices loaded with pollutants was developed as an alternative to the conventional thermal swing regeneration process, which is capital intensive. Ultrasonic enhancement of desorption of adsorbates from solid matrices is basically a mass transfer process and is limited by diffusion–convection in the system [202,203]. However, the intensity of ultrasound should not exceed the threshold value for damaging the adsorbent especially expensive adsorbents like polymeric resins [203].

It is known that ultrasound and its secondary effect, cavitation (which is nucleation, growth, and transient collapse of tiny gas bubbles driven by ultrasound wave) can enhance convection in a medium by physical phenomena such as micro-streaming, micro-turbulence, acoustic (or shock) waves, and microjets. Chakma and Moholkar [204] showed in their study that shock waves generate the necessary convection required for desorption via ultrasound, and cavitation does not boost desorption rate even though Rege et al. [205] had reported that it does. Both workers, however, acknowledge that the extent of desorption of a pollutant from an acknowledge via ultrasound technique is a strong function of the nature of the pollutant and adsorbent, and the interaction between them. They concluded that ultrasound is a useful tool for desorption in systems with favorable isotherm, where the intrinsic desorption kinetics is rather slow. However, there is enough scope for the enhancement of this kinetics by intensification of convection in the medium. Several researchers have used the ultrasound regeneration technique recently in desorption of pollutants from solid matrices and they include Hamdaoui et al. [206]; Midathana and Moholkar [207]; Rege et al. [205]; Schueller and Yang [208]; Hamdaoui et al. [209]; Zhu and Lei [210]; Choi et al. [211]; Zhang et al. [212] and Li et al. [213]. A schematic setup for ultrasound regeneration of an adsorbent is shown in Fig. 7.

One very important benefit of ultrasound regeneration is that attrition of the adsorbent due to cavitation could be prevented by operating a frequency ≥ 40 kHz and an intensity below the pulverization threshold value of the pulverization of adsorbent [205]. This technique can be used in a small-scale for counter-current regeneration of ultra-pure water. Other advantages of this technique are its low power consumption, simpler process equipment, and higher desorption efficiency compared with thermal regeneration technique [214].

10. DBDP regeneration

This regeneration technique is a recent tool that has been used by few researchers. The DBDB regeneration technique produces non-thermal plasma when high voltage is applied to electrodes (one of which is coated with a dielectric material) at atmospheric pressure. The plasma produces active species like O_3,

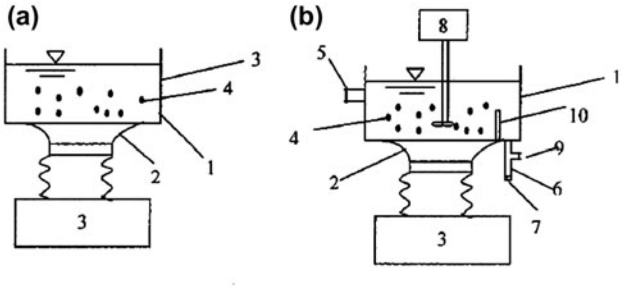


Fig. 7. Schematic diagrams for Ultrasound regeneration of an adsorbent. (a) Static experimental apparatus: 1-regeneration vessel; 2-piezoelectric ceramics transducer; 3-controller; 4-activated carbon. (b) Dynamic experimental apparatus: 1-regeneration vessel; 2-piezoelectric ceramics transducer; 3-controller; 4-activated carbon; 5-inlet of feed; 6-outlet of regeneration wastewater; 7–100 mesh nylon net; 8-Stirrer; 9-Outlet of activated carbon; 10-Baffle [215].

high-energy electron, and various chemical species with high oxidizing powers such as $^{\cdot}OH$, $^{\cdot}HO_2$, $^{\cdot}O_2$, etc. These species are responsible for the oxidation of organic pollutants on the surface of the adsorbent. Several factors such as regeneration time, electric field and type of gas used do influence the efficiency of the DBD regeneration process [215]. It was observed that O_2 was more efficient in the degradation of acid orange 7 dye than air or N_2. Similarly, increasing regeneration time and electric field increased the efficiency of the regeneration of acid orange 7 dye-loaded GAC [216] and nitrobenzene-loaded GAC [217]. Even though this process has been proven to be very efficient yet it is plagued with the problem of harmful by-products such as tri- and tetrachlorophenols, chlorides, glyoxalic acid, formic acid, maleic acid, etc. being formed in the process [16]. To handle these by products will require a secondary treatment step which makes the process less cost-effective. This technique needs further studies with more non-carbonaceous and non-porous adsorbents and more organic pollutants other than chlorophenols, which seems to be most studied. Besides, the question of its cost-effectiveness needs to be fully determined.

11. Future perspectives

From the foregoing discussions, it is clear that the relative ease of regeneration depends on the nature of the adsorbate on the adsorbent: physisorbed or chemisorbed. With physisorbed adsorbates, regeneration of the adsorbent can be achieved via the reduction of pressure or washing with solvent. However, with chemisorbed adsorbate, the adsorbent is regenerated via energy greater than the adsorptive energy such that bonds can be broken. In today’s world, for a regenerative technique to be adopted, it has to be cost-effective, environmental-friendly, easily operated, and very efficient even with an adsorbent loaded with a cocktail of adsorbates. Table 1 gives an overview of the various regeneration techniques discussed in this paper. It also shows factors influencing their operation, advantages and disadvantages. The microbial technique does fall short of one of the qualities required of an efficient adsorbent listed above. Though it has good regenerative ability, yet it is slow, largely suitable for degradable organic pollutants and efficiency of microbes could easily be compromised by cationic surfactants. Furthermore, microbial activity for adsorbates on activated carbon tends to differ for some adsorbates on non-carbonaceous adsorbents [215]. This calls for further studies. The microbial regeneration technique is well suited for spent adsorbents that are ready to be disposed off permanently. Although the microwave-assisted regenerative technique is a very efficient regeneration technique, the issue of adsorbent sintering due to hotspot formation [216] compromises this efficiency. This calls for more studies on how to circumvent it and further deepen the knowledge base of the dielectric properties of variety of adsorbents available such that in the nearest future the microwave regeneration technology becomes a more suitable candidate for large-scale adsorbent regeneration processes. Mathematical modeling can help to predict hotspot formation and how to avoid it [218].

Thermal regeneration technique which is currently the most applied technique for regeneration has the problem of adsorbent losses due to attrition which eventually leads to the loss of efficiency in addition to the high cost of energy and equipment required for the process. Besides, thermal regeneration technique increases the current global carbon footprint. Chemical regeneration basically by AOP is very effective with organic-loaded adsorbents but it is not very clear how toxic some of the by-products of degradation (which are perhaps refractory to oxidation) from the process is to humans and animals. The same is also true for photo-assisted regeneration technique. Besides, the presence of these by-products would require a secondary treatment step to take them out of aqueous solutions. Why it is true that for some adsorbates, they could be mineralized to CO_2 and H_2O it is certainly not the case with some other adsorbates, which may contain chlorine, nitrogen, and other substituents. While there has been so much studies on degradation of phenols there is a need to study the degradation of other adsorbates especially degradation of some of the emerging contaminants from adsorbents. Although Fe^{2+} can catalyze both Fenton and photo-Fenton organic degradation reactions, Fe^{2+} is known to foul the surface of the photocatalysts through the formation of $Fe(OH)_3$ while PO_4^{3-} in the nominal pH range fouls the active sites on TiO_2 surface and inhibits its photoactivity [2–6,10,11]. Although the AOPs are cost-effective, yet there is need for more scientific investigations to ascertain what the real by-products of degradation by AOPs are especially in adsorbents loaded with diverse pollutants and how to mitigate the presence of ions that inhibits their efficiencies. It is possible to suggest that to make photo-assisted regeneration, a more efficient technique, the catalyst requires improvement for high photoactivity over a wide solar spectra and an immobilization strategy that allows for cost-effective solid–liquid separation. It is also important that the photocatalytic process be improved on to span through a wide range of solution

Table 1
Overview of various adsorbent regeneration processes

Process	Factors influencing process	Advantage	Disadvantage	References
Microbial regeneration	Mineral components, biodegradability of adsorbate, adsorbent particle size, adsorbent porosity, nature of adsorbent, concentration of adsorbate, weight of adsorbent, type of microorganism, molecular structure of organic pollutants and type of adsorbent	Toxic organic pollutants that are biodegradable are converted to small non toxic molecules and moieties, leading to the permanent regeneration of the adsorbent More effective for chemically prepared adsorbents than thermally prepared adsorbents Appropriate for adsorbents that are to be discarded	Regeneration is very slow and only applicable to biodegradable pollutants, mainly organic pollutants Not suitable for some adsorbents especially surfactant modified adsorbents Possibility of fouling of adsorbent pores by some products of bioregeneration	[18,24,25–30, 42,53,54]
Microwave-assisted regeneration	Nature of adsorbate and adsorbent,	Tend to show stronger preference for adsorbates in multi-component Pore width of adsorbent not significantly affected Short regeneration time Improved adsorption capacity of adsorbent An energy saving process compared with the thermal process	More suitable for fluidized bed systems Adsorbent pore plugging from decomposition products Require a secondary treatment process for chlorinated loaded adsorbents	[65,71–75,87,87]
Thermal regeneration	Temperature, type of adsorbate and adsorbent, pressure	Useful for adsorbents loaded with heterogeneous mixture of adsorbates	Loss of adsorbent pore structure and hence loss of adsorption capacity due to attrition Air pollution problems associated with gases released during the process High energy requirement which is costly	[91–94,97–99, 103, 104]
			It is energy driven and hence commercially expensive compared with other regeneration methods	[89,90]
Chemical regeneration	Type of solvent, solubility of adsorbates Concentration of chemical reagents, chemical structure of adsorbent Done at room temperature and atmospheric pressure Utilizes reagents that are readily available, easily stored and handled and are safe	It is cost effective alternative to the traditional reactivation technique Easily coupled with other processes e.g. Sono-fenton, Sono-electro-fenton, photo-electro-fenton etc. Oxidation modes, effective for refractory compounds e.g. nitrophenols etc. Regeneration is fast	Alteration of adsorbent's chemical structure e.g. chemical reagent reacting with chemical species on the surface of the adsorbent Oxidant Wastage Continuous loss of ferrous/ferric ions and the formation of solid sludge Low solubility of adsorbate Sludge formation in some instances	[114,124,125,128]

(*Continued*)

Table 1 (*Continued*)

Process	Factors influencing process	Advantage	Disadvantage	References
Ozonation	Si/Al ratio of adsorbent, type of adsorbate	degrade organic pollutants even refractory organics like nitrobenzene improved adsorption capacity of adsorbent	Free radical may be scavenged by bicarbonate and carbonate ions in water Loss of adsorption capacity of adsorbent Surface modification of adsorbent Excess ozone usage could lead to the formation of acidic surface that interferes with the adsorption of anionic pollutants The adsorbents are calcined before reuse, thereby adding to the process cost	[140–143]
Photo-assisted oxidation	Type of photosensitizer, type of support,	Fast degradation of organic pollutants to very low concentrations Does not require the use of harmful chemicals i.e. environmentally friendly	Release of harmful by products from adsorbed chlorinated and nitro pollutants	[150,160]
Electrochemical oxidation	Type of electrode, electrolyte concentration, current intensity, time, adsorbent weight, effluent pH, and concentration of pollutant	Works well with low-porosity high conductivity carbonaceous adsorbents	Reduced electrode efficiency with time Decreased efficiency with subsequent regeneration cycle Long regeneration times	[162,165,170–172, 177,182, 183]
Supercritical fluids regeneration	Temperature, pressure, pollutant solubility in supercritical fluid and type of supercritical solvent	Very fast regeneration times,	Cost of pressure vessels	[187,188] [221,222]
Ultrasonic regeneration	Intensity of ultrasound, nature of pollutant and adsorbent	No attrition of adsorbent Lower power consumption Simpler process equipment Higher desorption efficiency when compared with thermal regeneration	[204, 205,214]	
Dielectric barrier discharge plasma regeneration	Electric field, type of gas regeneration time	Fast regeneration time	Release of harmful by-products e.g. tri-and tetra-chlorophenols, chlorides, glyoxalic acid, formic acid, maleic acid	[16,215]

pH to minimize the addition of oxidant additives which could produce undesirable secondary pollutants.

Ion-exchange regenerative technique is also efficient but is plagued with the question of what happens to the desorbed adsorbates? They cannot be returned to the environment and recovering them separately for possible reuse in the laboratory or for other purposes could be quite expensive, complex, and tedious.

The electrochemical regeneration technique is very attractive and very promising because of its potential to regenerate adsorbents loaded with both organic and inorganic species and because it has a better regeneration efficiency and porosity recovery compared with thermal or chemical regeneration [219] but has a slow rate of regeneration. Besides, the fact that the electrodes are easily fouled does add to the cost of regeneration. However, there have been attempts to coat the electrodes with active catalyst materials which still require further scientific studies on their efficiency in various organic pollutant media and at different electrolyte pH. Several other variants of electrochemical treatment of water, such as the electro-Fenton, photoelectron-Fenton, could as well be studied for their use as regenerative techniques of spent adsorbents [220]. While there is so much information about the electrochemical regeneration of organic-loaded adsorbents there is dearth of information for inorganic-loaded adsorbents. It is worth noting here that it will be quite interesting for further studies to be carried out on the efficiency of electrochemical regenerative systems in recovering an adsorbent loaded with both organic and inorganic pollutants. The success of this will open a new vista for the use of electrochemical cells for regeneration of adsorbents. The development of less expensive but efficient electrochemical cell systems could put the electrochemical systems ahead of others for use in water treatment.

The SCF technique is also very efficient but it is limited by the cost of temperature and pressure used in the process.

Of all the regeneration techniques discussed, ultrasound regeneration technique appears to have the best advantage because the regeneration process is with less adsorbent attrition and low-power consumption although controlling the temperature and intensity of the ultrasonic equipment is still a challenge. The ultrasound regeneration technique has the further advantage of safety, cleanliness of the process without the production of secondary pollutants unlike in the chemical regeneration technique.

It has become even more useful to use a combination of ultrasound with some other regeneration techniques to enhance regeneration efficiency at minimal cost [15]. It has been shown that the addition of hydrogen peroxide at optimized concentrations will greatly improve ultrasound/UV light regeneration efficiency [221]. The combination of ultrasound (US) with electrochemical oxidative (EO) regeneration could be very efficient when it is used along with the treatment of wastewater containing organic pollutants [10]. This technique will combine the mechanical effects of US (which enhances the efficiency of the electrodes surface via enhancement of mass transfer) and the chemical effects (oxidative degradation) of the EO to achieve very efficient and cost-effective regeneration of an adsorbent. However, a combination of US and O_3 may not be very effective because of intensified recombination of free radicals formed from sonoozonolysis which decrease the amount of free radicals available to attack pollutants thus reducing their reaction rates. Recently, a combination of microwave and ultrasound was used in the regeneration of phenol-loaded activated carbon [222] with a regeneration efficiency of ca. 96% in 4 min.

It is clear from this review that no single regeneration technique holds the key to an efficient regeneration of all the variety of adsorbents present today. Researchers and industries will need to identify the most suitable regeneration technique based on the type of adsorbent they are using, time of regeneration, and the cost of the entire adsorption–regeneration process while considering the environmental implications of their regeneration technique. A combination of regeneration techniques at minimal cost and better efficiency will certainly provide better adsorbent regeneration alternative. There is need to further broaden the knowledge base of the regeneration of non-carbonaceous but very efficient adsorbents, as there have been far more studies on regeneration of activated carbon than there are for non-carbonaceous adsorbents. This is in line with the current trend of increasing new low-cost adsorbents produced for water treatment purposes. Furthermore, the development of an efficient system that combines these effective regeneration strategies in an adsorption–regeneration mode (adsorption–degradation occurring simultaneously) for organic adsorbates, with the release of non-harmful by-products will surely reduce the current cost of water treatment and make potable water available to all. The question of how to effectively handle harmful by-products from oxidative degradations of organic pollutants from adsorbents should now be considered more critically by scientists.

Finally, apart from activated carbon and zeolites, other low-cost adsorbents are yet to be utilized for the treatment of water on a large scale. It would be useful to see an up-scale or a pilot study on the use of these adsorbents in the treatment of real-life water or wastewater so that a thorough regeneration assessment of these adsorbents can be carried out. More importantly, since most water and wastewater contain some amount of organic matter, studies on the influence of natural organic matter on their ability to be regenerated would be vital in understanding their potential use in the nearest future.

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