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A review on adsorptive removal study of organic pollutant(s) using activated sorbents from waste contaminated water

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There is a serious environmental concern being encountered for increase in the rate of water pollution occurs by the contamination of several industrial discharges. The key issue of the contamination water is owing to the content of various non degradable toxic components in it which lead to cause life threatening to both plants and animal lives. In particular, the industrial effluent bears substantial amount of waste dyes, pesticides and pharmaceuticals wastes and those are carcinogenic in nature. This review is an attempt to cover the adoption of various activated sorbents including, charcoal, activated carbon, clay materials, organic extracts of the plants and nanomaterials for sorption studies of waste contaminates from the different kinds of waste water. The origin of organic pollutants, their nature, development of numerous activated adsorbents, characteristics properties of the sorbents and their suitable adoption for removal of contaminates is systematically discussed. The significance of the sorption mechanism accomplishing the kinetics, isotherm and thermodynamics on interaction of the adsorbents with organic pollutants are extensively described and reported.

Keywords: Activated sorbent, Pollutants, Sorption, Kinetics, Thermodynamics, Isotherm

The increase in the rapid urbanization and industrialization has led the world in facing issues related to exhaustion of fresh and clean water. In general, majority of industries discharge out wastes as it is into the environment without treatment. The industrial effluent is in particular liberated out and contaminates the fresh water bodies of the environment up to significant level. The effluent discharged out of several industrial sectors contains a variety of organic, inorganic contaminants with pathogenic and nonpathogenic attributes constitutes number of pollutants and that substantially causes load on increasing the water pollution. As a result of which this waste water is not only causing an adverse effect on human health but also affects to the environment and its ecological territory up to a greater extent. The key pollutants found in wastewater effluents includes nutrients (nitrogenous and phosphorus based compounds), toxic heavy metals, microbes, organic matter, hydrocarbons and endocrine disruptors and those directly affect human morphology and so as to the environment[1]. Out of these, the non-degradable azo-organic dyes and toxic metals like As, Hg in water do cause carcinogenic effect on living species while affecting them directly or indirectly through a complex food chain mechanism. Moreover, the presence of several organic matters (plasticizers, fertilizers, bi-phenyls, herbicides, detergents, oils, grease, aromatic dyes, etc.) and the various other toxic heavy metals makes it a breeding ground for pathogenic organisms, which are directly accountable to water-borne infections; contributing to the necessity behind adequate treatment practices [2]. The suspended solids present in water resources reduce the entering of sun light into the water bodies and directly affecting to photosynthetic process to produce flora and fauna which disrupting the habitat of most invertebrates in aqueous systems. On the other hand, the Eutrophication is another such result of excessive nutrient proliferation leading to the inadvertent stimulation of algal growth. This causes depletion in the dissolved oxygen content interrupting the physiology and metabolism of aquatic organisms.

The EPA priority pollutants list classifies 129 priority pollutants (organic and inorganic) in 65 categories, regulated by systematic discharge standards. They are selected on the basis of their suspected carcinogenicity, mutagenicity, teratogenicity, or toxicity properties[3]. The persistent organic pollutants are incorporated in the priority pollutants category. They can be transported through air or water and can infect human as well as wildlife far from where they are released. They become recalcitrant over a period of time and can pass from one species to the next through the food chain. Some of these pollutants such as polychlorinated biphenyls, phenols, benzenes, and dichloro-diphenyl-trichloroethane (DDT) are highly resistant to biological degradation. Their biodegradation is possible only under exceptional circumstances by utilizing specialized micro-organism over an extended period of time or expending a combination of conventional chemical and biological techniques.

Types of organic pollutants

Azo dyes

Azo dye is a kind of pollutant which is having the azo linkages (R_1–N=N–R_2) shows various characteristics colours due to which they are extensively used in several industrial sectors and also in basic research laboratories. As of now over 10,000 dyes are commercially available across the globe and their production is increased up to ~7 X10^5 million tons. From these ~ 5–10% of dyes are becoming waste as they discharge out of these industries in the form of effluent[4,5]. Generally dyes categorized based on their chemical nature upon dissociation in an aqueous phases. They are of cationic (basic dyes), anionic (acidic and reactive dyes), and nonionic (disperse type dyes) dyes[6]. These dyes are of synthetic form having a complex chemical structure. Therefore upon contamination in water bodies of environments, they pose serious issues due to their high range stability towards light, oxidation and biodegradation leading to exist in environment for prolonged time limit. When these azo dyes are decomposing, it generates ~ 20 varieties of carcinogenic aromatic amines that could further change the structure of DNA and hence resulted to cause induced lesions and cancer[7-9].

Generally the textile industry consumes ample quantity of industrial water which bears huge numbers of chemicals in the form of detergents and caustic (used to remove dirt, oils, grit, and waxes), sizing agents, latex and glues (binder), dyes, fixing agents, and many in-organics, to impart vibrant colour. A special types of chemicals like softeners stain release agents, and wetting agents are found to be present at the above liberated waste water. Due to inadequate treatment of this polluted water, it could allow the pollutant to sustain in biological systems and environmental ecosystems for a relatively long period of time making them recalcitrant. The studies have indicated that textile effluents possess a very high concentration of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Dioxins from these sources can be transferred to other compartments through several pathways and contribute to bio magnification. Due to the synthetic nature and non-biodegradable property, they impart allergies, dermatitis, and skin irritation upon coming in contact with human tissue. Several azo dyes are responsible for damaging DNA leading to cause life threatening disease like cancer in human body. The past three decades revealed analytical data on global contamination of aquatic and terrestrial environments by these persistent contaminants and have exhibited concern to understand their ubiquitous environmental occurrence, toxic effects, health risk assessment and their subsequent removal.

Pharmaceuticals waste

The usages of pharmaceutical as well as personal care products in the healthcare and medical sectors have a major concern on water pollution because of the presence of nitrogenous, phosphorous and sulphur based organic compounds in aqueous medium. The pharmaceutical drugs are broadly classified as antibiotics, analgesics, anti-inflammatory, drugs, steroids and other related hormones, Beta blockers, and other cancer based therapeutics[10,11]. Diclofenac, Ciprofloxacin, Ibuprofen, Sulfamethoxazole, Ampicillin, Amoxicillin etc are some of the widely used compounds, on which studies show their presence in waste water. The total production of antibiotics in India was more than 2332 Mt in 2006 with a growth rate of 10%[12]. It is observed that 90% of antibiotics after injection into patients, gets excreted in the form of urine and faces in an un-metabolised state[13]. Hospital effluents are considered to be a major source of pharmaceutical residues. This is generally because of the hospital sewage system which is affected by admitted patients. Even though most of the researches on hospital effluents focus on antibiotic residues, however a large number of pharmaceutical compounds have shown that hospitals are one of the leading causes of water pollution with respect to pharmaceuticals in the environment. Different kind of residues such as radionuclides, solvents and antiseptic germicidal disinfectants, are mostly discharged from hospital waste. Apart from the regular medications and prescription drugs, even X-ray contrast media, diagnostics agents and other specific substances present in medical and research laboratories are considered as main primary sources for increasing the pharmaceutical load in the waste water[14-16]. These pollutants in their un-metabolised form remain highly toxic and hazardous with notably long term health risks to living beings[12, 17].

Persistent organic pollutants (POPs)

Persistent organic pollutants (POPs) are broad classes of an organic pollutant that are typically hydrophobic and lipophilic in nature which contribute strongly to organic solids in aquatic systems and accumulate in the fatty tissues continuing its fortuity in food chains. POPs chemicals are classified into families of chlorinated/brominated, aromatics, (polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins and-furans, poly brominateddiphenyl ethers and various chlorine based organic pesticides (DDT and its subsequent metabolites like toxaphene, chlordane, etc.). Off these chemical, some are of accidental byproducts due to combustion or from the synthesis of other industrially used chemicals (e.g. the PCDD/Fs). Some of other types of above chemicals are synthesized for an industrial utility like PCBs, chlorinated paraffin, PBDEs or for agro-industries (e.g. DDT, Lindane, chlordane). The other category of POPs are phenols (nonionic surfactants e.g. polyethoxylatedalkyl phenols), and chlorinated phenols. POPs have been deliberately manufactured over the years most of which is generated from agrochemical industries in the requirement of crop fertilizers and pesticides. Its multiple usages in a variety of industries make it a contemporary source for a prolonged period of time. The term "pesticide" is a broad category of POPs that are categorized depending on their ability to kill the living organisms. They include insecticides, herbicides, and fungicides. They are biologically active substances that occupy as omnipresent including living beings as well as in the environment leading to get more exposure of the major human population and that lead to cause major concern for human lives. Their structure mimics specific molecules in targeted biological reactions. Humans are exposed to the pesticide through a variety of routes and adversely affect all biological systems such as dermal contact, inhalation, and ingestion, Increasingly, exposure to pesticides have been corresponding to a wide spectrum of diseases and deformities, e.g, neurobehavioral disorders and developmental deformities in infants autoimmune disease, reproductive abnormalities, myeloma, leukemia, malignancy.

Therefore, it is very much essential to treat/remove theses pollutants from the industrial disgorges prior to their contaminations in the natural water bodies. Numbers of works are being investigated by researchers while adopting different techniques for removal of dye as well as other organic pollutants from waste contaminated water. Based on the degree of the level of pollutant contained in the contaminated wastes, many chemical and biological approaches have been applied for their removal studies to produce high pure water[18-24].

Adopted sorbent material and processes for remediation study of waste organic pollutants

Various technologies including coagulation-flocculation, sedimentation, membrane technologies (reverse osmosis, supported liquid membrane separation, and nanofiltration), microbiological decomposition, aerobic and/or anaerobic degradation, photo-catalytic oxidation and adsorption using numerous sorbents (activated carbon, silica or clays, ion exchange resins and composites, chitin-based adsorbents) are being practiced in due course of time for separation of these organic waste pollutants from the aqueous phases[25–30]. There is some advantages and disadvantages of the above processes, In shortcoming, the majority of these technologies (besides adsorption using natural sorbents) uses synthetic materials for examples nanocomposite, polymeric ion-exchangers and therefore the issues concerning to the resin poisoning and non-biodegradability nature of synthetic sorbent materials cannot be avoided. Apart of which in other applied approaches either the developed processes are of very slow and/or uses intensive energies. Thus, to overcome several such issues, adsorption process pronounced to be most preferred approach, in which a very low cost as well as advanced materials can easily be utilized for removal of targeted pollutant through π-complexation, π-π interaction, and electron donator-acceptor interaction. Nevertheless, major advantages of the process are its ease in operation, simplicity of process design, and complete separation of pollutant from aqueous media. Though the above mentioned processes showed a lot of efficacy and optimistic results in the removal of dyes still there is needed of surface modification of the adsorbent to enhance the efficiency of the adsorbent. This can be achieved by several treatments on the adsorbent. The prominent and widely used methods are generally chemical and physical treatments utilizing acids, alkalis, oxidizing agents, metal complexes etc. Metal impregnation, chemical grafting and functionalization techniques are the most important methods involved in the surface modification technique[31]. The main target of the surface modification technique is to increase the pore size of the adsorbent as well as the adsorption efficiency and increase the regeneration potential of the adsorbent.

Acid treatment

One of the most widely established methods for surface modification of adsorbents is the method of protonation by using acid treatments. The addition of positively charged ions on the substrate is resulted in more electrostatic attractions with negatively charged ions on the adsorbate which increases the efficacy of adsorption treatment. Generally this method of adsorption is mostly used on the modification of industrial and agricultural wastes. Hence this is widely recognized as a cost effective and popular technique of surface modification[32].

High temperature treatment process

Red mud is an industrial waste by product obtained by caustic digestion of bauxite ores by Bayer process in the production of alumina. For every ton of alumina produced, between 1 and 2 tons of dry red mud residue is obtained[33]. This red mud is strongly alkaline in nature and potentially very hazardous in nature. Many treatments have been going on for the utilization of this red mud in waste water treatment using adsorption technique. Red Mud is subjected to high temperature heat treatment, as well as acid treatment using nitric acid. It is observed that heat treatment can cause reduction of adsorption capacity due to the reduction of some hydroxyl and other organic carbon groups leading to less effective sites present for adsorption. However, they are still considered as good adsorbents for large scale waste water treatment.

Sorbent material

Fly Ash

Fly Ash is generally produced in a large scale, by burning of coal. Apart from its usual applications in cement production, road building and other civil engineering aspects, considerable research has also been done in using fly ash as a low cost adsorbent in the removal of organic pollutants, heavy metals and dyes from waste water. It is believed that the lime content in the fly ash plays a significant role in the adsorption as well as sorption capacities. According to experiments conducted, it is observed that fly ash shows great adsorption potential against Basic Blue 9, Acid Blue 29 as well as Acid Red 91(Ref. 34). Both basic as well as acidic dyes can be removed from waste water using the adsorptive capacity of fly ash[35]. However, surface modification using physical and chemical treatment showed far more adsorption efficiency in comparison to crude fly ash. The main components of fly ash are alumina and silica with some amounts of iron oxide and calcium oxide levels. Hence efforts were made to improve the adsorption efficiency following acid as well as heat treatment to the fly ash. High temperature results in the reduction of surface area as well as the surface pore volume which may impede with the adsorption capacity of the fly ash. However, nitric acid treatment can in turn dissolve many of the undissolved minerals present in the fly ash which may therefore lead to increase in adsorption efficiency[33].

Activated carbon

The carbon itself is the gift of nature for its various applications prospective. The pure form of carbon pose several usages for its characteristics features like surface behaviour besides its major utilization in thermal energy sector. The unique surface behaviour of carbon such as porosity and high surface area ensures on sorption strategy for removal of metals, non-metals and dyes. However, it was noticed that making pure carbon out of the natural precursor material is not easy. Moreover, the surface behaviour of the carbon surface can significantly be improved by activating it on formulating as a promising and suitable sorbent material. There are various chemical and biochemical routes are being practised to produce numbers of activated carbon. In these processes the natural sources such as the various plan extract (pericarf of fruits like orange peel, rice husk, various leaves, routes, stems, and several others part of plant) are used as precursor material for making activated carbon. The selection of activation agents for preparing activated carbon has been has the most challenging task, gained considerable attention around the world. One of the versatile method namely charring process has been dragged larger attention and the resulted products obtained through the charring approach are commonly called as activated carbon. The objective of making this is to bring the significant modifications on its surface enabling to improve the surface porosity for increasing the uptake ability while removing dyes.

Other Carbonaceous Materials

Carbon based materials have been emerged out to be as one of the oldest, widely researched areas for waste water treatment for removal of several organic as well as inorganic contaminants. Activated form of carbon is generally being adopted in an extensive manner due to its vast surface area as well as other surface textural properties that makes it a really good adsorbent. Moreover, one of the main reasons for its widespread utilization is availability of easy precursor materials as well as its cost effective approach in preparation. Activated carbons are generally prepared using carbonization process, where moisture, impurities and other volatile compounds are removed and what is left behind is char, which is further physically or chemically activated in order to be used as activated carbon[36]. This has a huge surface area and can therefore be used easily in adsorption process. However, to enhance the efficacy of adsorption, these activated carbons are allowed to treat under certain chemical modifications. This can again either be done through acidic treatment mineral acids (nitric acid, sulphuric acid and hydrochloric acid) for bringing out the acidic character of the carbonaceous surface. The most frequently used oxidation procedure is done by gas phase and liquid phase oxidation treatment. For example, an adsorption study was done using raw mango seeds as well as surface modified mango seed for the removal of methylene blue dye under optimal conditions. As per the results, even though the adsorbents showed good removal strategy, the surface modified concentrated sulphuric acid treated mango seed powder had the optimal results[37]. The other technique is being followed is base treatment route which induces a positive charge on the surface of the carbonaceous compound. This can be utilized to adsorb negatively charged surface moieties. The most preferred method of surface modification is the treatment with ammonia or hydrogen at high temperature range resulting in formation of basic nitrogen groups on the surface of the adsorbent, thereby adsorption efficiency can be improved. According to a study, granular activated carbons were subjected to ammonia tailoring at high temperatures for 60 min. This has resulted in both physical and chemical changes in the surface of the adsorbent that in turn resulted in increased percholate adsorption[38]. Hence heat, acidic and basic treatments as surface modifications on carbonaceous compounds can increase their adsorptive capacity by great extents.

Chemical Impregnation

Chemical impregnation is a method of uniform distribution of chemicals on the internal surface of activated carbon[39]. It is basically a method of introducing surface functional groups on the surface of the carbon without causing much significant changes in its properties like pH. These chemicals can be anything from polymers or metallic substances which play an important role in the adsorption efficiency. It has been observed that carbons generally do not exhibit much superior performance when it comes to removal of inorganic compounds. Hence the modification using impregnation technique is done to increase the performance of adsorption and greater selectivity as well as removal efficiency. In a study, adsorptive capacity of plain carbons were increased by impregnating them with silver and nickel. It was observed that silver impregnated carbons showed nearly twice the removal efficiency as compared to nickel impregnated carbons, with respect to cyanide removal from waste water[40]. In another such study, bismuth impregnated biochar was utlilised for the removal of arsenic, phosphorus and chromium from waste water. The studies showed that bismuth played a very important role in increasing micropore volume thereby resulting in increased surface area that aided in efficient adsorption. Moreover, phosphate adsorption resulted in formation of bismuth phosphate which was in turn utilised for the removal of methylene blue dye in solution. The study gave novel promising methods for using straw resources to prepare easy cost effective adsorbents that helped in anionic pollutant removal from waste water[41].

Surface modification of sorbents

Several efforts have been put forward about the surface modification of activated carbons as well as other chemical substances using anionic as well as cationic surfactants for removal study of wastes. Though, the direct application of surfactant modified adsorbents in waste water removal is relatively rare, limited studies have demonstrated good results. In a study, colloidal silica was used as an adsorbent for the removal of cationic dye, methylene blue as well as anionic dye, congo red[42]. The colloidal silica was then surfactant modified using a cationic surfactant cetyltrimethylammonium bromide (CTAB). The surface modification resulted in the formation of aggregates which favoured the congo red molecules to get adsorbed with a very small positive entropy.

However, the negligible amount of adsorption was observed over the modified surfactant surface with respect to cationic dye or methylene blue adsorption[42]. In another study, granular activated carbon was surface modified using, hexa-decyltrimethylammonium which showed much higher adsorption capacity for removal of hexavalent chromium, in comparison to granular activated carbon modified by cetylpyridinium. The modification of the activated carbon using a cationic surfactant leads to enhance almost 100 times higher adsorption capacity over raw activated carbon. Moreover, both the adsorption rates as well as adsorption capacities were greatly increased[43]. Similarly, another study showed that anionic surfactant modification of activated carbon using sodium dodecyl sulphate (SDS) as well as sodium lauryl sulphate showed much greater results than that with cationic CTAB surfactant for the removal of methylene blue[44].

Characterization study of activated sorbents

To understand the mechanism of adsorption process the adsorbent should be characterized by different analytical techniques which would provide information regarding the surface chemistry, structural framework, presence of functional groups and the active sites of adsorbent. One such technique is scanning electron microscopy (SEM), by which the surface morphology of the adopted sorbents can be ascertained. For instance in the investigation reported by Murmu et al.[45] in 2018, where they studied the adsorption of azo dye (bromocresol green) from waste water using activated *Phragmiteskarka* (activated carbon obtained after charring*)*. In this investigation they observed that the original bio-sorbent sample (*Phragmiteskarka* (PK)) before activation appears to be highly sturdy and dense. However, after the phase modification of the adsorbent by chemical charring process, there were observed significant changes in the porosity leads (to avail high surface area) over the non-activated adsorbent. The characteristic change in behaviour of the surface morphology of the bio-sorbent used for the dye removal study before and after activation is shown Fig. 1. In this investigation it was noticed that after chemical treatment of adsorbent PK, its surface modification was occurred and transformed from more shredder and denser surface to more porous form.

Another most useful technique such as X-ray powder diffraction (XRD) study has been commonly employed to ascertain the change in crystal phase of the adsorbent and its average crystallite size. After surface modification the crystallite size of the adsorbent may vary which will helpful for adsorption efficiency. Rath et al.[46] studied the adsorption of congo-red dye using magnesium doped zinc oxide nanoparticles. In this investigation it was observed that the size of ZnO nanoparticles decrease when doped with Mg. There was a shift of peak position observed because of Mg-doped ZnO owing to the change in inter-planar spacing after doping[46]. The characteristic pattern obtained for pure ZnO and 2% Mg-doped ZnO is as shown in Fig. 2.

FT-IR analysis has also been examined sorption process to infer the insight information regarding the kind of functional groups present on the adsorbent which is mainly responsible for establishing the mechanism of adsorption approach. To ensure the role of functional group present on adsorbent and adsorbate and its interaction in sorption process, a study of FT-IR spectra (shown in Fig. 3) of both *Phragmiteskarka* (PK) activated *Phragmiteskarka* (APK) and bromocresol green (BCG) dye was reported by Murmu et al.[45]. This activated carbon used in this study showed characteristics absorption bands of various functional group associated on binding of dye molecule. The peak observed at 1743 cm^{-1} is because of ν(C=O), and at 1605 cm^{-1} is due to ν(C=C) stretching frequency for APK before and after adsorption. The absorption band observed at 1424 cm^{-1} is owing to symmetric bending

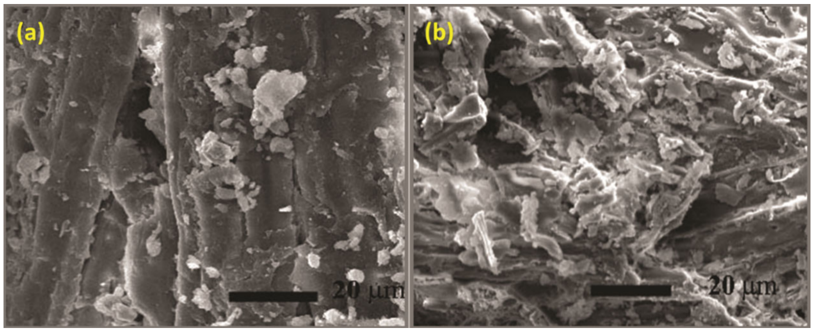

Fig. 1 — SEM analysis of (a) *Phragmiteskarka* and (b) activated *Phragmiteskarka*[45]

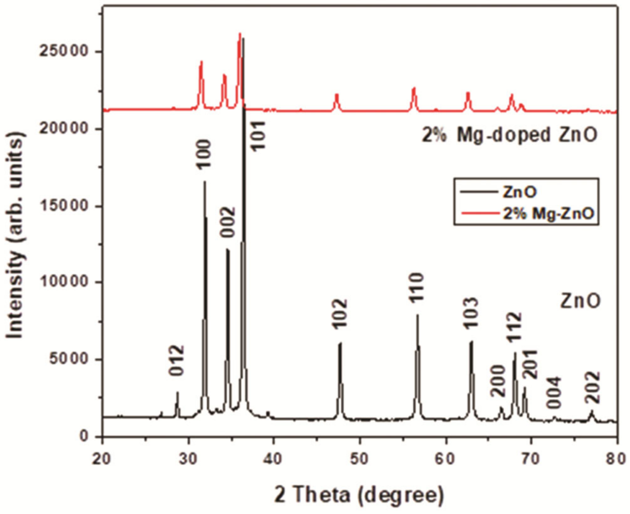

Fig. 2 — XRD of ZnO and 2% Mg-doped ZnO [46]

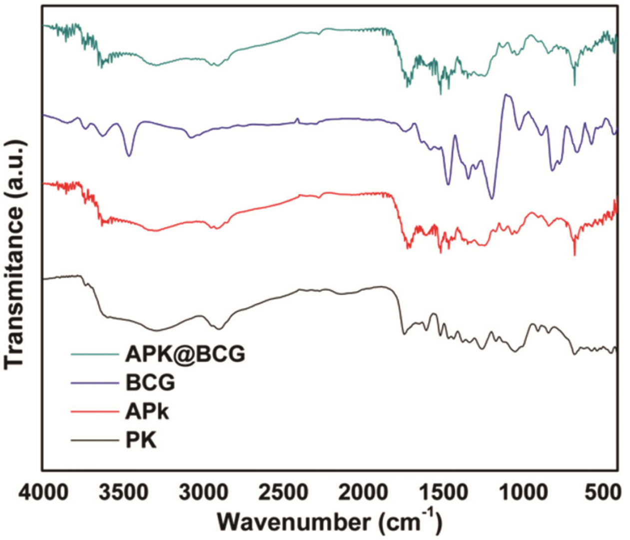

Fig. 3 — FTIR spectroscopy of PK, APK, BCG and BCG loaded APK[45]

of CH_3 group. There is a major shift of absorption band from 1200 cm^{-1} of BCG to 1150 cm^{-1} for BCG loaded APK for respective ν(S=O) frequency of $–SO_3^-$ group. The peak observed at 3450 cm^{-1} for ν($O\text{-}H_{str}$) of BCG shifted to a broad band at 3270 cm^{-1} may be due to conjugation of BCG molecule on activated carbon surface.

Studies on removal of dyes from wastewater

Majority of textile industries consumes large quantities of water for dyeing and has the roles over discharging of waste effluents for the contamination of fresh water. The lack of sustainable treatment systems makes it environmentally acute. Therefore proper treatment of this waste contaminated water is essentially urged. Among different treatment techniques are being adopted, the adsorption approach has been widely accepted for effective and clean removal dye(s) from wastewater[45]. Though, several sorbents appears to be promising candidate in separation of dyes, surface modification of these adsorbent materials have immensely contributed to improve the economic feasibility and adsorption yield of the material.

Almasian et al.[47], studied the synthesis of polyacrylonitrile (PAN) nanofibers by electrospinning technique and its adsorption behaviour for the removal of direct red 80 and direct red 23. Here the adsorption properties was studied by modifying the surface of the adsorbent using different sources of amine based compounds, namely, diethylamine, diethylenetriamine, and triethylenetetramine etc. for generating changes in chemical, morphological, and surface properties of nanofibers. It was noticed that the functionalized PAN nanofibers have high adsorption capacity over the non-fuctionalised one. Mahmoodi & Najafi[48], have studied the surface modified zinc oxide nanoparticle by amine functionalized for high adsorption capacity. In this study, the removal capacity of both the sorbents were investigated on separation of the dye like acid blue 25 (AB25), direct red 23 (DR23) and direct red 31 (DR31) and the maximum adsorption capacity was found to be 20 mg g^{-1}, 12 mg g^{-1} and 15 mg g^{-1} for ZnO and 1250 mg.g^{-1}, 1000 mg.g^{-1} and 1429 mg.g^{-1} for amine functionalized ZnO naoparticles, respectively. Mahmoodi & Saffar[49], have also examined the synthesis and modification of sodalite zeolite nanoparticle (SZN) using different amounts of (3-aminopropyl) tri-ethoxysilane and denoted as SZN(0.5), SZN(1) and SZN(1.5) for adsorbing direct red (DR23) and direct red 80 (DR80) from industrial waste effluent. The adsorption capacity of SZN(0.5) was observed to be very high compared to other SZN. Olusegun et al.[50], studied the adsorption efficiency of clay through its surface modification by spray drying of dispersed clay solution. The adsorbents were implemented on methylene blue for its effective removal in its aqueous state. The modified clay accomplished better adsorption capacity (168 mg g^{-1}) at 333K. Ge et al.[51], have studied the synthesis of silica with different channel structures and/or pore diameters through hydrothermal approach. Corresponding nitro/amine modified materials were obtained by nitrating reaction and grafting, respectively, for the removal of both Cu and methylene blue from aqueous solution. Mesoporous SBA-12-OH has exhibited superior uptake capacity (Q_{max} = 911 mg g^{-1}) for MB whereas SBA-12-NH_2 suggested excellent sorption behaviour toward Cu^{2+} (Q_{max} = 49.8 mg.g^{-1}). Xia et al. [52], examined the selective removal of the anionic dye congo red from aqueous solution using two modified hectorites which was synthesized by the application of two cationic surfactants namely CTAB and octadecylamine (ODA) and the adsorption capacities were 182 and 197 mg g^{-1} for the above modified adsorbents, respectively. Keyhanian et al.[53], studied the adsorption potential of Fe_3O_4 magnetic nanoparticles (MNPs) for efficient removal of methyl violet from aqueous solution. Here also the adsorption efficiency was enhanced with the surface modification of MNPs. The modification of MNPs was carried out with the help of surfactant like sodium dodecyl sulfate (SDS) and the maximum adsorption efficiency was observed to be 416.7 mg g^{-1} indicating that, SDS-MNPs can be used as a cost-efficient adsorbent for cationic dye. Zhang et al.[54] have investigated the modification of kaolinite through calcination, acid leaching, and ultrasonic dispersion followed by exposed to effective modification with amino functional groups through grafting with (3-aminopropyl) triethoxysilane (APTES) to test its efficacy for the removal of congo red from its aqueous solution and exhibited a high adsorption capacity of 437.6 mg g^{-1}. Mahmoodi[55] studied the surface modification of magnetic zinc ferrite nanoparticle (ZFN) using SDS for removal of basic Blue 41 (BB41), basic Red 18 (BR18) and Basic Violet 16 (BV16). The maximum adsorption capacity was found to be 42, 61 and 16 mg g^{-1} for BB41, BR18 and BV16, respectively. Wanga et al.[56], conducted a study for the synthesis of Fe_3O_4 nanoparticles by hydrothermal technique and its modification with tetraethyl orthosilicate to form $Fe_3O_4@SiO_2$ nanospheres for removal of congo red from aqueous solutions. Mahmoodi et al.[57], studied the surface modification of magnetic manganese ferrite nanoparticles (MFN) using CTAB to test its application in the removal of direct Red 80 (DR80), direct red 31 (DR31), and acid blue 92 (AB92). The maximum dye adsorption capacity (Q_0) of modified MFN-CTAB for DR80, DR31 and AB92 was 83 mg g^{-1}, 59 mg g^{-1}, and 70 mg g^{-1}, respectively. The summarized form of dye adsorption by different activated adsorbent and their adsorption efficiencies were given in Table 1.

Removal of pesticides and its derivatives from wastewater

Pesticides and their derivatives are one of the important class of organic pollutants.. These wastes are of major concern owing to their persistence in various ecosystems for a long period of time. In nature, the pesticide remainders gets expose to different chemical, physical, and biochemical degradation processes. However, due to their stability, the residues become recalcitrant. The removal of these pesticides can be

Table 1 — Adsorption efficiency of dye molecule using surface modified adsorbent

Sl No.	Adsorbent	Adsorbate	Adsorption efficiency	Reference
1	Amine functionalization surface modification of zinc oxide nanoparticle (AFZON)	Acid Blue 25 (AB25), Direct Red 23 (DR23) and Direct Red 31 (DR31).	1250 mg/g, 1000 mg/g and 1429 mg/g for AB25, DR23 and DR31, respectively	48
2	Sodalite zeolite nanoparticle (SZN)	Direct Red 23 (DR23) and Direct Red 80 (DR80)	2415 mg/g for DR80 and 4842 mg/g and DR23	49
3	Modified Clay	Methylene blue	168 mg/g	50
4	Modified Silica	Cu and Methylene blue	1.228 g mg^{-1} min^{-1} 0.048 g mg^{-1} min^{-1}	51
5	Modified hectorites	Congo red (CR)	182 and 197 mg/g for (CTAB-Hect) (ODA-Hect),	52
6	sodium dodecyl sulfate (SDS) modified Fe_3O_4 magnetic nanoparticles (MNPs)	Methyl violet	416.7 mg g^{-1}.	53
7	Modified kaolinite	Congo red (CR)	437.6 mg/g.	54
8	SDS modified Magnetic zinc ferrite nanoparticle (ZFN)	Basic Blue 41 (BB41), Basic Red 18 (BR18) and Basic Violet 16 (BV16)	42, 61 and16 mg/g for BB41, BR18 and BV16, respectively.	55
9	Tetraethyl orthosilicate modified Fe_3O_4 to form $Fe_3O_4@SiO_2$nanospheres	Congo red (CR)	54.64 mg/g	56
10	Cetyltrimethylammonium bromide modified magnetic manganese ferrite nanoparticles	Direct Red 80 (DR80), Direct Red 31 (DR31), and Acid Blue 92 (AB92)	83 mg/g, 59 mg/g, and 70 mg/g, respectively	57

achieved through several techniques such as biological, chemical, physical, and physicochemical processes with the usages of matrices. In a study[58] surface properties of granular activated carbon (GAC) was examined and compared with GAC modified by dielectric barrier discharge plasma to elevate for the removal of pentachlorophenol (PCP) from soil and water samples. From adsorption isotherms study it was revealed that the O_2 plasma could enhance the adsorption amount of PCP on GAC, while N_2 plasma significantly decreased the adsorption amount of PCP. Alila & Boufi[59] have used modified cellulose fibers for the removal of several aromatic organic compounds and three herbicides, i.e. Alachlor (ACH), Linuron (LNR) and Atrazine(ATR). The adsorption capacity was enhanced from 20 to 50 mg g^{-1} for the virgin fibers whereas the adsorption efficiency increases to 1000 mol g^{-1} for the modified substrates. Shankar et al.[60], have developed a bio-sorbent for the removal of PCP from aqueous media, utilizing functionalized chitosan (CHT) (I) with 2-hydroxy-1-naphthaldehyde which was further modified by grafting with $CuCl_2$ to prepare CHTAC. The surface modification of chitosan resulted remarkable changes due to the cross linking of chemically modified chitosan derivatives which improved their interaction with PCP and the uptake PCP was maximized. At neutral pH, the highest adsorption capacity displayed by CHTA (39.1 mg g^{-1}) followed by CHTAC (35.4 mg g^{-1}) and CHT (24.4 mg g^{-1}). The adsorption efficiency of a mixture of 15 pesticides from water samples was investigated by Taha et al.[61], using treated and untreated biochars and charcoal with phosphoric acid. The effect of treated biochars with phosphoric acid was higher than that by using charcoal. Phosphoric acid modified rice straw biochar shows high adsorption capacity of individual pollutant with faster kinetics except oxamyl at neutral pH range. However, the oxamyl can be easily removed from water by its degradation under the alkaline conditions of untreated biochar. Dhaouadi et al.[62], focused on the deletion of rotenone (insecticide) from wastewater using modified activated carbons. In order to enhance the removal efficiency, activated carbon was further modified chemically with NH_3 and $(NH_4)_2S_2O_8$ solutions. The maximum adsorption capacities of these modified activated carbon reached to 178.6, 217.4 and 270.3 mg g^{-1} for AC-P, AC, and AC-A, respectively. Alila et al.[63], studied the preparation of stearate impregnated starch nanocrystals for the adsorption of aromatic organic compounds from water samples. The maximum adsorption capacity enhanced ranges from 40 mg g^{-1} to 100 mg g^{-1} in consequence to the structure of the organic solute. Grafted modified thin alumina (c-Al_2O_3) nanofibres have been investigated by Paul et al.[64], where two organosilane grafting agents as 3-chloro-propyl-triethoxysilane (CPTES) and octyl-triethoxysilane (OTES) were used. These modified materials were effectively applied for removal of two herbicides like alachlor and imazaquin from water. It was observed that the modified nanofibres could absorb alachlor 1.6 mg $g^{-1}$of adsorbent at an initial lower concentration of 2 mg g^{-1} whereas CPTES grafted c-Al_2O_3 fibres absorb imazaquin about 1 mg g^{-1} of adsorbent at an initial concentration of 1 mg g^{-1}. Celis et al.[65], focused particularly on two montmorillonites (SWy-2 and SAz-1) which were modified with organic cations and were tested as adsorbents for the removal of herbicides: terbuthylazine, diuron, and MCPA. Among the three herbicides, SAz-1 exhibited strong affinities when exchanged with hexadecyl, -trimethyl ammonium cations. The unmodified clays removed less than 15% whereas after modification the adsorption efficiency was increased up to 95%. The pesticides adsorption taken up using various surface modified sorbents are summarized and presented in Table 2.

Pharmaceutical residues in waste water

At the present scenario pharmaceutical as well as personal care products in the healthcare and medical sectors have a major concern on water pollution because of the presence of nitrogenous, phosphorous and sulphur based organic compounds in aqueous medium. The pharmaceutical drugs are broadly classified as antibiotics, analgesics, anti-inflammatory, drugs, steroids and other related hormones, Beta blockers, and other Cancer based therapeutics[10, 11]. Diclofenac, ciprofloxacin, ibuprofen, sulfamethoxazole, ampicillin, amoxicillin etc are some of the widely used compounds, on which studies show their presence in wastewater. In a study on hospital effluents at Ujjaini district, India, it was observed that even though the sample groundwater was free from antibiotics, other pharmaceutical compounds such as norfloxacin, ciprofloxacin, orfloxacin etc. were present in extremely minute concentrations upto 236.6 ug^{-1} in hospital effluents[17]. Another study in effluents on the sewage treatment plant located in Delhi, on the effluent receiving Yamuna river showed that Ampicillin had the highest concentrations present upto 104.2±98.11 ug^{-1} followed by lower concentrations of cephalosporins and fluoroquinolones[12]. The summarized form of pesticides adsorption by different activated adsorbent and its adsorption efficiency was given in Table 3, below.

Role of process parameters affecting on sorption of organic dyes using activated sorbent

In the sorption process operational parameters such as time, shaking speed, pH, temperature, sorbate and sorbent dose plays key role on assuring the process and ascertaining the interaction mechanism of sorbate and sorption process. The illustrations on the

Table 2 — Summary of the studies for removal of pesticide(s) from waste water using surface modified sorbents

Sl No.	Adsorbent	Adsorbate	Adsorption efficiency	Reference
1	Grannular activated carbon (GAC) (modified through dielectric barrier discharge plasma	Pentachlorophenol (PCP)	98%	58
2	Modified cellulose fibers	Alachlor (ACH), Linuron (LNR) and Atrazine(ATR)	400 and 1000 mol g^{-1}	59
3	Modified chitosan material CHTA	Pentachlorophenol (PCP) pesticide	CHTA (39.1 mg g^{-1}) CHTAC (35.4 mg g^{-1}) and CHT (24.4 mg g^{-1})	60
4	Modified biochars and charcoal with phosphoric acid	Oxamyl	0.068 mg/l	61
5	Modified activated carbons	Rotenone	178.6 mg.g^{-1} for AC-P, 217.4 mg g^{-1} for AC and 270.3 mg g^{-1} for AC-A	62
6	Modified starch nanocrystals by impregnating with stearate moieties	Aromatic organic compounds	40 mg.g^{-1} to 100 mg.g^{-1}	63
7	Thin alumina (c-Al_2O_3) nanofibres with 3-chloro-propyl-triethoxysilane (CPTES) and octyl-triethoxysilane (OTES)	Alachlor and imazaquin	1.6 mg g^{-1}& 1 mg g^{-1}	64
8	Montmorillonites (SWy-2 and SAz-1) (modified using organic cations)	Terbuthylazine, diuron and MCPA	95%	65

Table 3 — Adsorption efficiency of pharmaceutical residues using surface modified adsorbent

Sl. No.	Pharmaceutical residue removed	Adsorbent	Adsorption efficiency (%)	Reference
1	Cationic-, Neutral-, and anionic- based compounds	Mesoporous silica SBA-15 and hydroxyl methyl (HM-SBA-15), aminopropyl (AP-SBA-15), and trimethylsilyl (TMS-SBA-15)	99	66
2	Ciprofloxacin	Chitosan/Biochar hydrogel beads	50	67
3	Acetaminophen, 17α-ethynyl estradiol, nalidixic acid, and norfloxacin	Silica, Alumina and Hydrophobic medium, Porapak P	99	68
4	Chlorophenols	Mesoporous silica	90	69
5	Acetaminophen	Double-oxidized graphene oxide	83	70
6	Carbamazepine, oxazepam, sulfamethoxazole, piroxicam, cetirizine, venlafaxine and paroxetine	activated carbon of paper mill sludge	90	71
7	Diclofenac, salicylic acid, ibuprofen and acetaminophen	Pyrolyzed pulp mill sludge	85	72
8	Flurbiprofen	Tetrabutylammoniummontmorillonite (TBAM)	90	73
9	Diclofenac	Cyclamen persicum tubers based activated carbon (CTAC)	72	74
10	Diclofenac	Activated carbon from potato peel waste	70	75
11	Ampicillin	Activated Carbon	73.	76
12	Ampicillin	Modified Ponorogobentonite	90	77
13	Ciprofloxacin	Dioctahedral clay minerals	93	78
14	Ciprofloxacin	Activated carbon, carbon xerogel and carbon nanotubes	95	79
15	Nitroimidiazole	Activated carbon	91	80

role of each of the parameters are described in the following sections.

Contact Time

The influence of time on adsorption of pollutant from waste contaminated water is an important factor which illustrates the adsorption capacity of the adopted sorbent and more importantly to establish the adsorption kinetics[45-50]. In this study stoichiometric amount of adsorbent is treated with a waste effluent at varying contact time. Since the adsorption process is usually very slow, therefore it becomes ease on ascertaining the establishment of kinetics behaviour. On the other hand, very slow kinetics does not rely on adopting in continuous system; therefore the strategies are taken up on reducing contact time while using more active sorbents. It was also noticed that the activated carbon based sorbents[7-12] are more preferred rather than their raw types and in which contact time could significantly reduce. In similar while using nanoparticles the doping of the particle is practiced and as a result loading affinity could be increased and thereby overall contact time has been shortened[45-50]. In our previous investigation for removing BCG and MG dyes it was noticed that almost 99.99% of adsorption efficiency was achieved in very short period[8,9,45]. The more important observation to be ensured from this study was that the moment sorption equilibrium reached to plateau further lingering of time should be avoided in the sorption experiments. In the study for adsorption of BCG it can be seen that due to greater availability active sites on sorbent surface initially reaction rate followed faster however it was steady till to reach the equilibrium (300 min). These results were further interpreted to ascertain sorption kinetics which is described in kinetics investigation section.

Shaking speed

Shaking period is one of the critical factors of sorption study as the particle behaves differently from static to dynamic mode. Most of the sorption experiments are operated under dynamic mode which can be attained by offering agitation/ shaking during sorption experimentation. Based on the degree of shaking speed, the adsorption behaviour either would follow the film diffusion or pore diffusion process that can easily be derived. Usually under lower shaking speed condition, the fluid film bearing the pollutant molecule around the sorbent particle is thicker and in which the film diffusion appears to be of rate limiting step[4]. This leads to have lowering of mass transfer of these organic pollutants as well as others into the internal surface of activated sorbent particles. Conversely by providing higher shaking speed the film diffusion increases above limiting value and where pore diffusion controls the rate of sorption[22,82]. In the study of BCG removal using AC, where the experiment was tested in the shaking speed ranges between 50-250 rpm using 0.1 g AC. The corresponding adsorption efficiency at the operated shaking speed was increased from 60.61% to 99.99% and then plateau was attained. This 250 rpm shaking speed assumed to be suitable dynamic condition for achieving maximum dye removal efficiency. From this result it was apparent on significance on the role of shaking speed /agitation on batch sorption process for effective removal of organic pollutants from the aqueous phase. Nevertheless, dynamic condition found to be more promising during sorption study.

pH Effect

To remove the organic pollutants using various activated carbons and other sorbents from the aqueous solution, it is essential to know the behaviour of the targeted molecule present in the aqueous solution. Therefore solution pH shows a critical parameter since the organic molecules (e.g. Dye, pesticides) may be present in ionized or non-ionized or other compound form. This leads to influence the surface properties of the adsorbent(s). It may not be easy to adsorb these organic components without understanding their state in aqueous media at the varying pH ranges of the solution. Thus maintaining a suitable pH condition of the solution ensures while favouring on attainment of higher selectivity affinity of sorbent molecule towards the sorbate(s) phases. Moreover, the outcome of this pH variation study does impart the key results on assuring the sorption mechanism (either of physo- or chemi-sorption). As a result of which the sorption interaction behaviour and mechanism could be established. The maximum BCG dye removal was obtained at acidic pH range of the solution (pH 0.5). In contrast the Mg removal was resulted at pH of using the same AC (activated *Phragmiteskarka*). This assures how same sorbent molecule behaves differently at the solution pH and this could be explained based on ionization behaviour of the dye molecules at the studied pH ranges of the solution[6,82].

Sorbent dose

In the organic pollutant removal study for batch adsorption investigations, the sorbent dose selection found as a vital operational factor since stochiometric requirement of sorbent for definite targeted sorbate molecule can be ascertained. Unlike other chemical processes, it is difficult to operate exact stochiometric dose for effective sorption of target organic molecules using AC type sorbents. Majority of these sorbents employed follows physosorption mechanism and therefore entire surface of the sorbent molecule under stochiometric condition may not effective for quantitative removal of organic pollutants. Therefore the requirement amount of sorbent dose becomes pretty higher(multi fold) over chemisorptions processes where most sorbent molecules are effective as they follows chemical mechanism (electrostatic force of attraction/ ion-exchange mechanism) in which stoichiometric amount of sorbent sometime becomes effective. Moreover, it determines the capacity of the adopted adsorbent at a given amount of organic pollutant /dye molecule in the solution. The adsorption efficiency generally enhances at higher adsorbent dose owing to the increase in active sites of the adsorbent[83,84].

Thermodynamics study for removal of organic pollutants using activated materials

To investigate the thermodynamics behaviour, generally effect of temperature on adsorption is examined based on physical and chemical nature of activated sorbent material. The activated materials like biosorbent and/or natural activated based materials sorbents can withstand their property at wider temperature ranges whereas the synthetic material based sorbents like ion exchange resins and nanomaterials may change their property at increased temperature conditions. Therefore, keeping in view of altering the property of sorbent material mostly experiments are performed between room temperatures to 60°C (unless otherwise specified). The other aspect of investigating the above effect is due to the fact of the high temperature condition observed for majority of effluents which are discharged from industries which can directly be taken up for removal studies. This study provides the observations of the nature of sorption process (endothermic/ exothermic) with feasibility of the approach and as a result the overall thermodynamic process could be established[6,9,85]. If the ΔH values reported to be positive that corresponds endothermic type sorption and vice versa. The ΔG values obtained for each of the sorption process should be –ve ensures about process feasibility. A study reported by Murmu et al.[45] for removal of BCG using AC and its thermodynamics behaviour at varying temperature range of 293-333 K has been demonstrated as shown in Fig. 4. It was noticed that significant increase in the adsorption rate which may be caused by three reasons:(i) Faster mobility of the dye molecule under high energy availed at high temperature resulting on penetration of sorbate molecules into the pores of adsorbent, (ii) increasing in interactions of sorbate and sorbent, and (iii) changing of the chemical potentials, based on solubility behaviour of sorbate species under temperatures conditions. The commonly used thermodynamic equations in sorption process are based upon Eqs. (1), (2) and (3) as given below.

$$\Delta G^o = -RTLn\ K_c \tag{1}$$

$$\Delta G^o = \Delta H^0 - T\Delta S^0 \tag{2}$$

$$\log K_c = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \tag{3}$$

Where K_c corresponds sorption equilibrium constant, ΔG^o is the standard change in free energy; ΔH^o and ΔS^o are the change in enthalpy and entropy, respectively, in the adsorption process. As shown in Fig. 4, the plot of the $\log K_c$ vs. 1/T from the van't Hoff relationship (Eq. 3, resulted a linearized trend).

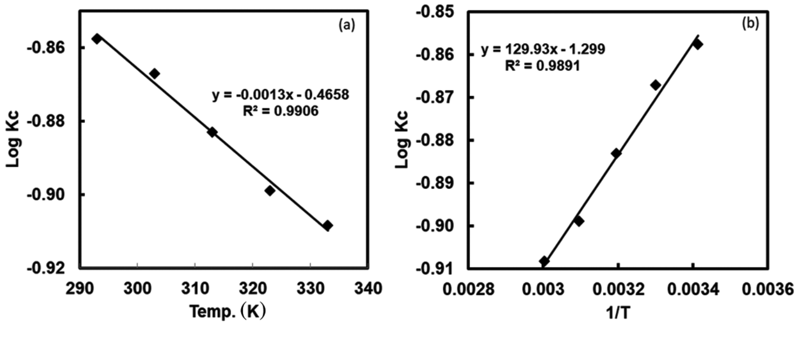

Fig. 4 — (a) Plot of equilibrium constants vs. temperature and (b) van't Hoff plot for exchange of BCG with APK[45]

The value of ΔH^o and ΔS^o were determined from the respective slope and intercept, respectively. The thermodynamics constants obtained from the above study are consistent and not dependent upon dye(sorbate) amount. The resulted negative value of ΔG^o ascertained on the feasibility of the adsorption process and also the spontaneous interaction of dye molecules with active sites AC(sorbent). On the other hand, the positive value of ΔH^o (+2.49) obtained in the above study corresponds on favouring of sorption by adsorption of energy with endothermic nature. The positive values of ΔS^o (+24.87) reveals on increase in the randomness of the dye molecule as well as the activated sorbent interface during sorption process[6,9,85,86].

Kinetics study

Based on the results of contact time on sorption of organic pollutants the rate of the sorption reaction can be derived. Usually the sorption processes are slower and therefore it becomes easier to ensure the sorption kinetics as the order of the reactions is depended on the slowest step associated in reaction. The kinetics study further ensures on establishing the sorption interaction mechanism due to sorbate and sorbent molecule. The sorption interaction mechanism for the removal of organic wastes can be explained based on some the assumptions as summarized below:

- Migration of pollutant(s) from the solution phase to the surface of activated sorbent
- Diffusion of pollutant(s) through the boundary layer to the surface of sorbent.
- Sorption of pollutant(s) at an active site over surface sorbent molecule
- Intra-particle diffusion of pollutants(s) into interior pores sorbent particle.

To ascertain the sorption mechanisms three basic kinetic models including pseudo-first order, pseudo-second order, and intraparticle or film diffusion models are employed and results are interpreted[7, 22, 84, 85].

Pseudo-first order and second order kinetics

Pseudo-first order kinetics equation can be described as per Eq. (4), where, q_e and q_t corresponds the dose (mg g^{-1}) of sorbate at equilibrium and at time t (min), respectively, and k_1 stands as rate constant (min^{-1}) of the Eq. (4).

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t \tag{4}$$

From the plot of $\log(q_e-q_t)$ vs.‘‘t’’ if a linear relationship is followed having regression factor(R^2) close to unity then probability of favouring pseudo first order kinetics can be ascertained. The rate constant k_1 and maximum loading capacity as q_e can be determined from respective slope and intercept value of above equation. On the other hand, if above kinetics model does not follow the linearity that indicates the deviation of above kinetics. Therefore, further pseudo second-order model is to be followed as per Eq. (5)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

Where k_2 (g mg^{-1} min^{-1}) is the rate constant and the other expressions and terms are same as presented in Eq. (5). The linear relationship of the plot of t/q_t as the function of t (min) can be presumed with the similar assumption like first order kinetics like observation of higher regression factor. The slope value results from the above plot can give rise to determine K_2. Thus to ensure such observation and validation of above two kinetic models an illustration of kinetics behaviour was represented as shown in Fig. 5(a & b). From the results, the pseudo-second-order model fits well having good correlation coefficient over pseudo-first-order model, indicated that the rate controlling step associated in sorption process supported by chemical sorption type of adsorption[9, 87, 88].

Intra-particle diffusion

It is apparent that most of the sorption behaviour follows either of the above two kinetics models. In addition, physo-/chemi-sorption behaviours of sorption are ascertained based upon the assumption of above kinetic models. Thus, further investigations are taken up to know whether the sorption can be restricted only on surface (mono layer with primary surface) or the sorption mechanism caused in inner core (multi-layer with inner surface) including surface of the sorbent molecules. To understand it in details further investigation has been put forward while employing intra-particle diffusion model of Weber-Morris model described by Eq. (6)[22, 87, 88].

$$q_t = X_i + k_p\, t^{1/2} \tag{6}$$

Where q_t is sorbate amount adsorbed at time t (min.), k_p (mg g^{-1} $min^{0.5}$) is rate constant due to intraparticle diffusion and X_i corresponds intercept. A study of intraparticle diffusion model for removal of dye using AC was presented. From the plot q_t vs $t^{0.5}$(Fig. 5c), K_p value was obtained. The linearity trend of the above plot is indicating on favouring of sorption of dye molecule on to the inner layer of the AC through intra particle diffusion approach. Therefore it was assured that most of chemisorptions type sorption there could be the possibility of intra-particle diffusion in addition the surface based sorption.

Adsorption Isotherms

The sorption isotherm is investigated on attaining maximum uptake capacity of the given sorbent after varying initial sorbet concentration under isotherm condition. Based on the above experimental results, different isotherm models such as Langmuir and Freundlich are attempted to fit so as to ensure the sorption mechanism. The sorption isotherm study provides the information in context of distribution of sorbate molecule between the liquid and the solid phase and thereby, the attainment of adsorption equilibrium state can easily be derived. The behaviour of the sorbent surface such as homogeneity, heterogeneity of the adsorbent and monolayer and multilayer of sorption process can be apprehended from the isotherm study. It is being noticed that after attaining sorption equilibrium the loading affinity of the activated sorbents reduces at increased initial concentration of sorbate (organic pollutants). The above observation has been attributed to the lack of available active sites needed for high initial concentration of the pollutants because of the fixed amount of activated adsorbent was used. In addition, the sorption sites are adsorbed the available solute more quickly at lower concentration range of sorbate (organic pollutants)[9,22,45]. Thus to establish the mechanism the two most common sorption isotherm models i.e., Langmuir and Freundlich is employed and results are discussed.

Langmuir Isotherm

The Langmuir isotherm model is adopted to ascertain the favouring of monolayer adsorption process. In this case sorption is of entirely homogeneous surface kind sorbent having a negligible interaction with adsorbed molecules, which can be represented in Eq. (11).

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + C_e(\frac{1}{q_m}) \qquad (11)$$

Where, b is the Langmuir adsorption constant (L mg^{-1}) and q_m is maximum sorption capacity (mg g^{-1}). The value of q_m, and b are calculated (given in Table 4) from the slope and intercept of plot between c_e/q_e vs c_e of above equation. Furthermore, the characteristics of the Langmuir isotherm is expressed by equilibrium parameter, R_L, as stated in Eq. (12).

Table 4 — Langmuir and Freundlich isotherm parameters for MV dye adsorption with APK[81]

	Langmuir isotherm			Freundlich isotherm		
Temp. (K)	q_m (mmol g^{-1})	b (mmol^{-1})	R^2	n	k_F	R^2
303	20000	5.005E-06	0.9991	1.001	0.1005	0.9999

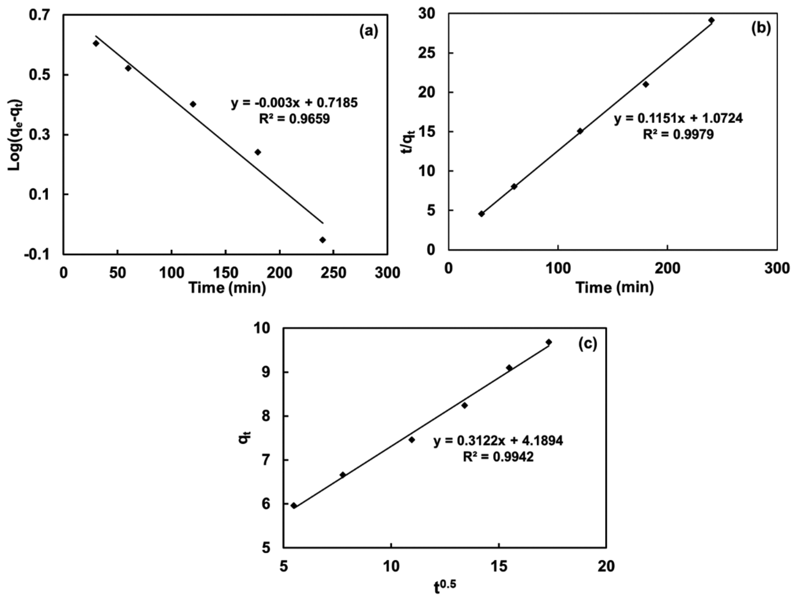

Fig. 5 — Sorption kinetics plots: (a) Pseudo-first order, (b) Pseudo-second order and (c) Intraparticle diffusion[45]

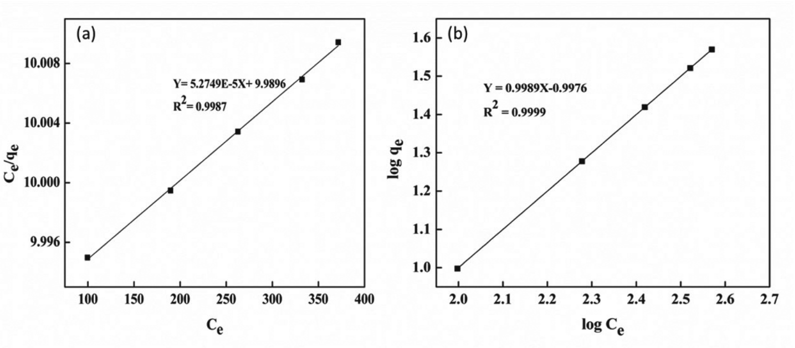

Fig. 6 — Plot of (a) Langmuir and (b) Freundlich isotherm for adsorption of MV by APK[81]

$$R_L = 1/(1 + bC_0) \quad (12)$$

Where C_0 is the highest initial dye concentration. Based on the assumption of R_L factor e.g., adsorption isotherm is of irreversible if R_L=0, the isotherm is favourable if $0 < R_L < 1$, linear if $R_L = 1$ or unfavourable if $R_L > 1$, the sorption behaviour and feasibility can be ensured. The results of a study for removal study of MV using AC were illustrated. The langmuir isotherm plot (Fig. 6a) revealed on determination of q_m, b and values. It was seen that R_L values obtained from the adsorption of MV dye on the APK was found in between 0 to 1, indicating on favouring of MV sorption on to AC surface and results are consistent[81-88]. If there would be the deviation on fitting of Langmuir model in the sorption investigations then the Freundlich Isotherm model is further investigated.

Freundlich Model

It is a model which is being investigated to validate the sorption process where sorption mechanism is favoured while adsorbing over the heterogeneous type sorbent sites having different energies. The linear form of Freundlich isotherm is as given in Eq. (13).

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (13)$$

Where, q_e is the amount of adsorbate (mg g^{-1}), c_e is the equilibrium concentration of adsorbent. The k_f and 1/n can be obtained from corresponding slope and intercept of log q_e vs log c_e plot. The k_f is of distribution coefficient and q_e represents amount of organic pollutants sorbed onto the activated sorbent at unit equilibrium concentration and 1/n represents the favourability of adsorption. Behera et al.[81] have investigated and demonstrated on the Freundlich isotherm results, results can be seen from Fig. 6b. Based on the assumption of the value of i/n value the possibility on favouring of Freundlich isotherm could be confirmed. For instance, in the study for removal of MV using AC [81], the value of 1/n for the Freundlich isotherm found in the range of zero and one (as given in Table.4), indicating that the dye molecule is favourably adsorbed activated carbon phase by following isotherm model. The observations like multilayer along with chemisorptions isotherm was ascertained in this isotherm model study.

Furthermore, the isotherm studies strongly provide the outcome on establishment of sorption mechanism (like physo-sorption, chemisorptions and/or combination of both) of numerous surface active sorbents. Thus the unique sorption behaviour of different sorbent adopted for removal of various organic pollutants can be ascertained through these adopted isotherm model investigations.

Conclusion

The present review comprises sorption of waste organic pollutants through sorption process with the conceptualization of waste to wealth covers the indepth insight of adopted sorption approach, used noble sorbent materials, activation strategy and critical sorption mechanism. The promising applications of several activated materials for removal of pharmaceutical wastes, azo dyes, pesticides and several other organic pollutants are summarized. The activation process adopted like doping and charring approach appears to be effective on enhancing the sorption ability of the respective sorbent materials as it is. The activation of the surface was mainly caused by improving the surface porosity of the sorbent material. The methodology of the sorption, its state of art, mechanism accomplishing process optimization, kinetics, thermodynamics and isotherms are systematically discussed for removal studies of these waste organic pollutants present in the waste contaminated waters. The surface behaviour and transportation of the organic pollutants into the activated sorbent phases are ensured from the FESEM, XRD and

FTIR study of sorbent material before and after sorption study. The activated carbon based material derived from the plant extract was demonstrated a case study for removal of the dye molecule namely bromo cresol green and malachite green from the aqueous phase. The interaction mechanisms of the activated material with the targeted organic pollutants are described. The model adsorption of above dye removal study ascertains on quantitative removal of organic pollutants using surface activated natural as well as synthetic materials.

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