Abstracts

Chapter 1: Water pollution by chemicals has become a major source of concern and a priority for all industrial sectors. In parallel, law and regulations in terms of effluent release and environmental impact are becoming increasingly stringent. This introduction gives a general scheme of wastewater treatment, briefly discusses the different types of effluents, and presents sorption processes as decontamination method for the removal of pollutants from industrial effluents.

Chapter 2: Sorption/adsorption is a key method for removing contaminants, particularly organics, from solutions. Activated carbon is extensively used not only for adsorbing contaminants from drinking water sources (rivers, lakes or reservoirs) but also for removing pollutants from wastewater streams. Other conventional and non-conventional sorbents/adsorbents can be also obtained and employed in the solid form. This chapter gives a general overview of liquid-solid sorption/adsorption processes for pollutant removal from wastewaters. It outlines some of the fundamental principles of pollutant sorption onto sorbent materials. The chapter also proposes a classification for the different types of sorbents used and discusses different mechanisms involved in the sorption processes.

Chapter 3: The treatment of high volumes of wastewater containing low concentrations of pollutants is of increasingly relevance as the awareness regarding the pollutants negative effects on human health and on the environment has led discharge regulations to become more stringent. Adsorption, as a unit operation for removing pollutants from effluents, has gained increasing popularity in recent years, because the process produces a high quality treated effluent, which can meet stringent environmental emission standards. Adsorption processes for purification of wastewaters can be carried out either discontinuously, in batch reactors, or continuously, in fixed-bed adsorbers (columns). Batch reactors are easier to operate than fixed-bed columns in laboratory studies, but are less convenient at industrial applications for discontinuous feeding is less economic than continuous feeding. Furthermore, other advantages of employing fixed-bed columns for industrial adsorption processes are higher residence times and better heat and mass transfer characteristics than batch reactors. Batch experiments provide fundamental information on the behavior of the adsorbents used (e.g. adsorbent capacity) and are thus necessarily carried out in all adsorption studies. However, discontinuous processes present distinct adsorption kinetics than continuous processes. Intra-particle diffusion is necessarily a more influential parameter on the adsorption mechanism and performance in continuous processes than it is in discontinuous processes, because the adsorbent particle size is usually larger in former, in order not to promote significant pressure drops throughout the bed of adsorbent. Also, because in dynamic column adsorption the solution continuously enters and leaves the column, a complete equilibrium is never established at any stage between the solute in solution and the amount adsorbed and, hence, high adsorption capacities in equilibrium with the influent concentration rather than the effluent concentration are achieved. Thus, continuous adsorption experiments should be carried out in order to determine operating parameters, such as feed flow rate and aspect ratio, if the fixed bed process is to be scaled-up to real industrial applications. The main information about an adsorbent performance in fixed-bed operations is obtained by making use of a breakthrough curve, which is basically a plot of the duration of the dynamic column experimental test against the concentration of the adsorbate in the effluent stream, i.e. it is the ultimate measure of an adsorbent working life. Thus, for a newly developed adsorbent to be proposed for utilization in an industrial adsorption process, dynamic column experimental tests should be carried out and the respective breakthrough curves be presented in order to attest its adsorption performance for a specific adsorbate. In view of the aforementioned, it is the objective of this essay to present a critical overview of the studies presented in the recent literature on the fixed-bed adsorption of pollutants using conventional and non-conventional adsorbents.

Chapter 4: Phenolic compounds belong to a group of most hazardous environmental pollutants. Since they are highly harmful to organisms even at low concentrations and, in general, not easy to remove by biological degradation, methods of their treatment have been continuously modified and developed. Adsorption is the most frequently used method to remove phenols from waters, and activated carbons are the most widely used adsorbents because of their excellent adsorption ability for relatively low molecular weight organic matter. However, it should be realized that there is a wide set of factors influencing the adsorption processes, such as the type of carbon material, the presence of surface functionalities, the pH value of the coexisting bulk liquid phase, the presence of oxygen, etc. In this review, we discuss the significance of the above-mentioned factors. This review also deals with structural and chemical characterization of the activated carbon from the point of view of application for phenols uptake. The selection of precursors of activated carbon as well as the generation of porosity and surface chemical composition are considered. Adsorption of phenolic compounds has been described critically, with an emphasis on the development of investigations on the subject and presenting some of the most relevant results. A special attention is paid to the effect of surface functionalities and pH of solution. The correlation between the structure of activated carbons and the adsorption behavior of phenol is highlighted. Problems associated with irreversible adsorption of phenols from aqueous solutions and their surface polymerization are also reported. The role of the oxygen and its influence on the adsorption capacity of activated carbons as well as the effects of different substituents of phenols are discussed.

Chapter 5: Activated carbons can be prepared using various precursors, and different experimental procedures, leading to different textural, chemical properties, and consequently to different adsorptive properties. Physical activation is a two-step process in which the precursor is developed into AC: the carbonization (or pyrolysis) of the carbonaceous material, followed by its activation. During the carbonization, which may be preceded by a pre-carbonization phase, the carbonaceous starting material is converted into carbon. Pyrolysis of the material removes non-carbon elements which are volatilized at low temperature species, thereby producing a fixed carbon mass having a rudimentary pore structure. The Activation step involves a controlled partial carbon oxidation. Oxidative species are believed to react with high energy sites in the non-graphitic carbon matrix to generate different pore sizes. Indeed, contacting the char with an oxidising gas results in the removal of the more disorganised carbon and the formation of a well developed micropore structure. Chemical activation is a one-step method used for the preparation of AC. In general, it involves impregnation of the carbonaceous material with activating chemicals, such as KOH, NaOH, H_3PO_4, $ZnCl_2$, H_2SO_4, $(NH_4)_2SO_4$,HCl, $MgCl_2$, HNO_3, or $CaCl_2$ followed by heating under a nitrogen flow at temperatures in the range 450-900°C, depending on the impregnant used. Carbonisation and activation proceed simultaneously and the method often leads to materials with higher micropore volumes and wider micropore sizes and these materials are therefore generally preferred for liquid phase applications. The performance of the activated carbons for water treatment is determined by both its textural and chemical properties. Therefore, the manufacturing process and the intended application of the carbon will be important considerations. The surface area, the pore size distribution, the presence of active functional groups, acido-basic sites and mechanical strength are very important properties to be considered for the adsorption of a given compound.

Chapter 6: The adsorption, adhesion, chemical and catalytic properties of silicas depend on chemistry and geometry of their surfaces. The physicochemical properties of amorphous silicas are compared. Functionalized silicas have been used as effective adsorbents because of their high surface area and the functionalized surface. The various modifying compounds, different methods of the silica surface modification and their effect on the pollutants adsorption process are described. The various types of organic and inorganic pollutants and their adsorption efficiency on the silica surface were presented.

Chapter 7: Sorption techniques are widely used to remove certain classes of pollutants from waters and wastewaters, especially those that are not easily biodegradable. Dyes represent one of the problematic groups. Although commercial activated carbon is a preferred conventional sorbent for dye removal, its widespread use is restricted due to high cost. As such, alternative non-conventional sorbents can be obtained and employed as inexpensive and efficient sorbents. In this chapter, an extensive list of non-conventional sorbent literature has been compiled. These include carbons from non-conventional resources, natural materials such as clays and zeolites, agricultural wastes, industrial by-products, biosorbents such as peat and chitosan, biomass, and other materials such as alginate beads, cyclodextrin and calixarenes. Results in terms of sorption capacities obtained from batch studies are compiled and discussed. It is evident from a literature survey of about 200 recently published papers that non-conventional sorbents have demonstrated outstanding removal capabilities for dye molecules.

Chapter 8: Wastewater treatment is a major problem in the current time. Water coming from houses, colonies, industries may contaminate both ground as well as surface water. Among all the pollutants, synthetic dyes are one of the most important pollutants. It comes from industries like textile, dyeing and fabricating units and disposes to the nature directly. To prevent this environmental pollution, proper treatment of this waste water is necessary. Adsorption is considered as one of the most important and easy method for cleaning these colored water. Adsorption with naturally available component is of great importance. Kaolin which is a clay, found naturally, is considered as good adsorbent for color removal and also economic. In this review, an extensive list of kaolin from vast literature has been compiled and their adsorption capacities for various dyes as available in the literature are presented. It is evident from the literature survey that kaolin has shown good potential for the removal of colored dyes. However, there are few issues and drawbacks on the use of kaolin in water treatment that have been discussed in this paper.

Chapter 9: The presence of textile dyes in the industrial aqueous effluents causes serious pollution of the environment because most of these are organic recalcitrant compounds, that are toxic and highly resistant to degradation and, therefore, their treatment is necessary. This review highlights the most important aspects of dye removal with wood sawdust, wood bark and wood chips that are relevant for the efficiency of the adsorption process (characterization of adsorbents, factors affecting the adsorption, kinetic and thermodynamic models). The results of adsorption studies on different types of dyes with natural and chemically modified forms of these materials in batch system are presented. The continuous-flow fixed bed columns are of great practical importance and from this point of view the design and optimization of dynamic processes have been investigated. These lignocellulosic waste materials from wood processing industry are available in large quantities. They are biodegradable, low cost and could be effective adsorbents for removal of dyes from wastewaters due to their physico-chemical characteristics. For possible practical applications variants with new inexpensive magnetically and chemically modified materials should be considered in order to facilitate adsorbent separation and efficient removal of dye. Combined adsorption methods using these adsorbents and the subsequent fungal degradation could also be extended in perspective.

Chapter 10: Chitosan, bearing amine groups, is very efficient for binding metal ions through different mechanisms including complexation/chelation of metal cations (at near neutral pH) or ion exchange (electrostatic attraction) of metal anions on protonated amine groups (in acidic solutions). Sorption properties are controlled by a wide range of parameters such as pH, metal speciation, particle size and characteristics of the biopolymer (degree of acetylation, crystallinity, porosity). The identification of the limiting steps in the process can help in designing new materials based on chitosan by chemical modification (bringing other reactive groups) or physical modification (to improve diffusion properties or design specific and original modes of application). Despite the abundant literature on the topic, biosorption on chitosan is not applied at industrial scale, several examples are cited to describe how these metal ion/chitosan interactions could be used for designing new materials with high added value.

Chapter 11: Heavy metals in liquid effluents are dangerous for both the human health and the environment, and their removal from wastewaters is an issue of great environmental relevance. To this end, adsorption is a consolidated technique since it is economical, effective, simple and versatile. To reduce the costs associated with the use of activated carbon as adsorbent, the employment of cheaper non-conventional adsorbents (like industrial residues, natural materials, agricultural by-products and other biomasses) has been proposed. This can also take advantage from proper beneficiation techniques (such as chemical modification, demineralization, gasification, mechanical sieving, pyrolysis) aimed at improving the physical, chemical and morphological characteristics of the material. The aim of this review is to critically report a selection of results, starting from the adsorbent properties and their (if any) beneficiation treatments, and then considering as relevant parameters the adsorption capacities, the thermodynamic and kinetic data. Finally, a discussion concerning the controlling mechanisms is dealt with.

Chapter 12: The surface-treatment industry consumes a broad range of chemicals that are considered harsh to humans and to the environment. This industrial sector is today considered to be one of the most polluting in spite of the considerable effort made to clean up the processes over the last 20 years. Because of increasingly stringent regulations, effluents polluted with heavy metals must be treated. The degree of detoxification may range from a main process stream for a seriously polluted industrial waste to a final purification to remove traces that can remain after the main treatment. Thus, the type of process or combination of processes used will depend on the metals involved and the ultimate concentration allowed. There are a variety of possible processes for the purification of wastewater from the surface-treatment industry but conventional detoxification systems mainly consist of pH adjustment, cyanide oxidization and chromium reduction (if relevant), followed by hydroxide precipitation, clarification, and sometimes filtration or sorption. The main focus of the present chapter is the sorption/separation processes used by surface industries for the treatment of their effluents. Sorption using activated carbons is examined for the removal of heavy metals and organic matter. However, carbon sorption is a relatively expensive process and, with environmental concern growing in developing countries, there has been considerable research interest in the use of alternative low-cost sorbents which can be considered as single-use solids. These have included biological materials from waste or natural products but biosorption on starch-based material is also a promising alternative process for environmental purposes.

Chapter 13: The removal of fluoride from water and wastewater is one of the most important issues due to the effect on human health and environment. Various defluoridation technologies based on the principle of precipitation, adsorption, ion exchange, membrane filtration and electrochemical methods have been proposed and developed to reduce/remove fluoride in drinking water and industrial effluents. Among the methods, adsorption onto activated alumina and activated carbons is considered a suitable and efficient technology. Recently, sorption and biosorption processes using non-conventional sorbents were demonstrated effective methods for fluoride removal from industrial wastewaters. The main objectives of this chapter are to summarize the developments related to the defluoridation of water/wastewater using non-conventional sorbents and to provide useful information about their most important features. In particular, chitosan might be a promising biosorbent for environmental purposes. When possibly the sorption capacity of various materials and chitosan derivatives used as sorbents under different experimental conditions is reported to help to compare the efficiency of the fluoride removal process.

Chapter 14: Water is a rare and precious commodity whose supply is becoming more acute every day. Increasing industrial development and urbanisation has resulted in generation of large quantities of toxic and persistent pollutants in aqueous streams that cause deleterious ecological effects and pose a serious threat to animals and humankind. In the last decades there has been an increasing concern on the aquatic pollution that drive efforts to decontaminate waters and to introduce stricter environmental regulations. A huge amount of research is needed to identify robust methods for purifying water at lower costs and with less energy, minimizing the use of chemicals and impact on the environment. Biosorption has been shown to be the most promising option for the removal of all the not easily degradable pollutants from aqueous streams. The kinds of biomass potentially available for biosorption purposes are enormous and fungi are the most promising ones thanks to their biological and physiological characteristics. Moreover many fungi are extensively used in large-scale industrial fermentation processes representing a potential source of cheap adsorbent materials. The chapter presents a brief introduction to the classification and characteristics of fungi with special reference to the cell wall composition and to the main functional groups involved in fungal biosorption. The effectiveness of fungal biomasses in biosorption of both organic and inorganic pollutants will be discussed and the effect of different biotic and abiotic parameters will be described. Moreover, an overview about the main applications of fungal biosorbents to real wastewaters will be given.

Chapter 15: The development of cross-linked cyclodextrin-based sorbents as complexing polymeric matrices is an expanding field in pollutant removal by sorption. The main objectives of this chapter are to summarize the developments in the use of these polymeric materials in decontamination applications and to provide useful information on their most important features. The synthesis of cross-linked cyclodextrin-based materials is presented and the various interactions occurring between pollutants and sorbent in the sorption processes are discussed.

Chapter 16: Sorption of cations as well as anions from aqueous media by calixarene based materials has been a widely developing area in material science and technology since last few decades. Mostly, it is achieved by the immobilization (physically or chemically) of modified calixarenes onto various supports such as polymers, silica, and resins. The calixarene macrocycles due to their bowl-shaped geometry are indeed used as hosts allowing organic and inorganic guests to coordinate/sorb onto their cavity. The possibility of designing versatile organic, coordination and organometallic architectures at the lower (narrow) and upper (wide) rims of the calixarenes are also very appealing for extending the cavity, or to take advantage of the proximity to promote substituent interactions. Thus, novel calixarene derivatives are continue to being synthesized and appended in polymeric materials in order to obtain regenerable resins for the recovery of various elements (metals/metalloids/ non-metals) and neutral molecules. The calixarene based sorbents are generally applied in various fields such as catalyst recovery, power plant, agriculture, metals finishing, microelectronics, biotechnology processes, rare earths speciation, and potable water. Besides this, they find applications in the area of selective ion extractions, receptors, catalysis, optical devices, chemical sensor devices, the stationary phase for capillary chromatography, ion transport membranes, biomimetics, and luminescence probes etc. This survey is focused to have an overview of calixarene based sorbents for the extraction of ions and neutral molecules. The article does not, however, attempt to cover all of the different approaches to extraction processes.

Chapter 17: Adsorption techniques are widely used to remove pollutants from waters and wastewaters, especially those of poor biodegradablity. Nanoparticle adsorbents exhibit attractive performance particularly for deep removal of pollutants as a result of high surface-area-to-volume ratio and quantum effect. Their widespread use is still limited by the poor separating performance and weak physicochemical stability. To overcome these technical bottlenecks, more and more porosinit-based nanocomposite adsorbents are now being developed. In this chapter, we present a critical review on these nanocomposite adsorbents, involving their preparation, adsorption characteristics, their potential advantages and limitations as well as the underlying mechanisms involved in adsorption.

Chapter 18: Many researchers have been employed with the sorption of different wastewater pollutants, but a limited number of studies were realized for their selective removal/binding by materials. The design of the modern sorbents is based on two properties/ abilities: (i) the sorption capacity presented, and (ii) the selective ability to recognize and sorb/bind the target molecules among different pollutants. This idea was applied through Molecular Imprinted Polymers (MIPs). The history of molecular imprinting is traced back in 1940s and 1950s, when there was an inspiration to create affinity for dye molecules in silica gel, which is considered to be the first imprinted material. MIPs represent a new class of materials (known as non-conventional adsorbents) that have artificially created receptor structures. Since their discovery in 1972, MIPs have attracted considerable interest from scientists and engineers involved in the development of chromatographic adsorbents, membranes, sensors, enzyme and receptor mimics. In particular, in the already published literature the application of MIPs is mainly in analytical fields, such as separation of enantiomers, binding assays, sensors, etc. Furthermore, the development of MIPs for solid-phase extraction (SPE) has been extensively reported in the areas of food and pharmaceuticals analysis, including their use as selective sorbents for the extraction (or clean-up) of different classes of compounds from various complex matrices. However, until nowadays, it has not been reported an overview of the particular application of MIPs in selective decontamination of wastewaters (composed of dyes or ions). Papers have been published disclosing the environmental side of MIPs, describing their binding mechanism and fitting their experimental sorption data to isotherm and kinetic models and being able to selectively remove environmental industrial pollutants (dyes), ions or pollutants resulted in environmental waterways (phenols, drugs, pesticides, insecticides). In this chapter, this review presents a critical analysis of these materials, and describes their characteristics, advantages and limitations, and discusses various mechanisms involved.

Chapter 19: Nanoscale material plays a fundamental role in the removal of pollutant. They posses the advantage of high surface area to volume ratio which enables an increased exposed sites of interaction between the pollutant and the nanoscale material surface. The capacity of pollutant removal increases by several folds when nanoscale martial are employed when compared to similar bulk material. In this chapter, we focused on the employment of two types of nanoscale -adsorbents; magnetic nanoparticles and carbon nanotubes. Magnetic nanoparticles provide the added advantage of facilitating the collection of the adsorbents by the employment of an external magnetic field. Carbon nanotubes are benefited with a large surface area allowing an increase in the removal capacity with small amount of adsorbent material. A combined particle that has the advantages of carbon and magnetic responsiveness provides an improved adsorption system for removal of pollutants.