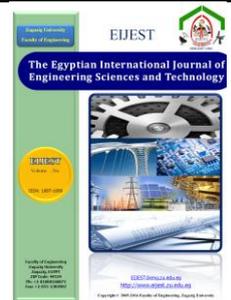




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## Adsorption technique for pollutants removal; current new trends and future challenges – A Review

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### ABSTRACT

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- 7<sup>th</sup> batch operation;
- continuous operation
- 8<sup>th</sup> interference pollutants

Water pollution is a challenging problem facing the human beings. In order to get treated water and wastewater, many techniques were proposed such as floatation, coagulation, ion exchange, biological treatment, adsorption, membrane etc. Among these methods, adsorption technique has proved to be an effective and low cost manner for the removal of inorganic pollutants (i.e heavy metals), synthetic dyes and organic pollutants (i.e phenols, methylene blue, methyl orange, benzene ...) from polluted water. This review summarizes the most used adsorbents such as Activated Carbon (AC), nanomaterials, natural adsorbents, industrial by-products, agricultural wastes and bio-sorbents and their performance, cost and regeneration studies. This review also discusses the mechanism of adsorption, kinetics and isotherms used in adsorption process. The effect of binary and ternary systems of ions was also discussed. The difference between batch mood and continuous flow mood (packed bed column studies) and the parameters considered in each type were also investigated. Future recommendations and trends were finally proposed to enhance the adsorption process from all aspects.

### 1. Introduction

Environmental pollution has increased to a noticeable level nowadays as a result of rapid industrialization, global population growth, industrial exploitation of natural resources and persistent droughts[1][2]. The growth of industry, agricultural and municipal activities has contributed directly to the rise in the continuous discharge of dyes, heavy metals, phenolic and phosphate compounds and inorganic chemicals into water bodies[3]. As a consequence of its use in various chemical and process industries such as metal plating, paints and dyes, textiles, fertilizers, tanneries, petroleum refining, pharmaceuticals, battery production and mineral processing industries, heavy metals are

discharged into effluents in large quantities [2][4][5]. Heavy metals are poisonous, bio-accumulative and non-biodegradable, and are harmful to both people and aquatic life, resulting in many diseases and chronic health disorders [6]. Organic pollution, which refers to a large number of organic compounds that could be emitted from wastewater treatment plants and industries, including food processing, pulp and paper making, textile production and agriculture, is also associated with the greatest concern [7]. Organic pollutants could be generated to environment due to pesticides, fertilizers, phenols, plasticizers, detergents, oils, pharmaceuticals, proteins and carbohydrates[8]. Organic compounds have many side effects and are considered carcinogenic so removing it from waterbodies is important to

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preserve the water quality and hence the aquatic fauna and flora[9].

Important attention has been devoted for effective techniques for eliminating harmful organic and inorganic compounds from water. A variety of techniques have been used for the removal of organic compounds from contaminated water and waste water, such as coagulation, filtration, electrocoagulation, precipitation, floatation, electrodialysis, membrane, adsorption, ion exchange, reverse osmosis, and advanced oxidation processes [1][7]. Although the traditional methods such as chemical precipitation, ion exchange, membrane separation process and electrocoagulation have been used to remove inorganic pollutants such as heavy metals, these methods have shown some limitations for high capital and operating cost [6][4][10]. For example, the process of precipitation generates harmful sludge that it furthermore, needs another treatment. The downside of ion exchange technique is the lack of recyclability. The key drawbacks of the membrane filtration system are the problems of regeneration, high cost and getting rid of the produced sludge [11]. The technique of flocculation and coagulation suffers from the volume of sludge produced, while the long duration needed is the downfall of the photocatalytic process. The method of electrodialysis is extremely successful, but requires high energy consumption and operating costs [12]. Owing to their relatively high expenditure and maintenance costs and the disposal of residual metal sludge, reverse osmosis and ion exchange don't seem to be low cost potential [13]. The previous methods from literature costs from US\$ 10 to US\$

450 for the treatment of one cubic meter, excluding adsorption. Water treatment with adsorption costs between US\$ 5.0 and US\$ 200 per m<sup>3</sup> [8].

Due to its universal existence, inexpensiveness in both initial costs and land requirements, easy design and ease of operation, adsorption is considered the best wastewater treatment process [5][7]. Adsorption can also reduce organic compounds that are soluble and insoluble [8]. Therefore, adsorption has been used for the treatment of a number of organic and inorganic contaminants from different polluted waterbodies.

The current review will illustrate the different types of adsorbents used for organics and inorganics removal and their mechanism. It will also explain the different moods of operation, kinetics, isotherms, the effect of multiple ions removal and the future needs for adsorption process.

## 2. Adsorption process and its mechanism

Adsorption is simply the accumulation on the surface or interface (solid or liquid) by a substance (gas or liquid) [14]. The process takes place in the case of water treatment at the interface between solid adsorbent and polluted water. When the solution and adsorbent contact together, the solute molecules attract to the surface of adsorbent via the functional groups over the surface [8]. Adsorbate is the solute that accumulates (on the solid interface) in adsorption processes, while the solid on which it is stored is named an adsorbent [15]. The basic terms of adsorption process are illustrated in Fig. (1)[14].

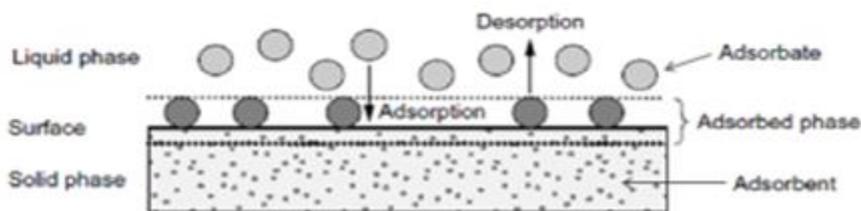


Fig. (1) Basic terms of adsorption [14].

Several adsorption mechanisms have been proposed for heavy metals removal. Adsorption process can be classified into two main mechanisms according to the type of attraction between adsorbate and adsorbent; first of all, physical adsorption or physisorption which is due to van-der-waals forces, dipole interaction and hydrogen binding force at

which the ions transfer from the solution to the surface of the adsorbent where an opposite surface charge was found. As a result, the metal ions are removed from the solution almost when they have passed from the boundary layer and attached to the surface of adsorbent[16]. Heavy metal ions diffuse into the adsorbent in the case of microporous

adsorbents. The ions, however, access the adsorbent pores and adsorb to the surfaces on the inside of the material. Fig. (2) illustrates this type of adsorption[17]. [18] describes the surface adsorption mechanism when studying the adsorption of Cr(VI) on LBR (Lignin based resin) as illustrated in Fig.(3). Firstly, during low pH conditions, the LBR surface became positively charged, allowing  $\text{HCrO}_4^-$  anions to diffuse through a boundary layer of LBR particles. Secondly, all adsorbed Cr(VI) anions transform to Cr(III) on the LBR surface as a result of the protons present on the surface. Finally, the interaction between the resulting Cr(III) species and the functional groups containing oxygen (such as the alcohol, ether, carbonyl, and carboxyl groups) were

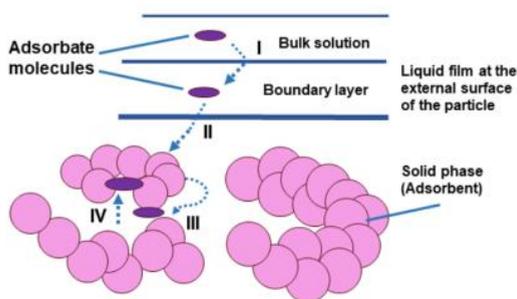


Fig. (2) Heavy metals removal via microporous adsorption[17].

formed. The other mechanism is chemical adsorption or chemisorption which is a result of electrostatic attraction due to the covalent bonding[14]. The adsorption mechanism occurs in chemisorption through a chemical interaction between the material being absorbed and the adsorbent, which is previously exposed to certain chemical modifications in this case to produce such surface functional groups (i.e. acidic functional groups such as carboxyl, carbonyl, hydroxyl, lactone and carboxylic anhydride), that are the most common types of surface functional groups. These functional groups thus retain the absorbed substance much more firmly in adsorption, that requires much more energy to release it [16].

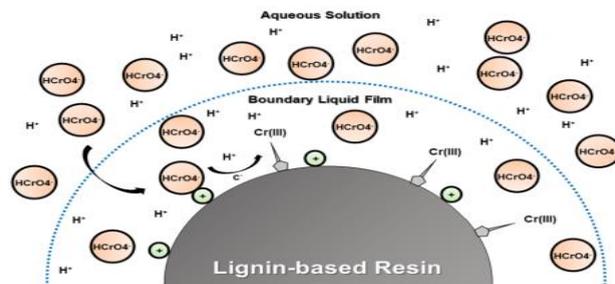


Fig. (3) Cr(VI) adsorption via surface adsorption [18].



Fig. (4) Cation exchange mechanism with the carbon surface carboxylic group[19]

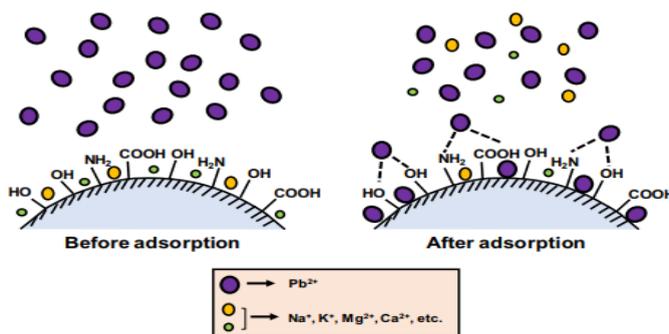
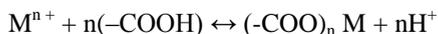


Fig. (5) Ion exchange mechanism for the adsorption of Pb(II) on FCCL [20].

The dominant mechanism, based on the activation energies of the reactions, is called ion exchange or cation exchange between the adsorbent and metal ions where the metal cation exchange site with hydrogen ions previously was attracted as a whole carboxylic group as shown in Fig. (4) [20]. The carbon substance is important for the adsorption of heavy metal ions (i.e. Pb(II), Cu(II), Mn(II), etc.) with unique functional groups due to the chelating characteristics of these groups in which alkaline earth metal cations can be incorporated with the groups to form complexes as shown in the following equation [19].



[20] describes the mechanism of ion exchange for the adsorption of Pb (II) on fallen Cinnamomum camphora leaves (FCCL) by Fig. (5) where the FCCL exchanges  $Na^+$ ,  $Ca^{+2}$ ,  $K^+$ ,  $Mg^{+2}$ , ... etc which exist on the leaves with the metal Pb (II) forming surface complexation as a result of the existence of many functional groups on the surface.

Also, electrostatic forces have been described as a factor that promotes heavy metal adsorption. The pH depends heavily on the presence of electrostatic forces. Lower pH values contribute to the protonation of the different functional groups associated with heavy metal adsorption, resulting in an overall positive charge on the adsorbent [21]. Electrostatic repulsion occurs as a consequence, preventing the adsorption of heavy metal ions that are positively charged. Conversely, with rising pH, electrostatic repulsion decreases, which is obvious because of the rise in heavy metal adsorption [22]. In determining the removal efficiency of the adsorbent relative to the pH value representing the point of zero charge ( $pH_{PZC}$ ) of the adsorbent, the effect of electrostatic forces during adsorption can be clearly seen. The  $pH_{PZC}$  is defined as the pH value at which the surface charge of the adsorbent is neutral [23]. When the pH of the solution is less than  $pH_{PZC}$ , the surface charge of the adsorbent is positive, while its surface charge is negative when the pH of the solution is greater than  $pH_{PZC}$ . As a consequence, when  $pH < pH_{PZC}$ , the removal of heavy metals, particularly those in cationic form, is low and increases when  $pH > pH_{PZC}$ , indicating a significant presence of electrostatic forces in the adsorption process [24][23].

### 3. Materials and Methods

Various types of adsorbents have been used for the process of adsorption of different pollutants. The

main difference between these adsorbents is the method of preparation, surface modification and cost. All the previous studies try to find a cheap and effective adsorbent for both organics and inorganics removal. The main purpose of the surface modification processes is to enhance the adsorption process through increasing the number of active functional groups on the adsorbent surface and to increase the surface area of it.

There are two types of modification; chemical and physical modification. Chemical modification is widely used with agricultural residuals and wastes using different chemical reagents such as sulfuric acid, phosphoric acid, hydrochloric acid and sodium hydroxide. while physical modifications are used in the preparation of activated carbon. [25] used 0.1 N NaOH and 0.5 N NaOH as a chemical preparation for Banana Waste (BW) to increase its adsorption capacity. Modifications on sugarcane bagasse was done through carbonization under  $N_2$  flow [26] or through chemical modification using  $H_2SO_4$  to increase its surface area and the degree of micro porosity[27]. Modified Phragmites Australis with 1% HCl is used as a new low cost adsorbent for the removal of COD, BOD, TSS and TDS as it is available around drains and also causes environmental problems [28]. Biochar was produced using pyrolysis process in the presence of nitrogen gas on Green Pea Pod Peels (GPPP) to be used in Cr (IV) removal under different conditions[29]. [30] used the modification of PPP with NaOH and HCl to increase the adsorptive characteristics of PPP. Many methods for modification of Rice Straw were done to increase its adsorption of heavy metals. First of all is the biochar production at different temperatures of 300, 500 and 700°C as investigated by [31]. [32] modified RS with acid treatment using nitric acid and CaO and alkali treatment using NaOH and urea. Modification with NaOH only is used by [33]. [34] modified the rice husk with tartaric acid while [35] used KOH for the production of rice straw carbon (RSC) and rice straw activated carbon (RSAC). The next section shows the different adsorbents used and their operating conditions and preparation method of each.

Many researches use chemical modification with acid or alkali treatment or both of them to improve the adsorption of ions on different agricultural waste surfaces. [36] uses thioglycolic acid to treat onion skin while [37] uses onion dust without modification. Pomelo peels are grafted by citrate to remove methylene blue from aqueous solution [38]. [39] used

chemical pretreatment using HCl and NaOH as modification for banana peels and peapod peels which shows satisfying results for adsorption capacity. [31] uses HCl, NaOH and deionized water or ethanol as a pretreatment for rice straw biochar while [35] modified the rice straw with 10% KOH solution to prepare rice straw carbon (RSC). [40] used citric acid to treat sugarcane bagasse which increased the adsorption capacity to 13.5 mg/g.

#### 4. Different types of adsorbents

Many adsorbents have been used to remove pollutants from polluted water and in various research and review articles their mechanisms have been reviewed. It is possible to classify such adsorbents into natural adsorbents and synthetic adsorbents. Charcoal, cement, clay minerals, chitin, chitosan, ash, peat, zeolite, and ores are all types of natural adsorbents. The benefits of these natural adsorbents are that they are relatively inexpensive, plentiful in supply and have considerable potential to modify and eventually boost their adsorption capabilities. Synthetic adsorbents are adsorbents produced from agricultural products and waste, marine adsorbents, adsorbents for forest waste, household waste, industrial waste, sewage sludge and polymer adsorbents. Each adsorbent is characterized by many features such as porosity, pore structure and nature of its adsorbing surfaces. Many waste materials used as low cost adsorbents include fruit wastes, sawdust, rice husk, fertilizer wastes, fly ash, petroleum wastes, coconut shell, sugar industry wastes blast furnace slag, chitosan and seafood processing wastes, seaweed and algae, peat moss, clays, red mud, zeolites, sediment and soil, ore minerals and other adsorbents are shown in Fig. (6) [3] [41]. On the other hand, nanomaterials and activated carbon are the most widely used adsorbents, as they have wide surface area, adsorption capability and microporous structure, but their costs are high. [42].

##### 4.1. Activated carbon (AC)

Activated carbon are classified into two main categories according to production; commercial activated carbon and AC produced from waste materials and four types according to shape or size namely; granular activated carbon (GAC), powder activated carbon (PAC), fibrous activated carbon (FAC) and cloth activated carbon (CAC) [41]. Due to the large internal surface area, the availability of pores and high micro-porousness, Activated Carbon

(AC) is considered the strongest heavy metal adsorbent [43]. AC's key advantages are: very large surface areas, porous sorbent, functional groups, high adsorption capacity and high rate, great ability to adsorb a broad range of contaminants, good kinetics and high quality treated effluent [44]. The major limitations of AC, on the other hand, are that it is very costly and needs complexing agents to enhance its removal efficiency [45] [46].

In addition, thermal, chemical, oxidation, electrochemical methods are needed to be regenerated, but again this whole regeneration process adds additional costs, and any regeneration process results in a reduction in the ability of adsorption [47]. Table (1) shows some used activated carbon adsorbent for heavy metals removal and their adsorption capacity and optimum operating conditions. From Table (1) it is evident that the modification of AC increases the adsorption capacity of Cr(VI) from 4.75 to 9.95 and from 10.88 to 15.47 mg/g respectively [48] [49]. The maximum adsorption capacity for Cr(VI) from literature was 97.96 mg/g for Cucumis melo peel [50]. Similarly, for Cd(II) the adsorption capacity was highest (227.27 mg/g) for AC impregnated with phosphoric acid and microwave induced [51]. These results show the value added for AC through different modification processes.

In addition, AC has been used to absorb various forms of dyes from industrial waste water. Dyes are regarded as a type of organic pollutants derived primarily from the clothing, clothing, pulp and paper, food coloring, cosmetics and carpet industries. In solution, dyes could be categorized according to chemical structure, color, application and particle charge. We may typically divide the dyes into natural dyes and synthetic dyes. Natural colors are typically derived from animals and minerals. Natural dyes, however, could not meet the needs of the demand of citizens as the enhancement of industrial activities. Synthetic dyes are then produced and natural dyes have gradually been replaced, especially in the textile and textile industries. Dyes are not biologically degradable and can be toxic or carcinogenic to mammal animals and has toxic effects on microbial populations[7][52]. Table (2) shows some types of activated carbons used in the removal of dyes such as methylene blue. The results from literature shows that maximum adsorption capacity of methylene blue was 580 mg/g for bituminous coal-based activated carbon which have high micro-pore surface area of 801.8 m<sup>2</sup>/g and high carbon content of 81.8 % [53]

**Table (1):** Activated carbon adsorbents for heavy metals removal and their optimum conditions.

Pollutant removed	Adsorbent	Optimum operating conditions						
		$q_m$ (mg/g)	Isotherm followed	Kinetics followed	pH	adsorbent dosage	Equilibrium time	Reference
Cr (VI)	Coconut shell activated carbon CAC	4.75	Freundlich	Pseudo-second-order	2	1 gm/50ml	60 min.	[48]
Cr (VI)	Phosphorus acid modified coconut shell CAC	5.95	Freundlich	Pseudo-second-order	2	1 gm/50ml	60 min	[48]
Cr (VI)	Coconut shell charcoal treated with nitric acid	10.88	Langmuir	–	4	12 gm/L	3hrs	[49]
Cr (VI)	Nitric acid oxidized commercial activated carbon	15.47	Langmuir	–	7	2 gm/L	60 min.	[49]
Cr (VI)	Activated Carbon Apple Peels	36.01	Freundlich	Pseudo-second-order	2	0.15 gm/50ml	4 hrs	[76]
Cr(VI)	Cucumis melo peel	97.96	–	Pseudo-first-order	3.0	250 mg/50ml	180mins.	[50]
Cr (VI)	Mango kernel activated with $H_3PO_4$	7.8	Langmuir	Pseudo-second-order	2	0.25gm/100ml	150 min.	[77]
Cr (VI)	Activated carbon from Fox nutshell	43.45	Langmuir	–	2	0.05 gm/100ml	60 min.	[78]
Cr (VI)	peanut shell	8.31	Langmuir	Pseudo-second& first order	2	0.1 gm/40ml	20 hrs.	[79]
Cr (VI)	Activated carbon	19.305	Langmuir	Pseudo-second-order	3.0	0.2 gm/30ml	150 mins.	[80]
Cd(II)	Cucumis melo peel	97.96	–	Pseudo-first-order	6.0	250 mg/50ml	180mins.	[50]
Cd(II)	Activated carbon	19.380	Langmuir	Pseudo-second-order	6.0	0.2 gm/30ml	150 mins.	[80]
Cd(II)	phosphoric acid-impregnated microwave-induced mesoporous activated carbon	227.27	Langmuir	Pseudo-second-order	6.0	0.5 gm /500ml	6 hrs	[51]
Cd(II)	NAOH activated palm kernel shell charcoal	22.37	Langmuir & Freundlich	Pseudo-first-order	–	1 gm/100ml	150 mins.	[81]

AC is also used for the removal of phenols from industrial wastewaters such as chemical pesticides, pharmaceuticals, petrochemical industries. The main source of phenolic compounds are petroleum refineries, paints, coke oven plants, pharmaceuticals, steel mills, petrochemical, coal gas, plywood industries and synthetic resins. The maximum phenols production i.e about more than 1000 mg/L is produced from coke oven plants, while it should not exceed 0.1 mg / L for wastewater according to the Environmental Protection Agency (EPA) and the World Health Organization (WHO) has also set a limit of 0.001 mg / L for phenols in

drinking water [54]. Table (3) includes some used activated carbon adsorbents used for the removal of phenols from wastewater. The maximum adsorption capacity for phenols removal was 191.87 mg/g using activated carbon obtained from chicken eggshell because of the large surface area up to 113 m<sup>2</sup>/g and high pores volume up to 0.97 cm<sup>3</sup>/g [55]. For 2-chlorophenol, the maximum capacity was 549.5 mg/g of using granulated activated carbon [56].

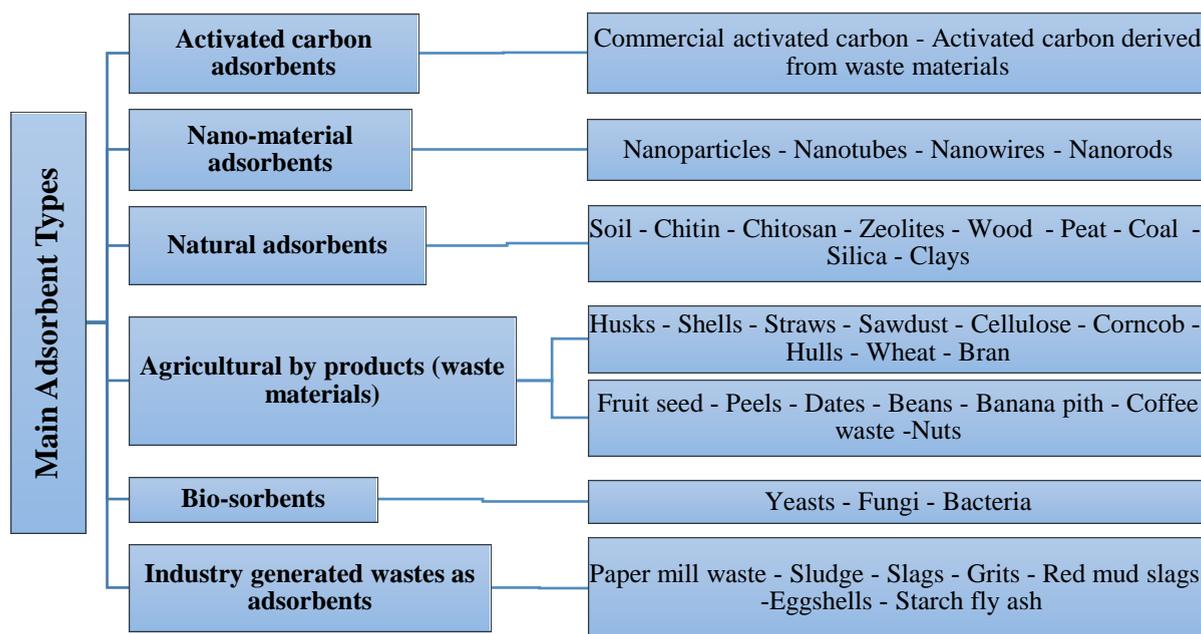


Fig. (6) Different adsorbents used for organic and inorganic pollutants [3] [41]

#### 4.2. Nano material adsorbents

Nanomaterials are those metal-oxides at a very small size up to nanoscale. These adsorbents are highly efficient in the removal of heavy metals (arsenic, cadmium, mercury, iron, chromium, lead, cobalt, copper, selenium, etc) and other organic pollutants from aqueous solutions [66]. As a result of high surface area, high surface to volume ratio, catalytic properties and other favorable properties, these adsorbents showed an excellent adsorption capacity toward many pollutants in water and wastewater. The most used metal oxide nanomaterials are magnesium oxides, titanium oxides, ferric oxides, manganese oxides, aluminum oxides, cerium oxides, etc [67] [68] [69].

To enhance the adsorption capabilities of nanomaterials to be efficient in the elimination of heavy metals and other organic compounds, various chemical and physical modifications or functionalization with a lot of agents are allowed to magnetic metal oxides [70] [5]. Many methods are used for the modification of the surface of nanoparticles such as grafting, hydrothermal and/or

hydrothermal reduction, covalent binding, co-precipitation, co-condensation, surface coating, method of ligand exchange, modified method of Stober and method of sol-gel [4].

Carbon nanotubes (CNTs) are a type of nanomaterials used in the adsorption of pollutants from contaminated water and wastewater. CNTs consist of one or more cylinder-shaped sheets with a length of more than 20  $\mu\text{m}$  and a radius of less than 100 nanometers (nm) [71]. Functionalizing CNTs are used to increase their effectiveness. Two functionalization groups exist: covalent and non-covalent. Functional groups that by chemical reaction covalently bind to the frame of CNTs form a string of covalent functionalization. While the other type takes place when the functional groups coat the walls of CNTs. Table (4) shows different heavy metals eliminated by different nanomaterial adsorbents. As shown in Table (4), the maximum adsorption capacity is 96.79 mg/g for the adsorption of lead using amino functionalized silica nano hollow sphere ( $\text{NH}_2\text{-SNHS}$ ) [72].

**Table (2):** AC adsorbents for dyes removal from polluted water and their capacities.

Dye	Adsorbent	Adsorption capacity	Reference
Methylene Blue	bituminous coal-based activated carbon	580 mg/g	[53]
Methylene Blue	activated carbon from Cotton stalk-based	180.0 mg/g	[57]
Methylene Blue	coal-based activated carbon & coal-based activated carbon(KOH washed)	(252 mg/g & 234.0 mg/g)	[58]

**Table (3):** Adsorption capacities of AC adsorbents for phenols removal from polluted water.

Phenol	Adsorbent	Adsorption capacity	Reference
phenol	Activated carbon from dates stone (DS)	97 mg/g	[59]
phenol	Carbon rich bagasse fly (BFA)	9.49 mg/g	[60]
phenol	Activated carbon commercial grade (ACC)	7.06 mg/g	[60]
phenol	Activated carbon laboratory grade (ACL)	9.64 mg/g	[60]
phenol	Activated carbon from rattan sawdust (ACR)	149.25 mg/g	[61]
phenol	zeolite X/activated carbon composite (X/AC)	37.92 mg/g	[62]
phenol	granulated activated carbon	283.3 mg/g	[56]
phenol	Activated carbon obtained from chicken eggshell	191.87 mg/g	[55]
phenol	Activated carbon from coconut shells	58.07 mg/g	[63]
phenol	diethylenetriamine-modified activated carbon	18.12 mg/g	[64]
phenol	Banana Peels Activated Carbon (BPAC)	48.58 mg/g	[65]
2-chlorophenol	granulated activated carbon	549.5 mg/g	[56]
4-chlorophenol	granulated activated carbon	280 mg/g	[56]

#### 4.3. Natural adsorbents

Many studies were done on the usage of natural adsorbents for the elimination of organic pollutants such as dyes and inorganic heavy metals such as Pb, Cr, Cu, Zn, etc. The most used natural adsorbents in the removal of heavy metals, dyes and organic compounds are clay minerals and its derivatives, chitin and chitosan, zeolite, wood and coal.

Chitin is one of the most promising natural biopolymers for application in adsorption. It is the primary constituent of the exoskeleton, cuticle, and cell wall of crustaceans, insects, and microorganisms, respectively. Chitin de-acetylation also contributes to the development of chitosan and its derivatives that are even more promising than chitin for adsorption [73]. The high adsorption capacity of chitosan is due to the presence of large number of active sites, flexible structure of the polymer chain, specific physico-chemical characteristics, excellent chelation behavior, high reactivity and high selectivity toward metal ions [74]. In molecular structure, chitosan is similar to cellulose, thus exhibiting properties identical to those of cellulose. It contains a large number of hydroxyl bonds which make it a good ion exchanger [73].

Soil and other mineral deposits are also used for heavy metals removal from polluted aqueous

solutions. The removal efficiency of heavy metals using natural soils differ a bit from using mineral deposits [75]. The difference in their attraction to heavy metals is due to the solubility of heavy metals ( $K_{sp}$ ), which may lead to metal carbonates and hydroxides being precipitated, along with other physical and chemical characteristics, such as density of charge and electronegativity.

Clays (Hydrated alumina silicate), which are mainly montmorillonite, bentonite and kaolinite can be effective in the removal of heavy metals, dyes and phosphate. Because of the large number of cations ( $Ca^{2+}$ ,  $Mg^{2+}$ ,  $H^+$ ,  $K^+$ ,  $NH_4^+$ ,  $Na^+$ ) and anions ( $SO_4^{2-}$ ,  $Cl^-$ ,  $PO_4^{3-}$  and  $NO_3^-$ ) present on clay surface which can be easily replaced with ions present in adsorbate, it is considered as an effective low cost adsorbent [82] [83]. Chemicals treatment or acid or alkali treatment are methods used to improve the adsorption characteristics of clay minerals such as surface functional group, CEC, pore size, high surface area per unit mass, and volume of pores[84].

Zeolites are microporous, crystalline aluminosilicates, usually consisting of symmetrically stacked tetrahedra of alumina ( $Al^{3+}$ ) and silica ( $Si^{4+}$ ), which easily form an open and stable three-dimensional structure with a negative charge ion. Clinoptilolite is the most commonly used type of zeolite. The availability of zeolites makes it a low

cost adsorbent for the removal of both organic and inorganic pollutants. Like clay and clay minerals, zeolites have cation exchange availability and molecular sieve properties so it can be used in water purification [85].

Peat and wood are naturally available materials that have large surface area and found in abundance. The two materials are inexpensive and has high adsorption capacities toward many pollutants so they can be used in water and wastewater treatment. Peat is mainly composed of lignin, cellulose and humic acid which contain bear polar functional groups that help in the adsorption process [86]. Table (5) shows the different natural adsorbents used in the literature and their adsorption capacities. From Table (5), it is clear that the maximum adsorption capacity for dyes (Acid orang 12 (AO12)) is 973.3 mg/g using chitosan, derived from deacetylated crab shell chitin which is very high compared to other natural adsorbents [87]. On the other hand, For Cr(VI) removal, kaolin was the best adsorbent with capacity of 256 mg/g compared to natural clay and roasted clay [75].

#### 4.4. Agricultural by products (waste materials)

The discarded waste materials are farm residues, fruits and vegetable peels that do not find any further use anywhere and thus develop an environmental disposal problem. They can be used as low cost adsorbent after some chemical treatment methods [73]. Because of their unique structure and chemical properties, agricultural waste is mainly composed of lignin and cellulose that serve as attractive alternative adsorbents. In their polymer chains, unique functional groups such as alcohol, phenol, aldehyde, carboxyl and ketone are present that help to remove different contaminants from water [88]. Various number of agricultural wastes in literature are used to remove pollutants from water and wastewater. Banana peels [89] [90] [25], pea pod peels [29] [39], citrus peels [91] [92] [93], pomelo peels [94] [95] [38], orange peels [96] [97], rice husk and straw [31] [35] [33] [98] [32], onion peels [99] [36] [37], sugarcane bagasse [26] [40] [100] and others were used as low cost adsorbents for the removal of heavy metals, organics and dyes from contaminated water.

Table (6) shows different pollutants removed by agricultural waste in literature and their capacities. Agricultural wastes prove high removal efficiency for

dyes such as methylene blue and the maximum capacity reported in literature according to Table (6) was 7041.52 mg/g using pomelo peels with ultrasound pretreatment [94]. For Heavy metals, Cr(VI) and Pb(II) were removed using different agricultural residuals. The optimum removal from literature for Cr(VI) was 89.9 mg/g using chemical pretreated biochar while that of Pb(II) was 2840.91 using sweet lemon peel biochar (*Citrus limetta*) which is considered the optimum removal capacity reached by agricultural wastes [31] [92].

#### 4.5. Industry generated wastes as adsorbents

Industrial wastes are byproducts of different industries that are available in large quantities and have low cost. Therefore, they can be used as low cost adsorbents for heavy metals, dyes and other organic compounds. Various industries produces byproducts such as palm oil ash [101] [102] [103], red mud (aluminum industry waste) [104] [105] [106] [107], coffee waste [108] [109] [110], fly ash [111] [112] [113] [114], bagasse ash [115], olive oil industry waste [116] [117], tea factory waste [118] [119] and blast furnace slag [120] can be reused after some treatment or as it is for removal of pollutants from polluted water. Table (7) shows the most used industrial byproducts for the removal of heavy metals, dyes and organics with their adsorption capacities.

#### 4.6. Biomass adsorbents

Biosorption and bioaccumulation are also considered as a promising adsorption method to eliminate many toxic pollutants such as heavy metals, phenolic, pesticides and dyes [158]. Many researchers studied the use of both dead and live microorganisms such as fungi [159] [160] [161], alga [162] [163], yeast [164] [165], bacteria [166] [167], etc. for the removal of organic and inorganic pollutants from polluted water.

Algae are one of the most effective bio-sorbents as they possess large adsorption potential and are widely existing in large amounts in the seas and oceans [168]. Algae bio-sorption is primarily based on the composition of the cell wall of the algae, which consists of a variety of polysaccharides: mannan, xylene, alginate, chitin, etc. Acid binding sites such as amino, amine, hydroxyl, imidazole, phosphate and sulphate groups are found due to these compounds and proteins present in the algae wall [169].

**Table (4):** Different nanomaterial adsorbents used in removal of heavy metals.

Material	Functional group	Modification method	Adsorption capacity (mg/g)								Reference
			Cu	Cd	Co	Ni	Pb	As	Cr	Hg	
NH <sub>2</sub> -SNHS (Amino functionalized silica nano hollow sphere)	Amino-	Covalent attachment	-	40.73	-	31.29	96.79	-	-	-	[72]
NH <sub>2</sub> -MCM-41	Amino-	Grafting	-	18.25	-	12.36	57.74	-	-	-	[121]
Fe <sub>3</sub> O <sub>4</sub> -NH <sub>2</sub>	Amino-	Hydrothermal reduction	-	-	-	-	40.10	-	-	-	[6]
NS Aminopropyl (H <sub>2</sub> N(CH <sub>2</sub> ) <sub>3</sub> -)	Amino-	Post grafting	6.35	0.00	0.00	0.059	-	-	5.20	-	[122]
NNS amino-ethylamino]propyl-(H <sub>2</sub> N-(CH <sub>2</sub> ) <sub>2</sub> -NH(CH <sub>2</sub> ) <sub>3</sub> )	Amino-	Post grafting	31.77	1.12	3.54	8.80	-	-	10.40	-	[122]
Fe <sub>3</sub> O <sub>4</sub> -NH <sub>2</sub>	Amino-	Covalent binding	25.77	-	-	-	-	-	-	-	[123]
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub>	SiO <sub>2</sub> -	Surface coating	12.71	-	-	-	82.88	-	-	-	[124]
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -TETA	TETA-	Covalent binding	30.50	-	-	-	62.16	-	-	-	[124]
PPhSi-Fe <sub>3</sub> O <sub>4</sub>	PPhSi-	Covalent Grafting	-	-	-	-	-	50.50	35.21	-	[5]
FeAA	Fe <sub>3</sub> O <sub>4</sub>	FBR-Fenton Reaction	-	-	-	-	28.08	-	-	-	[125]

**Table (5):** Different natural low cost adsorbents and their capacities for removal of organic and inorganic pollutants.

Pollutant removed	Natural Adsorbent	Adsorption capacity (mg/g)	Reference
Acid orange 12	Chitosan	973.3	[87]
Ethoprophos	Chitosan	85.47	[126]
Safranin -O (dye)	Kaolinite clay	16.23	[127]
Phenol	Organommodified bentonite	22.68	[128]
Benzene	Clay	37.59	[129]
Phenanthrene, Napthalene, Acenaphthene and Pyrene	Pine wood (raw)	2.318, 2.820, 1.497 and 0.417	[130]
Cr <sup>6+</sup>	Kaolin	256	[75]
Cr <sup>6+</sup>	Natural clay	19	[131]
Cr <sup>6+</sup>	Zeolite	70	[132]
Cr <sup>6+</sup>	Roasted clay	14.18	[133]
Cd <sup>2+</sup>	Modified chitosan coated bentonite	217.4	[134]
Zn <sup>2+</sup> and As <sup>5+</sup>	Shrimp shell (chitin)	270.27 and 11.57	[135]
Cd <sup>2+</sup> and Pb <sup>2+</sup>	Soil (Entisols)	3.4 and 9.3	[136]
Cu <sup>2+</sup> , Co <sup>2+</sup> , Ni <sup>2+</sup> , Pb <sup>2+</sup> and Cd <sup>2+</sup>	Chitosan/Glucan	342, 232, 184, 395, 269	[137]
Cu <sup>2+</sup> , Hg <sup>2+</sup> , Ag <sup>1+</sup> , Cr <sup>3+</sup> and Cr <sup>6+</sup>	Magnetic chitosan beads	122, 306, 107, 63 and 81	[138]
Pb <sup>2+</sup> , Cu <sup>2+</sup> , Cd <sup>2+</sup> , Ni <sup>2+</sup> and Mn <sup>2+</sup>	Zeolite	65.75, 56.06, 52.12, 34.40 and 30.89	[139]
Cr <sup>6+</sup> , Cu <sup>2+</sup> and Ni <sup>2+</sup>	Oak sawdust	1.7, 3.22 and 3.29	[140]

**Table (6):** Agricultural waste adsorbents and their adsorption capacity towards different pollutants.

Pollutant removed	Agricultural waste Adsorbent	Adsorption capacity (mg/g)	Reference
Methylene Blue	Pine cone (Pinus Radiate)	109.89	[141]
Methylene blue	Pine tree leaves	126.58	[142]
Methylene Blue	Pomelo peels (pretreated with ultrasound)	7041.52 at 30 % ultrasound amplitude	[94]
Methylene Blue	Pomelo peel modified with citrate	199.2	[38]
Methyl violet 2B	Casuarina equisetifolia needle	164.99	[143]
Methyl orange	Orange peel (dried)	149.26	[97]
Methyl orange	Orange peel activated carbon	2342.91	[97]
Crystal violet	Rice Husk (modified)	37.83	[144]
Congo red	Pine cone	500	[145]
Reactive black 5	Peanut hull	50, 52.63 and 55.55 for 20, 40 and 60 °C	[146]
Basic blue 9	Guava leaf	295	[147]
Oil-byproducts	Sugarcane Bagasse	12.30	[148]
Benzene	Rice husk activated carbon	365	[149]
P-Cresol	Canola stalk	41.6	[150]
Phenolic compound	Wheat bran	487.3	[151]
2,4- dichlorophenol	Banana peel	65.7	[152]
Nitrate ions	Onion peel dust (OPD)	5.93	[37]
phenol	Pomelo peel biomass	10.35 using 0.02 g/20 mL	[95]
Cr <sup>6+</sup>	Grafted banana peel	6.17	[89]
Cr <sup>6+</sup>	Banana peel	26.46	[90]
Cr <sup>6+</sup>	Green pea pod (Pisum Sativum)	33.33	[29]
Cr <sup>6+</sup>	Pea pod peels	4.33	[39]
Cr <sup>6+</sup>	Chemical pretreated rice straw biochar	89.90 at pH = 2	[31]
Cr <sup>6+</sup>	Fine Rice straw	7.99	[35]
Cr <sup>6+</sup>	Rice straw carbon	18.83	[35]
Cr <sup>6+</sup>	Rice straw activated carbon	40.32	[35]
Cr <sup>6+</sup>	Citric acid modified Sugarcane bagasse	13.5	[40]
Cr <sup>3+</sup>	Rice husk biochar	26.31	[98]
Cu <sup>2+</sup> and Ni <sup>2+</sup>	Sugarcane Bagasse	7.88 and 14.31	[153]
Cu <sup>2+</sup>	Bengal gram husk	330	[154]
Cu <sup>2+</sup>	Orange peels	63	[96]
Pb <sup>2+</sup>	Sweet lemon peel biochar (Citrus limetta)	2840.91	[92]
Pb <sup>2+</sup>	Unmodified Onion skins	6.173	[99]
Pb <sup>2+</sup>	Modified Onion skins with thioglycolic acid	4.878	[99]
Cd <sup>2+</sup>	Unmodified Onion skins	21.28	[36]
Cd <sup>2+</sup>	Modified Onion skins with thioglycolic acid	17.86	[36]
Ni and Cr	Untreated Rice straw	50 and 15.87	[33]
Ni and Cr	Treated Rice straw	71.43 and 19.23	[33]
Zr <sup>6+</sup>	Citrus peel waste biomass	42.02	[93]

**Table (7):** Various industrial byproducts and their capacities for pollutants removal from contaminated water.

Pollutant removed	Industry waste (byproduct)	Adsorption capacity (mg/g)	Reference
Cr <sup>6+</sup>	Palm oil fuel ash	0.464	[102]
As <sup>3+</sup> and As <sup>5+</sup>	Palm oil fuel ash	91.2 and 99.4	[103]
Pb <sup>2+</sup>	Red mud	6.03	[104]
Cu <sup>2+</sup>	Red mud	5.35	[105]
Hg <sup>2+</sup>	Coal fly ash	0.44	[114]
Pb, Cu, Cd, Cr and Zn	Blast furnace slag	5.11, 5.22, 5.05, 4.83 and 4.26	[120]
Pb <sup>2+</sup> , Cd <sup>2+</sup> , Ni <sup>2+</sup> and Cu <sup>2+</sup>	Paper mill waste	14.1, 14.8, 13.7 and 13.9	[155]
Cr <sup>6+</sup>	Leather industry waste	65.35	[156]
Phosphate ions	Red mud	38.46	[107]
Methyl orange (MO)	Coffee waste	62.5	[109]

Toluidine blue (TB) and Crystal violet (CV)	Coffee waste	142.5 and 125	[110]
Pb <sup>2+</sup> and Cr <sup>6+</sup>	Fly ash	78.13 and 15.70	[111]
Crystal violet (CV) and Methylene blue (MB)	Fly ash	172.41 and 151.52	[112]
2,4-dichlorophenoxyacetic acid	Bagasse fly ash	7.14 at 328 °K	[113]
Congo red	tea factory waste	3	[118]
Phenol	Activated red mud	1.58	[157]

Like algae, sorption of fungi and yeast also relies on their cell wall, which consists primarily of the amount of polysaccharides, chitins, glucans and proteins, etc. Phosphate, carboxylate, sulphate, hydroxyl and amino groups are the functional groups that could be found on the cell wall of them [160].

For the elimination of harmful contaminants, bacteria are often used as biosorbents. Several forms of bacteria are used, such as Bacillus, Pseudomonas, Streptomyces, Escherichia, Micrococcus, etc., which have been used effectively for pigment, metal or organic removal [14]. The key advantages of bacteria are that they are small, ubiquitous, able to grow under various environmental conditions and provide amino,

carboxyl, phosphate and sulphate groups through polysaccharide slime layers for metal biosorption.

Research has shown that biomass adsorption potential can be improved by some physical or chemical pretreatment procedures. These methods of pretreatment included, in particular, drying, autoclaving, interaction with organic chemicals such as formaldehyde, or inorganic chemicals such as NaOH, H<sub>2</sub>SO<sub>4</sub>, NaHCO<sub>3</sub>, and CaCl<sub>2</sub> [158]. Biosorbents can also be regenerated for reuse by organic solvents such as ethanol and methanol or surfactants such as NaOH and nonionic tween solutions. The summary of most used biosorbents for pollutants removal are tabulated in Table (8).

**Table (8):** Biosorbents used for different pollutants removal and their adsorption capacity.

Pollutant removed	Biosorbent	Adsorption capacity (mg/g)	Reference
crystal violet (CV)	Fungus Diaporthe schini	642.3 at 328 °K	[159]
Phenol	Sargassum and Chaetomorpha	88.1 and 17.7	[170]
Phenol	Saccharomyces cerevisiae	26.95	[171]
Pb <sup>2+</sup> , Cd <sup>2+</sup>	Green Algae (Ulva lactuca)	34.7 and 29.2	[162]
Cu	Yeast (Saccharomyces cerevisiae)	4.73	[164]
Cd <sup>2+</sup> , Cu <sup>2+</sup> , Ni <sup>2+</sup> , Zn <sup>2+</sup> and Mn <sup>2+</sup>	Geobacillus toebii	29.2, 48.5, 21, 21.1 and 13.9	[172]
Cd <sup>2+</sup> , Cu <sup>2+</sup> , Ni <sup>2+</sup> , Zn <sup>2+</sup> and Mn <sup>2+</sup>	Geobacillus thermoleovorans	38.8, 41.5, 42, 29 and 23.2	[172]
Zn <sup>2+</sup> and Cu <sup>2+</sup>	Thiobacillus thiooxidans	172.4 and 39.84 at 40 °C	[173]

## 5. Effect of interference of other Pollutants

The effect of presence of more than pollutant in the same water is studied in some researches to show the influence of interference between them in adsorption process. Being single ion in water, enhances the adsorption process as the active sites are available for only one ion adsorbed. In real samples, for example industrial wastewater from tanneries, electroplating, mining, etc contains more than one ion such as Cr, Ni(II), Pb(II), Cu(II), Zn(II) and other heavy metals that can compete and hinder a single

metal from binding to an active site. [174] studied the effect of Pb(II) removal in the presence of Cu(II) or Zn(II) or both of them. The presence of constant Cu(II) decrease the adsorption of Pb(II) whereas the presence of constant Zn(II) or both of Zn(II) and Cu(II) have no effect on the sorption of Pb. Zn(II) and Cu(II) ions compete with each other as they are very similar in molecular mass, ionic radius and electronegativity and this decrease the competition effect on lead for active sites. Similar trends was investigated by [175]. [176] studied the effect of competitive adsorption of Pb(II), Cd(II) and Zn(II) on

Eichhornia crassipes in binary and ternary system. The study investigated that all ions have competitive effect on the metal binding of other for both binary and ternary system. The maximum suppression effect of Pb(II) ions on Cd(II) ions adsorption  $q_e/q_e = 0.24$  for binary system and 0.2 for the effect of Zn(II) and Pb(II) on Cd(II) in ternary system.

## 6. Cost analysis

Cost is considered one of the most important parameters governing the choice of the adsorbent. As for real application of the adsorption process, we should use the most effective adsorbent and also the most economic one. In comparison to nano-materials and AC, the modified low cost adsorbent could be considered as a promising solution for the treatment process. The cost of preparation of these adsorbents is only concerned with the chemicals used such as HCl and NaOH and the process of drying in an oven that don't consume more energy.

## 7. Regeneration and Reuse

During the adsorption process, the efficiency of the adsorbent is reduced by the time due to the accumulation of pollutants on the surface of adsorbent. Therefore, a process of regeneration of the exhausted ions on the surface should be applied to make the process economically feasible. There are many studies in the literature that use many different eluents such as HCl, NaOH, H<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>,.... etc. to extract the adsorbed pollutant from the surface of adsorbent. [35] uses NaOH then HCl and distilled water to desorb chromium from rice straw carbon while [42] uses 1N NaOH only for the desorption of chromium from modified sawdust. [177] uses 1M HCl for the regeneration of tea waste to be used for 5 times. [178] studied the regeneration and reuse of CoFe<sub>2</sub>O<sub>4</sub>/MgAl-LDH using Na<sub>2</sub>CO<sub>3</sub> to be used in the removal of chromium for the sixth cycle. [179] also uses 0.02 mol/L solution of NaOH to regenerate GO/PAMAMs for 5 successive cycles for the removal of chromium.

## 8. Mood of operation

The adsorption method of certain undesirable toxic materials such as heavy metals and synthetic dyes on various adsorbents may be performed in a laboratory using either batch mode or adsorption techniques for fixed bed columns. Batch laboratory adsorption studies can be helpful when using adsorption for removing specific pollutant

components [180]. On the other hand, continuous column studies provide the most practical use of the adsorption technique in the treatment of wastewater. The continuous adsorption method is more appropriate and suitable in real water treatment industries because of its low operating costs and the ability of columns to adapt to versatile processes, as stated in some scientific studies [181].

### 8.1. Batch studies

Most of the previous studies were conducted in batch mode as it is more suitable for researchers to use in laboratory, but definitely do not simulate the actual treatment or pilot scale work in industrial treatment. Batch techniques studies the effect of some parameters on the adsorption process such as the effect of pH, adsorbent dosage, pollutant initial concentration, contact time, temperature surface morphology and modification method, etc. The obtained adsorption capacity from batch equilibrium studies is beneficial for giving information about the interaction between adsorbate and adsorbent. Nevertheless, in general, the data obtained from such a technique may not refer to most treatment processes (i.e. the column process), since the contact time in the batch process is not adequate to achieve equilibrium in the continuous flow process. Another drawback for batch technique is that it deals with small volume of wastewater and don not fits to large flow. Fig. (7) shows a schematic diagram for batch adsorption process, where  $C_0$  is the pollutant initial concentration that goes to  $C_1$  after adsorption process. For adsorption process,  $W$  indicates the mass of adsorbent used and  $V$  is volume of solution studied and  $q_0$  &  $q_1$  are the adsorption capacity (pollutant concentration on solid) for initial and final stage. The mass balance for the process is given in equation (1)

$$V(C_0 - C_1) = W(q_0 - q_1) \quad (1)$$

Under equilibrium conditions:  $C_1 \rightarrow C_e$  and  $q_1 \rightarrow q_e$  so the equation will be

$$V(C_0 - C_e) = W(q_0 - q_e) \quad (2)$$

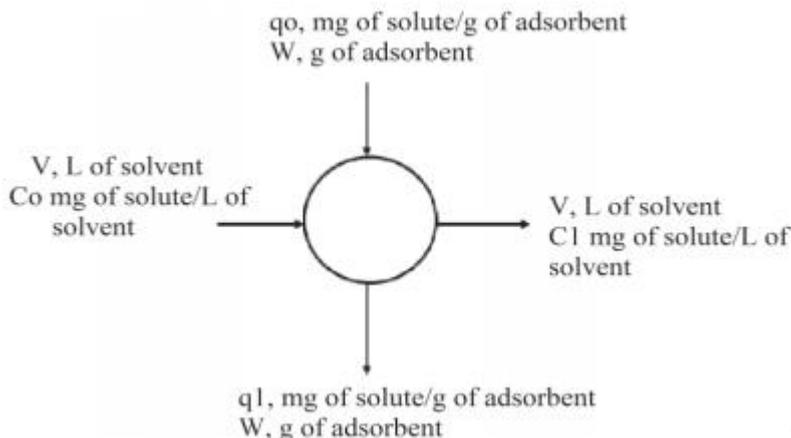


Fig. (7) Batch adsorption schematic diagram [16].

### 8.2. Continuous studies

In addition, the fixed-bed columns shown in Fig. (8), because of their simple operation are widely used in various chemical industries. In addition, continuous treatment is much more time-efficient in contrast to batch treatment with the high volume of wastewater to be processed. [181]. For evaluating the experimental breakthrough curve, the fixed-bed column approach is used. Breakthrough time ( $t_b$ ) is characterized as the time to achieve  $C_b$  (i.e. (1-5) percent of the initial concentration ( $C_0$ )) for a particular breakthrough concentration. The effluent concentration from the column is increased with time till it reaches the initial concentration at which the time is called the exhaust time. The output of the column is assessed by plotting the relative pollutant concentration, which is defined as the ratio of the

pollutant concentration in the effluent to the influencing concentration ( $C_t / C_0$ ) with regard to flow time,  $t$  [182]. The same solution stays in contact with a given amount of adsorbent in batch mode adsorption studies (static mode). The adsorption process, however, continues until the equilibrium between the solute concentration in solution and the solute adsorbed per unit adsorbent weight is reached. Equilibrium is unchanged in nature in this scenario, since it does not shift further over time. Nevertheless, the solution proceeds to access and simultaneously exit the column in dynamic column adsorption, and equilibrium can never be achieved at any point or time. Equilibrium must be continually maintained as it reaches the new concentration each time and thus equilibrium in column mode is called dynamic equilibrium. The adsorption capacity in continuous mode is given by equation (3)

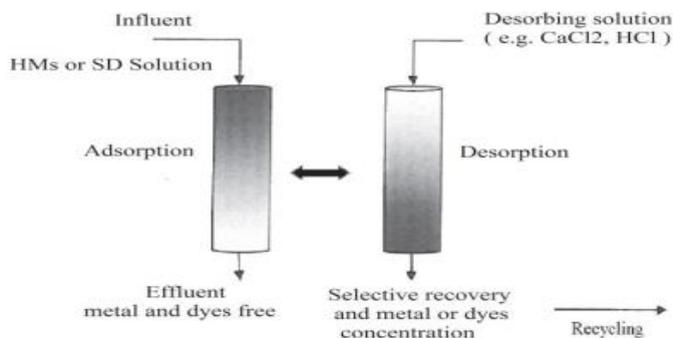


Fig. (8): Fixed be column studies for adsorption and desorption [16].

$$q((1 - 5)\%) = \frac{t_b * Q * C_o}{M} * 90\% \quad (3)$$

### 9. Adsorption Kinetics

Kinetics of sorption describes the rate of solute adsorption which in turn control the residence time of sorption reaction that defines efficiency of sorption [21]. The most used kinetic models are Pseudo-first-order, Pseudo-second- order and Intraparticle diffusion models.

#### 9.1. Pseudo-first-order

Lagregren, 1898 derived the Pseudo-first-order equation to calculate the rate of adsorption. The rate of adsorption is given by equation (4)

$$\frac{dq_t}{dt} = k(q_e - q_t) \quad (4)$$

The linear form of the equation after integration with boundary condition from  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$  becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k}{2.303} t \quad (5)$$

The values of  $q_e$  and  $k$  at different initial concentrations are calculated from the slope and intercept of the plots of  $\log (q_e - q_t)$  versus  $t$  which gives a straight line if the kinetic data correlate with Pseudo-first-order [90].

#### 9.2. Pseudo-second-order

The rate of adsorption for Pseudo-second-order is given by equation (6)

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (6)$$

Where,  $q((1-5)\%)$  is the capacity of adsorbent (mg/g) when the concentration of solution reach  $C_b$ ,  $Q$  is the flow rate (ml/min), and  $M$  is adsorption mass packed in the column (g).

By applying the boundary conditions after integration of both sides from  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$ , the integrated form of the equation becomes:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

The rate constant  $k_2$  (g/mg.min) and equilibrium adsorption capacity  $q_e$  are calculated from the slope and intercept of the linear plot of  $t$  (time) Vs  $t/q_t$  [89] [65].

#### 9.3. Intraparticle diffusion model

When the film diffusion resistance is negligible, the adsorption of a solute from a liquid to the surface of a solid adsorbent is solely regulated by Intraparticle diffusion. The Intraparticle diffusion model can be derived from the second law of Fick, assuming that the diffusivity of the Intraparticle  $D$  is constant and that the adsorbent's absorption of sorbate is small compared to the total amount of sorbate present in the solution [59]. The mathematical expression thus obtained for the Intraparticle diffusion model is given by equation (8)

$$q = K_p t^{0.5} + I \quad (8)$$

$k_p$  is related to the Intraparticle diffusivity ( $D$ ) as in equation (9):

$$K_p = \frac{3q_e}{d_p} * \sqrt{D/\pi} \quad (9)$$

Table (9) shows the three kinetic models explained and their linear forms and parameter

**Table (9):** Kinetic models along with their linear equations.

Kinetic Model	Linear Equation	Straight Line
Pseudo-first-order	$\log(q_e - q_t) = \log q_e - \frac{k}{2.303} t$	A plot of $\log (q_e - q_t)$ versus $t$
Pseudo-second-order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	A plot of $t/q_t$ versus $t$
Intraparticle Diffusion	$q = K_p t^{0.5} + I$	A plot of $q$ versus $\ln t^{0.5}$

## 10. Adsorption Isotherms

An adsorption isotherm is usually a significant curve that defines the retention (or release) or mobility of a substance at a constant temperature and pH from aqueous porous media or aquatic environments to a solid phase [183] [184]. Adsorption equilibrium (the ratio of the amount of adsorbed to the remainder of the solution) is reached when the phase-containing adsorbent has been contacted with the adsorbent for a reasonable period of time and its adsorbate concentration in the bulk solution is dynamically balanced with the interface concentration [185] [186]. Concentration of the equilibrium solution remains unchanged. The equilibrium adsorption isotherm is graphically described by plotting solid-phase concentrations against liquid-phase concentrations. Over the years, many equilibrium isotherm models (Langmuir, Freundlich, Brunauer–Emmett–Teller, Redlich–Peterson, Dubinin–Radushkevich, Temkin, Toth, Koble–Corrigan, Sips, Khan, Hill, Flory–Huggins and Radke–Prausnitz isotherm), have been formulated in the study of adsorption process [187]. The most common used isotherm models are Langmuir, Freundlich, Temkin and Dubinin–Radushkevich [188].

### 10.1. Langmuir Isotherm Model

One of the best known, scientifically understood, and commonly used models is the Langmuir model, introduced in 1916 by Langmuir. The Langmuir equation is based on the assumption that maximal adsorption occurs on the adsorbent surface of a saturated mono-layer of adsorbate molecules (there is no interaction between adsorbed molecules at the neighboring adsorption sites) and that the adsorption energy is constant [61] [90]. The linearized form is given in equation (10)

$$\frac{C_e}{q_e} = \frac{1}{b Q_m} + \frac{1}{Q_m} C_e \quad (10)$$

The plot of  $C_e$  versus  $C_e/q_e$  gives a linear form if the adsorption equilibrium obeys Langmuir equation.

### 10.2. Freundlich Isotherm Model

Freundlich equation is an empirical equation that commonly describes the procedure of adsorption from wastewater for heavy metals and organics. It is based on heterogeneous or multilayer adsorption sites. [18] [189]. It also implies that before the lesser

one, the stronger binding sites are occupied and that the adsorption strength decreases with the degree of occupation [188]. The linear form for Freundlich equation is given by equation (12)

$$\log q_e = \log K + \frac{1}{n} \log C_e \quad (12)$$

The value of  $1/n$  is between 0 and 1 if the value of  $1/n$  below the unit means that the process of adsorption is chemical; if the value is above the unit, the more the physical process is adsorbed; the more heterogeneous the surface, the more the value of  $1/n$  approaches zero [189].

### 10.3. Temkin Isotherm Model

The effects of indirect adsorbent / adsorbate interactions on isotherms of adsorption were considered by Temkin. Due to adsorbent / adsorbate interactions, the heat of adsorption of all the molecules in the layer will drop linearly with coverage. This isotherm assumes that (i) the adsorption heat of all molecules in the layer decreases linearly due to adsorbent-adsorbate interactions with coverage, and that (ii) the adsorption is characterized by a uniform distribution of binding energies, up to a certain maximum binding energy. [61] [189]. The linear form of Temkin isotherm is given in equation (13)

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (13)$$

### 10.4. Dubinin–Radushkevich Isotherm Model

The isothermal model of Dubinin–Radushkevich is used to predict the nature of the adsorption process, i.e. physical or chemical, by sorption energy value [61]. The linear form of the model is described as in equation (14)

$$\ln q_e = \ln q_{max} - B\varepsilon^2 \quad (14)$$

Where,  $\varepsilon$  is the Polanyi potential that can be calculated as follow:

$$\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (15)$$

The constant B ( $\text{mol}^2 / \text{kJ}^2$ ), gives the mean free energy E of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed by using the relationship [23]:

$$E = \frac{1}{\sqrt{2B}} \quad (16)$$

The E (kJ/mol) value gives the information about sorption type, physical or chemical. If  $E < 8$  kJ/mol,

the adsorption process was physical in nature and in the 8–16 kJ/mol range, and it was chemical in nature [190]. Table (10) summarizes the equilibrium isotherm models mentioned above and their linear form.

**Table (10):** Isotherm models along with their linear equations and parameters.

Isotherm Model	Linear Equation	Straight Line
Langmuir	$\frac{C_e}{q_e} = \frac{1}{b Q_m} + \frac{1}{Q_m} C_e$	A plot of $C_e$ versus $C_e/q_e$
Freundlich	$\log q_e = \log K + \frac{1}{n} \log C_e$	A plot of $\log q_e$ versus $\log C_e$
Tempkin	$q_e = B_T \ln A_T + B_T \ln C_e$	A plot of $q_e$ versus $\ln C_e$
Dubinin–Radushkevich	$\ln q_e = \ln q_{max} - B\epsilon^2$	A plot of $\ln(q_e)$ versus $\epsilon^2$

## 11. Future needs in adsorption process

More attention should be given to fixed bed column –continuous- studies and pilot-scale models as it represents the actual case study for real treatment systems. The study of combination of pollutants should be enlarged because the behavior of an adsorbent will differ in the presence of multi-species pollutants. Kinetic and isotherm models for multi-species pollutants should be established to describe the behavior of adsorbents at these conditions. Regeneration is also a point of interest that should be improved to exploit the adsorbents more than one time and to eco-friendly materials. For AC and nano-adsorbents, more researches should be executed in order to decrease the cost of their production to be an effective source for large scale application especially in developing countries. Effective approaches should be investigated to separate spent nanomaterials from aqueous solution. The important thermodynamic parameters, e.g. adsorption free energy and surface energy, should be characterized or discussed in details. For packed bed column studies, the effectiveness of using multi-media adsorbent should be investigated. In order to understand the actual adsorption mechanism at the solid-water interface, more spectroscopic studies using zeta potential calculation, attenuated total reflection, Fourier transform infra-red, X-ray photoelectron spectroscopy, extended X-ray absorption

fine structure, and X-ray absorption near edge structure are required.

## 12. Conclusion

Organic and inorganic pollutants for waste water has increased widely due to the modern industrialization occurred in past few years. Adsorption process is a promising method for the removal of these pollutants. The largest adsorption capacity for heavy metals from literature was 2840.9 mg/g for sweet lemon peel biochar (Citrus limetta) for the removal of  $Pb^{+2}$ . low cost adsorbents can be used as alternative for activated carbon due to the high cost of AC preparation. Regeneration and recovery studies can be done to the adsorbents after adsorption process. The presence of two or more than one pollutant could affect the adsorption capacity of an adsorbent. Batch mood is suitable for investigating the adsorption capacity for an adsorbent but cannot be considered in the design of adsorption column studies. Langmuir and Freundlich are the most used isotherm models that fit the adsorption process of organic and inorganic compounds. Pseudo-first-order and Pseudo-second-order kinetic models are the most used kinetic models in adsorption process. The mechanism of adsorption process depends on the type of functional groups on the surface of adsorbent and adsorption capacity can be improved via chemical modification methods.

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