INTRODUCTION
1. INTRODUCTION

1.1 Waste Production over the world

Poland is inhabited by 38.2 million people with an average population density of 122 persons per square kilometer, and has a territory of 322,577 km\(^2\), of which 311,904 km\(^2\) is occupied by land. In the year 2008, in 3090 (both municipal and industrial) Polish sewage-treatment plants more than 1100 thousand tons (d.b.) of municipal and industrial sewage sludge was produced. In 2008, wastewater treatment plants serviced only 63% of the population (87% in urban areas and 26% in rural areas, where about 39% of the population lives); by comparison, in the countries of Western Europe, more than 78% of the population is serviced by waste treatment plants. In Poland, only 456 cities and 559 rural communities possessed a modern waste water treatment plant with enhanced nitrogen and phosphorus removal. In these plants, 918 \(\text{hm}^3\) of waste was treated, which accounts for 73% of the waste discharged through urban and rural sewerage systems. This ratio fluctuates around 70% in most countries. The average unit index of sewage sludge generated in Polish wastewater treatment plants amounts to 0.25 kg d.b./m\(^3\) of treated wastewater. Presents the quantities of municipal sewage sludge produced in Poland in the years 1999–2007 along with the anticipated amount in the future. According to the Polish Environmental Policy and the objectives of the National Waste Management Plan 2010 (NWMP) as well as the National Urban Wastewater Treatment Program (NUWTP) the quantity of sewage treated in Poland is systematically increasing. A measurable effect of this is, first of all, the increasing proportion of the population being served by waste water treatment, but also the growth of the amount of produced sewage sludge (and sewage).

On the basis of demographic projections, it is estimated that the quantity of sludge which will be produced in Poland between the years 2010 and 2018 will increase from 612.8 thousand tons (d.b.) to 706.6 thousand tons (d.b.). Currently, the predominant method for the
disposal of sewage sludge is its storage and agricultural application. Sewage sludge is deposited in landfill sites dedicated exclusively to this sludge, in lagoons or jointly with municipal waste. In terms of the commitments derived from the introduction of European Union (EU) Directives, this structure of sewage-sludge utilization in Poland is highly unfavorable. The main problems are the high percentage of stored sewage sludge and a lack of installations for its thermal utilization. Thermal processes can be used for the conversion of large quantities of sewage sludge (e.g., in large urban areas) into useful energy. Processes for thermal utilization of sludge can be developed at existing installations (e.g., heating plants, power plants, or cement plants) or in newly built facilities. Thermal methods of sewage-sludge utilization should be preceded by dehydration and drying of sludge. In Poland, 98% of municipal sewage-treatment plants use a biological treatment and among them 36% with enhanced biogenic removal. In the EU, 50% of sewage treatment plants have anaerobic digestion, 18% incorporate aerobic digestion and 4% lime stabilization, whereas 24% of the plants undertake no sludge stabilization; the same tendencies are observed in Poland (Werther and Ogada, 1995).

1.2. Waste Disposal Problem and Management

Rapid industrialization and population explosion in India has led to the migration of people from villages to cities, which generate thousands of tons of MSW daily. The MSW amount is expected to increase significantly in the near future as the country strives to attain an industrialized nation status by the year 2020. Poor collection and inadequate transportation are responsible for the accumulation of MSW (municipal solid waste) at every nook and corner. The management of MSW is going through a critical phase, due to the unavailability of suitable facilities to treat and dispose of the larger amount of MSW generated daily in metropolitan cities. Unscientific disposal causes an adverse impact on all components of the environment and human health (Sharholy et al., 2005). Generally, MSW is disposed of in
low-lying areas without taking any precautions or operational controls. Therefore, MSWM (municipal solid waste management) is one of the major environmental problems of Indian megacities. It involves activities associated with generation, storage, collection, transfer and transport, processing and disposal of solid wastes. But, in most cities, the MSWM system comprises only four activities, i.e., waste generation, collection, transportation, and disposal. The management of MSW requires proper infrastructure, maintenance and upgrade for all activities. This becomes increasingly expensive and complex due to the continuous and unplanned growth of urban centers. The difficulties in providing the desired level of public service in the urban centers are often attributed to the poor financial status of the managing municipal corporations (Mor et al., 2006; Siddiqui et al., 2006; Raje et al., 2001; Ahsan 1999).

1.3 Methods of Waste Disposal

There is a strong demand for environmentally safe reuse and effective disposal methods for sludge due to the increasing amount of sludge generated by the wastewater treatment plants in Taiwan. While sanitary landfills are commonly used for disposal or sewage sludge in Taiwan, rapid urbanization has made it increasingly difficult to find suitable landfill sites. Therefore, incineration has become one of the few alternatives available for disposal of sewage sludge. The ultimate disposal of incinerated sludge ash can be accomplished by using it as engineering construction materials. Use of sludge as construction and building material converts the waste into useful products that can alleviate the disposal problems (Tay and Show 1999). The use of digested sludge mixed with limestone powder to produce a “biocement” has been proposed by (Tay and Show 1993). Several studies have shown that sludge or sludge ash could blend with clay to produce brick (Tay 1987; Alleman et al., 1990; Trauner 1993; Okuno and Takahashi 1997; Wiebusch and Seyfried 1997) that both oven-dried sludge and incinerated sludge ash could be used as brickmaking materials.
He reported that the dried sludge in the mixture might create uneven surfaces when the organic component was burned off during the firing process. The results indicated that the maximum amount of sludge ash for brick making is 50% by weight. Up to 10% ash could be added to the bricks to produce the strength of equivalent normal clay bricks. In order to obtain the suitable manufacturing conditions, the proportion of sludge ash in the brick and the firing temperature that might affect the qualities of bricks.

1.4 Types of Waste

1.4.1 Sewage Sludge

Sewage sludge is a by-product from wastewater treatment plants, and contains significant amounts of heavy metals, organic toxins and pathogenic microorganisms, which are considered to be harmful to the environment and all living organisms (Jindarom et al., 2007). There has been a significant increase in sewage sludge generation from wastewater treatment plants over the past decades due to the major limitations in wastewater disposal and the increase in the percentage of households connected to central treatment plants. An alternative practice for the management of sewage sludge is its composting in order to produce an end-product with added value. In India, the informal sector and secondary industries recycle 15–20% of solid wastes in various building components (Pappu et al., 2007).

1.4.2 Waste from Steel Slag

Slag is the molten by-product or coproduct of many metallurgi operations, that is subsequently cooled (air, pelletized, foamed or granulated) for use or unfortunately in too many cases, disposal. Ferrous (iron and steel) and nonferrous (copper and nickel for instance) metals are the most commonly used, world-wide as structural and functional materials. The resulting large quantities of slags produced and their potential impact on the environment have prompted materials scientists and civil engineers to explore the technically sound, cost-
effective and environmentally acceptable use of a wide range of slags in civil and highway construction. The use of steel slag to replace natural aggregate in concrete is initially based on consideration of availability of natural resources and the good characteristics of steel slag. In nature, the resources of natural mineral aggregates of high engineering quality which can be used ultimately will become exhausted. In Japan, the proposition of natural mineral aggregates in concrete diminishes year by year and is being replaced by artificial aggregates and industrial by-product. In US, shortages of high quality natural aggregates have been experienced in number of areas and the resources are becoming less accessible. Steel slag possesses good physical properties which can be utilized in construction to enhance the characteristics of end products. In contrast to blast furnace slag, which is volumetrically stable and straight forward in its construction uses, steel slag contains hydratable oxides (CaO and/or MgO) that can result in volumetric instability (expansion) that must be dealt with through appropriate steel slag aging and quality control, especially appropriate testing to ensure its appropriate use in construction. Particular care must be taken to prevent potential steel slag expansive behaviour in confined applications, Portland cement concrete, for instance. In the last 30 years, researches have been conducted on steel slag use as aggregates in concrete and its advantageous properties have been reported (Kawamura, 1983; Montgomery and Wang, 1991; Maslehuddin et al., 2003; Manso et al., 2006; Li et al., 2009). However, a technical opinion unsupported by thorough characterization and performance testing is not sufficient to encourage the use of a steel slag in the construction industry without misgivings or concerns. The reason for steel slag not currently being fully utilized is often due to a general lack of quantification work on the properties of steel slag (expansion potential for instance) and the performance required for the end products. Appropriate test method to quantify the expansive properties of steel slag is the first and important step to develop technical guidance, criteria and specifications for practical utilization of steel slag in
concrete construction. The current ASTM standard test method for potential expansion of steel slag aggregate from hydration gives the method to determine the volume expansion of steel slag aggregate that can be used to evaluate the use of steel slag as an unbound granular material. However the volume expansion data are not directly related to the expansion behavior of steel slag under confined conditions such as in Portland cement concrete. In order to use steel slag as an aggregate in concrete, expansion force of steel slag during its hydration reaction should be considered and measured.

1.4.3. Municipal Solid Waste

Annually, Asia alone generates 4.4 billion tonnes of solid wastes and MSW comprise 790 million tones (MT) of which about 48 (6%) MT is generated in India. By the year 2047, MSW generation in India, is expected to reach 300 MT and land requirement for disposal of this waste would be 169.6 km² as against which only 20.2 km² were occupied in 1997 for management of 48 MT. Traditionally materials like clay, sand, stone, gravels, brick, cement, block, distemper, paint, timber, and steel are being used as major building components in construction sector. All these materials have been produced from the existing natural resources and will have intrinsic distinctiveness for damaging the environment due to their continuous exploitation. Nevertheless, during the process of manufacturing various building materials, especially decomposition of calcium carbonate, lime and cement manufacturing, high concentration of carbon monoxide, oxides of sulphur, oxides of nitrogen and suspended particulate matter are invariably emitted in the atmosphere. Exposure to such toxic gases escaping into the environment does lead to major contamination of air, water, soil, flora, fauna, and aquatic life and finally influences human health and their living conditions. The cost of construction materials is increasing incrementally. In India, the cost of cement during 1995 was Rs. 1.25/kg and in 2005 the price increased three times. In case of bricks the price was Rs. 0.66 per brick in 1995 and the present rate is Rs. 1.9 per brick. Similarly, over a
period of 10 years from the year 1995 the price of sand has increased four times. Also due to high transportation costs of these raw materials, demand, environmental restrictions, it is essential to find functional substitutes for conventional building materials in the construction industry. In view of the importance of saving of energy and conservation of resources, efficient recycling of all these solid wastes is now a global concern requiring extensive R&D work towards exploring newer applications and maximizing use of existing technologies for a sustainable and environmentally sound management. As a result, in India, the informal sector and secondary industries recycle 15-20% of solid wastes in various building components (Shekdar et al., 2004; Bhattacharyya et al., 2004).

1.4.4. Construction and Demolition Waste (CDW)

Construction and Demolition Waste (CDW) is produced from the construction, renovation, repair and demolition of technical structures, such as residential and commercial buildings, roads, bridges, etc. The composition of CDW varies for these different activities and structures. CDW often contains bulky and heavy materials, including concrete, wood (from buildings), asphalt (from roads and roofing shingles), gypsum (the main component of drywall), metals, bricks, glass, plastics, salvaged building components (doors, windows, and plumbing fixtures), earth and rock from clearing sites. More importantly, CDW may contain hazardous materials, such as asbestos and heavy metals. All these different materials need to be managed in an environmentally sound and economic feasible manner. Construction industry is probably one of most significant fields on a global scale, with respect to its economic, technological, and environmental impact. In the European Union (EU-25), there are about 2.3 million construction companies, contributing 9.8% to the overall GDP and employing around 12 million people, which account for 7.1% of the total European workforce. The rapid growth of the construction industry worldwide has resulted to an enormous increase of the produced CDW globally. In particular, CDW constitutes the largest
stream within the EU accounting for more than 450 million tonnes per year. Excluding earth and excavated road material, the amount of CDW generated is estimated to be roughly 180 million tonnes per year. Despite the significance of this particular waste stream, in many countries there is still a lack of accurate information on the field, as CDW is not studied separately from the rest municipal solid waste (MSW). Up to recently, the most common practice in the field of CDW management was to discard all waste materials and debris to landfills, frequently in the same landfills that were used for the disposal of MSW (Garrido et al., 2005). This practice cannot in any case be considered as a proper management practice for end-of-life building materials. Even worse, there are many cases reported where CDW ended up in uncontrolled open dumps, not taking into account the severe burden imposed upon the environment (Fatta et al., 2003). The environmental and health impacts of such disposal and treatment methods for CDW include apart from the aesthetic degradation, soil and water contamination, air pollution as a result of resulting fires, reduced land and property values, destruction of open spaces and landscape blight. In addition, heaps of CDW may include asbestos waste, which poses a significant health risk, especially in building sites which are later converted into playgrounds and residential buildings. The aforementioned practice has expanded to all the stages of building materials’ lifecycles; production, construction, use, but most significantly their end of life management majority of existing buildings in modern cities have not been designed so that building materials are reused or recycled at the end of their useful life. There are already many countries that have recognised the problem and the significance of environmentally sound CDW management. However, changes still occur in a rather slow pace (Moussiopoulos et al., 2007). To date, a lot of effort has been directed towards assessing multiple criteria in several thematic areas in the field of building environment, such as the identification of available end of life building materials reuse options, improvements in the building’s life cycle performance through their better
design (Wang et al., 2005b), or overall eco-efficiency evaluation of technical structures (Li et al., 2010). However, CDW optimal end of life management constitutes also a critical issue for building materials’ life cycle, and consequently minimising environmental impacts of uncontrolled discard would substantially reinforce sustainability in the building environment.

Adequate infrastructure is a prerequisite and one of the most crucial aspects of an efficient waste management scheme (Achillas et al., 2010). Taking into account the investment costs for the development of a reverse supply chain network, one of the vital aspects for any CDW collective take-back and recycling scheme relates to the required Units of Alternative Management (UAMs).

In the material to follow, a multicriteria assessment aiming towards optimal location of UAMs is developed and demonstrated, combining environmental, economical and social criteria, in an effort to interlace local acceptance and financial viability. In contrast to the majority of the currently employed methodologies, the presented creates a tractable interface between mathematical modelling and policy making since the Multicriteria Methodology Framework (MMF) enables the evaluation of sites for the location of CDW management facilities in terms of their combined impact on environmental, social and economic aspects of alternative scenarios. In addition, waste management models have been thoroughly employed in the past, with a thorough review to be presented in the work of Morrissey and Browne (Morrissey and Browne, 2004). Not withstanding the fact that it has been since early 1980’s that Ross and Soland stated that practical problems involving the location of public facilities are multicriteria problems and ought to be modelled as such, literature hardly studied the problem of special waste streams, such as CDW, focussing mostly on municipal solid waste management. In this light, emphasis needs to be given also to social criteria, e.g. Not In My Back Yard syndrome, which is often neglected (Morrissey and Browne, 2004).
The increased interest in multifunctional materials and structures is driven by the need for the development of new materials and structures that simultaneously perform (a) multiple structural functions, (b) combined non-structural and structural functions, or (c) both. One example of a multifunctional structure of type (a) would be a composite structure that has high strength, high stiffness, high fracture toughness and high damping. An example of type (b) would be a load-bearing structure that has the capability of providing its own noise and vibration control, self-repair, thermal insulation, and energy harvesting/storage, whereas an example of type (c) would be a structure combining the functions of both type (a) and type (b). Most of the recent developments in multifunctional materials and structures tend to be of type (b). Multifunctional materials are necessarily composite materials, and the strong growth in the use of composites has been greatly influenced by multifunctional design requirements. The traditional approach to the development of structures is to address the load-carrying function and other functional requirements separately, resulting in a suboptimal load-bearing structure with add-on attachments which perform the non-structural functions with the penalty of added weight. Recently, however, there has been increased interest in the development of load-bearing materials and structures which have integral non-load-bearing functions, guided by recent discoveries about how multifunctional biological systems work. Due to the interdisciplinary nature of multifunctional materials and structures, and the need to avoid duplication in the current review, it is appropriate to cite several relevant previous review articles.

Baur and Silverman (Baur and Silverman, 2007) reviewed the challenges and opportunities in multifunctional nano composite aerospace structures, while (Ye et al., 2005) reviewed developments in the application of artificial intelligence to functionalize composite air-frames. By definition, a multifunctional material must be a composite, and it is becoming increasingly apparent that nano-structured composites can produce and/or enhance
multifunctionality in ways that conventional composites could not. Thostenson et al. (2001) and Chou et al. (2010) reviewed recent advances related to the science and technology of carbon nanotubes and their composites; (Breuer and Sundararaj, 2004) reviewed recent studies on polymer/carbon nanotube composites; (Li et al., 2008) surveyed the recent advances related to the use of carbon nanotubes and their composites as sensors and actuators, while (Gibson et al., 2007) reviewed recent publications dealing with vibrations of carbon nanotubes and their composites, and (Sun et al., 2009) reviewed articles dealing with various types of energy absorption in nano composites. With the addition of very small amounts of carbon nanotubes, non-conducting polymers and polymer composites can be transformed to conducting materials, thus enhancing their multifunctionality. Accordingly (Bauhofer and Kovacs 2009) have reviewed relevant research on electrical percolation in carbon nanotube polymer composites. Modeling and analysis of functionally graded materials (FGM) have been reviewed by (Birman and Byrd, 2007). The field of structural health monitoring (SHM) is highly relevant here, and several review articles have appeared recently. Montalvao et al. (2006) reviewed vibration based SHM of composite materials, while a similar review with emphasis on composite delamination identification had been published earlier by Zou et al. (2000).

1.5. Waste treatment Materials

1.5.1 Structured Materials for waste treatment

One of the most innovative elements that have appeared in recent decades in the context of technologies for treating polluted effluents before their emission to the environment are the so-called structured materials (Cybulski and Moulijn, 1998). This is a new family of reaction systems whose open and ordered structure avoids the main problems of conventional packed bed reactors, which are the random and structural maldistributions that originate from the looser packing of particles near the reactor walls. This results in a
tendency to bypass the core of the bed, even if the initial distribution of fluid(s) is uniform, drastically altering its residence time from the design value. Among structured materials, honeycomb monoliths are by far the most popular adopted form, the literature devoted to them being really vast (Forzatti et al., 1998; Williams 2001; Heck et al., 2001; Toma and Sic, 2007). Consisting of continuous unitary structures that contain a large number of straight, identical, parallel channels, equally accessible to the contact with the flow, they have been found to be effective in the cleaning of exhaust gases from stationary and mobile sources. This is because they offer very low pressure drop, high resistance to plugging, and a high geometric area per unit volume, which make them very useful in solid catalyzed gas phase chemical reactions (Heck et al., 2001). They are extensively used in automotive and stationary emission control, but they are also increasingly used in many other applications, such as in chemical processing industries, catalytic combustion, pollution abatement of volatile organic chemicals, and oxidation of carbon monoxide and unburned hydrocarbons, among others. There is no doubt that over many years honeycomb monoliths have become the standard catalyst shape in most applications of environmental catalysis. In addition, more recently the application of monolithic catalysts has been proposed as an intensification method in some classical processes of the industrial chemistry. In fact, the adoption of structured catalysts with highly conductive supports makes it possible to remove (in the case of exothermic processes) or supply (in the case of endothermic processes) the heat of reaction easily, allowing these processes to be carried out on an industrial scale with small temperature gradients both in the axial and in the radial direction, with specific productivity similar to or higher than conventional reactors (Cristiani et al., 2009).

Nowadays, the interest of the scientific community in this kind of materials is so evident that an international conference specifically focused on structured catalysts and reactors is held on a regular basis. From the very beginning of their use in technological
applications, their rheological properties have made clays and clay minerals ideal raw materials for preparing structured supports and catalysts (Gippini 1979; Benbow and Bridgwater, 1993; Graczyk and Gleissie, 1990) being a better alternative to metallic ones. However, most of the work performed in this regard has dealt with the production of the very well known synthetic ceramic called “cordierite” (Forzatti et al., 1998; Williams, 2001; Komova, 2007).

(i) Composition of structured materials

Compositions based on this material, 2MgO·2Al₂O₃·5SiO₂, possess a unique combination of several critical characteristics: (a) thermal shock resistance due to a low thermal expansion coefficient; (b) porosity and pore size distribution suitable for ease of wash coat application and good wash coat adherence; (c) sufficient refractoriness because the melting point exceeds 1450°C; (d) sufficient strength for survival in an automotive exhaust environment; and compatibility with wash coat and catalysts. In particular, cordierites are the source of inspiration for patents. Nevertheless, from the processing perspective, cordierite substrates are clay based structured materials with a high energy demand as they are the result of firing previously moulded ceramic pastes at very high temperatures (usually above 1300°C). Moreover, these pastes are basically prepared from a mixture of talc with alumina to which clays are just added to favour the extrusion process. In a similar way, there are many studies in which clays, although part of a structured support, are not the majority component but mere binders to shape other materials into ceramic bodies. The list of these materials is long and includes carbon, mainly activated (Yates et al., 2002; Yates et al., 2003) but also in the form of coals (Gatica et al., 2004), carbon black (Mitchell et al., 2008) and even carbon fibres (Oku, 1991), TiO₂ (Yurchenko et al., 1997; Ismagilov et al., 2001; Ismagilov et al., 2001; Ismagilov et al., 2003), Al₂O₃ (Ismagilov et al., 1997), zeolites (Li et al., 2001; Madhusoodana et al., 2005), mullite (Song et al., 2003), SiC, Al₂O₃–SiO₂ (Ismagilov et al.,
2001; Barannik, 1997), ZrSiO₄ (Haenel and Kaiser 2005), FeTiO₃ (Yoshimoto et al., 1990), B₂O₃ (Yamaguchi and Wakabayashi, 1993), Fe₂O₃–Cr₂O₃ (Yokota and Arai, 1987), Al₂TiO₅, LiAlSi₄O₁₀ (Chijiiwa, 2003), etc. The purpose of this review is to show a broader reality that extends beyond the limits of these materials and, in general, of cordierites. They present a selection of cases of clay based structured materials in which clays are the main component, both from the compositional and functional viewpoint. First, the most common procedures to prepare them are briefly described. Then their application in environmental uses is discussed, putting the emphasis on the key role played by the clayey fraction of the structure. The plastic properties of clays make them very appropriate materials for processing through extrusion, i.e. to elaborate pastes that can be first forced in a press to pass through a die to acquire a determined geometry, and then, after appropriate subsequent drying and heating treatments, become rigid solids with good physicochemical properties (Benbow et al., 1998; Yashnik et al., 2005). Therefore, it is not surprising that screw type or hydraulic piston extruders are used to shape clays into structured materials. Moreover, although it depends on the die used, supports with many different configurations can be shaped, such as disks or pellets (Rodriguez and Hernandez, 1999; Kawasaki, 1993). Nevertheless, honeycomb monoliths are the typical form adopted for claybased extrudates due to their inherent advantages, (Yokota and Arai, 1987; Yashnik et al., 2005; Harti et al., 2009). On the other hand, the preparation of structured materials by extrusion is a much more complex process than it may appear at first sigh (Avila et al., 2005). It comprises more steps than the mere shaping mentioned above, and each step influences the quality of the final material. Therefore, it is important to know the correlations between process parameters and the relevant properties of the catalysts or of the catalyst substrates that can be obtained as resulting products (Yashnik et al., 2005). This is particularly true for extruded monolithic ceramic catalysts if we consider that the precision required for these materials may be in the range of microns, which is much higher than that of
traditional items that are also formed by extrusion of ceramic pastes, such as bricks and pipes.

According to the extensive description in literature (Williams, 2001; Avila et al., 2005), the fabrication of ceramic extrudates in general can be summarized in the five following consecutive steps: (i) dry mixing of the solid raw materials; (ii) wet mixing and plasticizing with water and additives; (iii) extrusion of the paste; (iv) drying uniformly; and (v) calcining at high temperatures. In the particular case of honeycomb monoliths, the structures can be prepared with many different types of cross section and channel shape, although the most typically manufactured are circular and square. Also remarkable, in the case of clays as raw material to be extruded, it is that additives are not always necessary. Sometimes extrusion can be achieved with just water (Chafik et al., 2009 & 2007), which implies significant cost reduction, not only in terms of additives and solvents, but also the energy consumption required for further elimination by thermal treatment (step v). In this regard, it is also important to note that the preparation of non cordierite clay based honeycombs does not require severe final firing either.

The thermal treatment determines their operational properties such as mechanical strength, specific surface area and pore structure. So, although it may change depending on the application, calcination can be performed at much lower temperatures than those employed to synthesize cordierite, for example: 210 °C, 240 °C (Mendioroz et al., 1999), 440 °C (Cifredo et al., 2010), 450 °C (Ariga, 1997), 500 °C (Mohino et al., 2005; Mohino et al., 2005; RosaBrussin et al., 2003) or 650 °C (Bahamonde et al., 2001). As it is not always easy to find the adequate conditions for extrusion, especially when this is performed with a new material, preliminary studies should be developed to avoid a trial and error methodology (Mohino et al., 2005). In this sense, one of the simplest strategies reported is Casagrande's technique (Gippini, 1979). This enables the extrudability of the paste to be predicted by just measuring two parameters known as liquid limit and plasticity index (Gatica et al., 2004;
The methodology is also clearly much simpler than other methods based on capillary rheometry and/or structure mechanical characteristics, which are used to investigate the formability behaviour of ceramic pastes (Yurchenko et al., 1997). Another refinement of the extrusion process consists of improving the final textural properties of the extrudates. In this regard, although acid activation is the conventional method employed to activate clays (Christidis et al., 1997; Korichi et al., 2009), in the case of clay honeycomb monoliths, attractive alternatives have recently been proposed, such as doping the clay with carbon in the first step and burning off the carbon after extrusion to create a new porosity network (Rodriguez-Izquierdo et al., 2009). This author has prepared composite honeycomb monoliths by coextrusion of clays and alumina–silica finding that definite porosity control can be achieved as a function of the relative composition selected—3/2, 2/3 or 1/1. A monodisperse pore structure with extremely different pore radii or a desired bimodal pore structure can be obtained. Similar results, i.e. control of porous structures in a monolithic support without burning additives but by a variation of the ratio between the matrix materials, have been obtained by extruding Al₂O₃ with clay (Ismagilov et al., 1997). In both cases, the resulting materials were consequently proposed as being of interest for application in membranes.

(ii) Foams Clay-based structured materials

Foams Clay-based structured materials can also be prepared in the form of foam (Carty and Lednor, 1996; Buciuman and Kraushaar, 2003; Vasquez et al., 2008). These are three-dimensional cellular structures in which the cells are connected by open windows, giving high porosity with 80–90% void space. These materials, also referred to as reticulated foams and which were originally developed three decades ago to filter out impurities from molten metals, can also be highly suitable catalytic carriers when a low pressure drop is mandatory (Buciuman and Kraushaar, 2003). In fact, foams possess certain advantages with respect to
the honeycombs: the possibility of a much wider range of shapes due to their preparation method; more tortuous porosity, which improves reactant mixing, and favours surface reactions; and significantly improved radial transport within the monolith. The main disadvantage is their weakness, and that is precisely the reason why, contrary to honeycombs, sintering at high temperature is systematically applied and a real ceramic obtained in all cases. Nevertheless, new processing techniques are continuously being assayed to improve their strength (Carty and Lednor, 1996). There are several ways to manufacture ceramic foams. Among these, the polymer sponge replication method is used mostly as it is suitable for making foams with easily accessible open cells (Vásquez et al., 2008). The method consists of coating an elastic open cell polymer sponge with a slip containing the precursors of the ceramic material together with other additives. Coating is achieved by immersing the polymer sponge in to the slip, expelling the excess (e.g. by compression), and drying. Subsequently, the green body is exposed to temperature treatment. In a first stage, the organic skeleton is burned off in air. At temperatures above 1400°C, the particles forming the ceramic replica are sintered. The cell size of the finished foam depends on the so-called pore count of the original polymer sponge and the degree of shrinkage during the drying and sintering of the green body. The phase composition of the ceramic is established by choosing the appropriate combination of raw materials and sintering temperature. As with honeycombs, foams can also be modified, for instance coating them with oxide layers to increase their surface area or to alter the chemical nature of the surface (Carty and Lednor, 1996). Others besides the two major methods above described, other options can be adopted to obtain clay based structured materials. One of them consists of depositing the clay over a preformed metallic (Martinez et al., 2009) or ceramic (Xu et al., 2006; Sakata et al., 1999) honeycomb to obtain what is called a claycoated monolith, to differentiate it from the integral clay monoliths mentioned before. Coatedtype monoliths are preferred when a substrate with a
low surface area but high thermal stability is used so the film of clay coating permits the better further dispersion of an active phase for catalysis, while also possessing certain functionality by itself (Avila et al., 2005). Although there are different procedures for incorporating a phase to a structured support (Cybulski and Moulijn, 1998; Avila et al., 2005), the most common is wet impregnation, also known as the wash coating method. This is normally selected due to its ease of use, the better control of the total amount of phase incorporated and the lower preparation time needed. This method is based on the adhesion of the phase dispersed in slurry on the monolithic surface.

First, a stable aqueous suspension is prepared, by dispersing the right amount of clay containing solid in deionised water and submitting the mixture to ultrasound for several hours. Then, a cationic polymer in aqueous solution is added to the suspension to improve its stability. The mixture is kept under vigorous stirring for about 24 h after which the monolith is immersed in it for approximately 1 min and withdrawn at a constant speed. The excess of colloidal solution is removed by centrifugation (e.g. 400 rpm for 10 min). Then, the monolith is dried (typically at 120°C during 1 h) and finally calcined at mild temperature (e.g. 400°C for 2 h). To increase the amount of phase loaded on the monolith, successive coating, drying and calcination procedures can be carried out. Finally, in the last few years, a very interesting new family of materials with a controllable structure, the so called clay aerogels (Wan and Zhang 2009; Bandi et al., 2005; Arndt et al., 2007), have emerged abruptly in clay literature. They are synthesized by a method that comprises four steps: (i) a stable dispersed clay suspension is prepared; (ii) one or a mixture of amination polyhedral oligomeric silsesquioxane, alkyl ammonium salt and alkylphosphonium salt is added as an intercalation modifier (iii) a clay gel solution with modified intercalation is obtained through ion exchange reaction, and (iv) a freeze drying technique or supercritical drying technology is used to directly carry out drying treatment on the clay gel solution to obtain the clay aerogel This has
the characteristics of large interlayer spacing (1–4 nm), a high porosity factor (50–80%), and a large specific surface area (100–800 m² g⁻¹), and can be used as a catalyst carrier or filling, and for insulating and sound proof materials. By adjusting parameters such as the variety and dosage of the modifier, the acidity–basicity of the gel, the synthesis process, and so on, the method can effectively adjust and control the structure, porosity factor, thermal stability and surface activity of the clay aerogel so as to meet different application requirements. Meanwhile, the preparation process is simple and does not pollute the environment, as well as being suitable for industrial production. As can be deduced, although many clay minerals are present in the formulation of structured materials, montmorillonites are perhaps the most versatile type of clays. In their Ca and Na forms they are especially attractive for obtaining honeycombs by extrusion as they show no defects during drying (Gippini, 1979; Ismagilov et al., 2001). In general, bentonites ensure monoliths have good radial crushing properties because their fibres are oriented in the direction of the extrusion. Moreover, associated to their layer charge, their influence on the viscosity of the ceramic paste can be finely controlled by pH (Forzatti et al., 1998). Montmorillonites are also ideal for producing aerogels due to their hydrophilic ordered nature that permits good and stable dispersion and the ability to exfoliate in the polymer used for the synthesis. On the other hand, kaolinites are the most typically employed clays to create ceramic foams as they sinterize at very high temperatures so enhancing mechanical resistance, one of intrinsic weaknesses of these structures (Gippini, 1979; Carty and Lednor, 1996). They are becoming more competitive in relation to other ceramic foams based on cordierite, mullite, Al₂O₃, SiO₂ or ZrO₂ (Leonov et al., 1997). Environmental applications adsorption several studies have shown that noncordierite claybased structured materials can be good adsorbents of different pollutants, both in gas and liquid phase.
The relationship between clays, health and environment is as ancient as it is diverse (Bergaya et al., 2006). For a very long time, these materials have been known to be beneficial to human health due to their characteristic surface properties, such as large specific surface area compared with other natural resources, their layer charge, and swelling capacity. As a result, they have been extensively employed as active principles, or as excipients in pharmaceutical formulations, spas, and aesthetic medicine. Being good adsorbents and mucostabilizers, clay minerals are also useful as drugs in the treatment of intestinal disorders. Furthermore, as recognition of the need to develop technologies for pollution control grew worldwide, new applications were found for them in this field, because of their large propensity for adsorbing and immobilizing extraneous species. Summarizes the most classic applications reported for clays in environmental protection, which are mainly, although not exclusively, related to pollute soil and wastewater treatments. Nowadays, due to their abundance and low cost, clays are also used in atmospheric pollution control. In this sense, an example of their ever growing versatility is that some clay has recently been proposed as good candidates for CO₂ sequestration to reduce the greenhouse effect (Azzouz et al., 2010).

1.5.2. Parameters for controlling the materials properties

A description was provided of the manufacturing conditions (paste composition) under which the resulting extruded materials offer the proper combination of physicochemical and mechanical properties to be used as catalysts or catalytic supports. Some characterization techniques were used to control the materials' properties throughout the successive steps of preparation. Special attention was given to axial crushing strength testing in order to know the changes in the mechanical properties of the monoliths with temperature and pH. The influence of these parameters was studied bearing in mind the use of the monoliths as catalysts carriers, which require a certain contact with the solutions in which the element to be incorporated is dissolved, and also considering the subsequent
thermal treatment needed to activate the supported phase. Surface areas above 220 m²g⁻¹ and crushing strengths above 180 m²cm⁻² were preserved in the 2.5–9.5 pH range and at temperatures up to 500°C when the proper combination of ceramic paste components, for AlPILC/ bentonite/water, and the applied thermal treatment were used to manufacture the monoliths. After impregnation of the PILC monolithic supports with different noble metals, such as Rh, Pd or Pt (0.6 wt. %) (Bahamonde et al., 2001) performed activity tests on the SCR of NO reaction in the presence of oxygen (1.2 vol %). The influence of the reaction temperature (300–500°C) on methane (reducing agent) and nitric oxide molar conversions was analyzed. Other operating conditions were an initial NO concentration of 500 ppm and total flow of 3600 cm³ min⁻¹. A comparative study with zirconia based monolithic supports was carried out, trying to correlate the catalytic activity with the physicochemical properties of the catalysts. The results obtained indicated that structure and surface acidity of the support plays an important role in the selectivity to NO reduction, although properties such as the surface area or pore volume could also determine the overall activity of the monolithic catalysts. In further research (Mohino et al., 2005) the same group performed a more in depth study of the catalytic system described above by using the same raw material used to synthesize the pillared clays during the preparation of the monolithic support as a permanent inorganic binder. The authors observed that this confers high surface area and acidity to the extrudates, in addition to high hydrothermal resistance and mechanical strength. The influence of the method used for active phase incorporation on the physicochemical properties and DeNOx activity and selectivity was also studied. Conclusions were drawn from the use of different solution pH values (2.7–9.5) and precursors (acetate or chloride) of the noble metal (Pd, 0.2–0.6 wt %) in relation to the isoelectric point of the solid. The contribution of to the application of claybased honeycomb monoliths for the oxidation of VOCs (RosaBrussin et al., 2003; RosaBrussin et al., 2005) is also remarkable. Starting from
natural clay mixtures from Venezuela containing vermiculite, chlorite, muscovite and plagioclase, the authors extruded monoliths of 2–6 cm in length with square shaped channels. To do this, pastes with alumina (30 wt %) and the right amount of water to obtain plasticity of the material were first prepared. The resulting monoliths were dried at 110°C and then calcined in air at 500°C for 5 h. Then the monoliths were coimpregnated with aqueous solutions of salts from transition metals such as Pt, Pd, Fe and Cu. The first two were introduced to act as active phases and the two latter as promoters. In particular, three series of bimetallic catalytic monoliths were prepared, each with two different metal compositions: PtFe (0.24–4.00 and 0.13–3.50 wt. %), Pd, Fe (0.16–3.50 and 0.03–4.44 wt %), and Pt, Cu (0.17–0.19 and 0.12–0.22 wt %). Scanning Electron Microscopy (SEM), used to evaluate possible Pt Fe and Pd Fe interactions, confirmed the coexistence of these bimetallic pairs (RosaBrussin et al., 2003). Subsequently (RosaBrussin et al., 2005) the oxidation activity of the monoliths was tested under dynamic conditions in the presence of acetone, toluene, chlorobenzene, trichloroethylene and tetra chloroethylene. At the same time, a comparison with catalysts based on perovskitetype mixed oxides containing variable amounts of La, Sr, Mn and Co supported over the same clay monoliths was studied at the 150–300°C temperature interval. For the noble metal based catalysts, Pt crystals were found to be relatively large but well dispersed over the monoliths' channel walls. On the other hand, for perovskite based catalysts, a specific activity pattern was observed for complete toluene oxidation being the most active. Finally, the authors compared the catalytic activity of the structured bimetallic catalysts Pt Fe, Pd Fe and Pt Cu in the oxidation of toluene and ethyl acetate. VOC concentrations were 2400 ppm for toluene and 8500 ppm for ethyl acetate. In the case of the latter, at relatively low temperatures partial oxidation products such as ethanol, ethers, acetic acid and acetaldehyde were formed, while oxidation was complete above 280°C. For PtFe catalysts, the influence of the catalytic bed size in the activity.
The longest monolith (6 cm) was the most efficient, reaching toluene conversion over 90%, at an elevated flow rate (230 cm$^3\text{min}^{-1}$) and lower temperatures (110 °C) than those of the Pd Fe and PtCu catalysts. The existence of extensive surface zones where Pt (or Pd) and Fe were associated was determined by the SEM (mapping) technique. Iron was found to improve dispersion of Pt micro crystals, and XPS results obtained for the Pt Fe catalyst indicated an electronic promoter effect between Pt and Fe. Clay coated honeycomb metallic monoliths have also proven to be useful as support for catalytic oxidation reactions. Martinez et al. (Korichi et al., 2009) used a commercial type natural bentonite from Colombia as starting clay. It was first pillared with iron and then coated with gold by the deposition-precipitation method originally developed by Tsubota and co-workers (Tsubota et al., 1995). The above solid was deposited over a preformed stainless steel (Fe Cr Alloy) monolith by rolling around a spindle alternate flat and corrugated sheets are evaluated (Avila et al., 2005). The metallic monolith was a 30mm high cylinder with a16 mm diameter and a cell density of 55 cellcm$^{-2}$. AlFe pillared bentonite and Au supported on Al, Fe pillared bentonite catalysts deposed on these Fe Cr Alloy monoliths were further characterized and tested in two oxidation reactions: gaseous oxidation of CO (in the range 25–400°C) and phenol oxidation in an aqueous medium (at room temperature and atmospheric pressure). For the former, a mixture was used containing 3.4% CO and 21% O$_2$ in Helium at a total flow rate of 42 ml min$^{-1}$. For the latter, a semi batch type reactor was loaded with 100 ml of phenol solution (5×10$^{-4}$ M) and a submerged monolith, bubbling air at room temperature at a constant flow (2l h$^{-1}$) with continuous stirring of the solution. A 0.1 M H$_2$O$_2$ solution was added at a rate of 2ml h$^{-1}$ during a reaction time of 4 h, with continuous adjustment of pH to 3.7 in order to improve the activity of iron species. This investigation was performed knowing previously that supporting gold on Fe and Al pillared clays results in a solid with an improved catalytic activity towards CO oxidation, due to the coexistence of active Fe and Au sites. However, no
similar study had yet been performed to make the most of this advantageous monolithic design. The authors found that deposition of the solid (with and without gold) on the metallic substrate does not alter its structural characteristics. Also, the use of monoliths improved the activity in the reactions, both in the gas phase (CO) and the liquid phase (phenol), with this improvement being more evident in the oxidation of phenol. In addition, the use of a structured support in the reaction taking place in aqueous medium offered the additional advantage of facilitating the separation of the catalyst from the reaction medium. Extrudates developed from Al Fe and Al Ce Fe pillared bentonites were shaped as pellets, Raschig rings and cylindrical honeycomb monoliths and tested as catalysts in the oxidation of phenol. Naor Cabentonite was also used as binder. The extruded pellets had a diameter of 1.96 mm and were cut to lengths of around 6 mm. The Raschig rings, with an internal diameter of 4.25 mm and an internal diameter of 1.96 mm, were also cut to a length of 6 mm. The cylindrical monoliths had an outside diameter of 16.25 mm, a wall thickness of 0.85 mm and square open channels of 1.72 mm. This gave a cell density of 11.7 celles cm$^{-2}$. These monoliths were cut to lengths of 15 mm. The mechanical stability of the extrudates, measured as breaking force, was evaluated as a function of thermal treatment (105, 400 and 500°C) together with the stability to water immersion. Calcination at 500°C was needed to obtain water stable materials. The specific surface area and the micro and mesopore volume of the extrudates depended on the calcination temperature as well. Regarding catalytic activity, the tests were performed at 25°C and atmospheric pressure in the following way: (i) in the case of pellets and Raschig rings, a glass thermo stated semibatch reactor, with 4 plastic mesh bas16 kets attached to a stainless steel shaft connected to a motor, was used; (ii) in the case of monoliths, these were packed between two layers of glass Raschig rings inside a fixed bed reactor with a phenol recirculation flow of 150 ml min$^{-1}$. For the reaction, 250 ml of a $5 \times 10^{-4}$ phenol solution, 2.08 g of extruded material and a solution of 0.1 M H$_2$O$_2$ (20 ml, 2.22 ml h$^{-1}$) was
used, adjusting the pH of the reacting medium to 3.7. The conversion rate for phenol oxidation of the extrudates was generally lower than for powders, due to an increased induction period and diffusion limitations. It was also lower than that reported (Martinez et al., 2009) for similar experimental conditions but it should be noted that clay, and no supported metal, was the active phase. As with adsorption applications, the use of noncordierite claybased structured materials in catalysis is also present in patented works. As an example, Yao and Kimble from the Conocophillips company in USA (Yao and Kimble, 2004) demonstrated that carbon monoxide can be selectively oxidized to carbon dioxide in a feed stream containing hydrogen over a catalyst based on platinum and iron (molar ratio from 0.5:1 to 4:1) supported on clay monoliths at 60–100°C. The deactivated Pt Fe catalyst was regenerated by increasing the temperature to 175–225°C.

The construction, use and demolition of buildings are sources of a significant part of human-induced environmental burden (Levine et al., 2007). In the EU-25 countries, 70% of the existing housing stock was built before 1980 and 23% before 1945. In 2004, an average of approximately 1% of the existing housing stock was newly built, while up to 0.75% of the existing stock was demolished (Itard et al., 2008). On average, about 100 times more houses are in use than are built annually, meaning that the existing housing stock is both slowly growing and ageing. Moreover, the energy efficiency of the existing housing stock is, on average, lower than that of new housing (Itard et al., 2008; Beerepoot, 2007). Thus, in order to lessen the annual negative impact of housing on the environment, it would be more efficient to improve the environmental quality of the existing housing stock than to focus only on new houses. The IPCC report on climate change (Levine et al., 2007; Treloar et al., 2000) stress that when analysing a building’s energy use over its lifespan it is important to take the building’s operational phase and its inhabitants’ activities into account. During the operational phase of dwellings, negative environmental impact results from activities such
as maintenance, the replacement of building components and energy used for both climate control and household appliances. The magnitude of the impact depends on physical building characteristics such as applied building services and materials, as well as other factors such as the rate of deterioration and maintenance activities. Activities that take place frequently but have a low environmental impact themselves may still contribute significantly to the total environmental impact in the use phase of dwellings due to their high rate of occurrence. High impact activities that occur only during the service life of a building may also contribute significantly.

Recent developments in self-healing polymeric materials were reviewed by Wu et al. (2008). Articles on energy harvesting for sensor networks in SHM were reviewed by (Park et al., 2008). Piezoelectric materials are often utilized for energy harvesting, and publications on this topic have been reviewed by (Sodano et al., 2004; Anton and Sodano, 2007; Cook-Chennault et al., 2008). Closely related to SHM is the study of shape memory polymers (SMP), and reviews of recent advances in SMP have been published by (Ratna and Karger-Kocsis 2008; Gibson et al., 2008) edited the Proceedings of the 2008 SAMPE Fall Technical Conference entitled “Multifunctional Materials: Working Smarter Together”. (Lau et al., 2009) have archived selected papers from the 2008 International Conference on Multifunctional Materials and Structures (MFMS 08), which was held in Hong Kong.

1.6. Dye Removal by Adsorption

Dyes are widely used in different industrial area for colouring the final products in textile, leather, paper, and plastics industries. Disposal of dyes into receiving waters causes damage to the environment. In textile processing, a significant proportion of synthetic organic dyestuffs are released annually to waste streams, which eventually enter the environment. Elimination of dyes in the textile dying process is very difficult by conventional wastewater
treatment methods. These dyes are stable under the environmental effects, such as light, pH and microbial attack. Dye wastewaters are usually treated by physical or chemical processes including coagulation, flocculation, biosorption, ultrafiltration, oxidation and ozonation, etc. (Gulnaz et al., 2006). Among them, the adsorption techniques have been shown to be a reasonable way to treat textile dyeing effluents. Dye adsorption is a process of transfer of dye molecule form bulk solution phase to the surface/interface. The adsorption of dyes at the solid-liquid interface plays an important role in much technological and industrial application. The solid-liquid interface is considered to develop a surface charge as a determining ions which give rise to positive, negative and for some system neutral surface sites. This would have the potential advantage of allowing recovery of the dyestuffs in concentrated form. The adsorption of dyes on different adsorbents has been studied in detail such as peat, chitin/chitosan. Polymeric adsorbent rice husk and various microbial biomasses used as adsorbent. Different types of low cost sewage sludge have been used as biosorbent for the removal of dye and metal ions from aqueous water.

1.7. Adsorbent Materials

1.7.1 Porous Adsorbent for adsorption of dye

Recently, research efforts have been directed towards the use of industrial waste as an adsorbent material in an attempt to minimize processing costs. The solid residue usually has a porous structure and surface area that is appropriate for use as an adsorbent. Adsorption capacity of a material depends not only on the porous structure of the adsorbent but also on its chemical structure.

1.7.2 Monolithic Adsorbents

Mendioroz et al. (Mendioroz et al., 1999) investigated mercury retrieval from flue gas by monolithic adsorbents based on sulphurized sepiolite. Sepiolite is a fibrous hydrated magnesium silicate clay that is very cheap (around D 75/ton) and abundant, with unique
textural and structural characteristics: SBET, 150–300m² g⁻¹; pore volume, 0.3–0.8cm³ g⁻¹; density, 0.8 g cm⁻³. Therefore, this material was presented as a cheaper alternative to sulphur-impregnated activated carbons, which are extremely costly sorbents in mercury control technologies. Samples of 10% S supported on monolithic sepiolite were used to retain 90ppm mercury in air at 47°C an ambient pressure. The honeycomb monoliths obtained were square channelled with a length of 9.5cm and wall width of 0.04cm as the main geometrical dimensions, and had a cell density of 34–43 cell cm⁻². The experimentation was carried out in a dynamic system at flow rates in the 600–3600 cm³ min⁻¹ range. A comparative study was performed of the performance of the monoliths against a fixed bed reactor of powders of 0.026cm in size, and kinetical equations were assessed, finding the process was governed by mass transfer, under the work conditions. The importance of the adsorbents’ texture and, consequently, of the preparative method for obtaining monoliths was also demonstrated. In particular, the samples’ capacity per mass unit was better when impregnation was the last preparation step because porosity was better preserved and the sulphur was more uniformly distributed. Chafik et al. (Chafik et al., 2009) tested honeycomb monoliths prepared from natural Moroccan clays on the adsorption of volatile organic compounds (VOCs). The raw material consisted of a mixture of mineral clays such as muscovite, kaolinite, vermiculite and illite, and, contrary to the authors’ previous experience with other clays (Harti et al., 2007) it was easily extruded without the need for chemical binders and plasticizers. This result itself was highlighted as possibly offering a significant economic impact in terms of feedstock additives and the energy needed for their elimination. In addition, it was found of interest because it fits the recent green chemistry concept, which is required more and more nowadays in production processes involving chemistry. Moreover, the extrusion and conformation of the monoliths into rigid structures was achieved through thermal drying at moderate temperatures, yielding geometrical strength and mechanical properties that might
be sufficient for VOC elimination by adsorption. The extruded monoliths presented the following geometric properties: square section of 13.7 cells cm$^{-2}$, wall thickness of 0.08 cm and geometric surface area of 10.4 cm$^2$ cm$^{-3}$ with an open frontal area of 49%. Besides their textural, structural and physicochemical characterization, the adsorptive behavior of the clay monoliths towards oxylene was evaluated. The experiments were carried out at room temperature under dynamic conditions using a flow stream of 100 cm$^3$ min$^{-1}$ containing 3600 ppm of pollutant.

The monoliths exhibited a total adsorption capacity around 150 mmol g$^{-1}$. According to the authors, although this result could not compete with those of activated carbon, the most common adsorbent for VOC removal, the use of clay monoliths allowed VOC retention with, mainly, physical adsorption, which permits easier solvent recovery and adsorbent regeneration with less energy consumption. It was also concluded that monoliths extrusion with narrower channels was still needed in order to enhance the overall adsorption efficiency in terms of breakthrough time. This might help us to benefit from the important advantage of clay monoliths over activated carbon adsorbents with respect to operational safety, as they enable the suppression of the fire hazard. More recently, the same authors (Cifredo et al., 2010; Rodriguezlzquierdo et al., 2009) investigated the capacity of clay honeycomb monoliths, with the same configuration as above, to adsorb methylene blue from aqueous solutions. In this case, the clay employed consisted of a Spanish mixture of sepiolite, montmorillonite, kaolinite and illitemuscovite. The experiments were performed in a homemade system in which lab scale monoliths were subjected at room temperature to a recirculated 1200 cm$^3$ min$^{-1}$ flow-of the solution initially containing 10 or 100 mg l$^{-1}$ of the pollutant. The study indicated that the adsorption capacity doubled or tripled in those honeycomb monoliths that had been prepared by mixing the clay with coal before the extrusion, and further removing the coal from the monoliths by heating them under air at a
temperature as low as 440°C. The mechanical resistance of the monoliths in aqueous solutions remained acceptable for liquid phase applications. Consequently, the process followed in this study to activate clay monoliths was proposed as an alternative to acid activation methodologies. In particular, the results were interesting for those applications in which the combination of the honeycomb monolithic design and improvement of macroporosity may represent an advantage. An analysis was performed of the efficiency of porous ceramic filters in the adsorption of heavy metals, lead, cadmium and chromium, present in urban residuals waters and dissolutions prepared in laboratories (Vasquez et al., 2008).

Filters of 3.3cm in length, 1.3cm wide and 0.5cm thick were elaborated from diatomite clay (50 wt.%) mixed with other urban and industrial wastes such as bone meal and limestone. The clay came from beer industry sludge and was selected as a low cost raw material for obtaining a final adsorbent with high porosity and thermo chemical stability while allowing the conformation into a rigid structure of a natural precursor of hydroxyapatite, a well known immobilizer of heavy metals. For the preparation, the authors used the polymeric sponge method to obtain porous structures, using polyurethane sponges with density of 14 and 20 kgm\(^{-3}\). Milling and homogenization of the suspensions were carried out in two stages, the first one at 500°C, to ensure elimination of polymeric substrates and organic additives, and then at 1200°C, the mixture sintering point. Retention tests of heavy metals were performed in batch conditions starting from initial concentrations in a 5–10 ppm range and monitoring the evolution with exposure time. A percentage of adsorption of 98.4% was found for the lead in treated residual waters, and of 99.6% for the lead, 93.2% for the cadmium and 18.0% for the chromium in the laboratory solutions. Also on the subject of patents, references can be found on the use of structured clays in adsorption applications. For instance, the Sharp Corporation in Japan (Ariga, 1997) developed ceramic materials
which acted as adsorbents for purification of air and water. In particular, the materials were manufactured from honeycomb structured ceramics containing kaolinitic clays (Kibushi type), fillers such as Al(OH)_3 (of about 1mm medium particle diameter), and additives for the extrusion such as aluminium primary phosphate. The structured clayey material was fabricated by kneading the three mentioned components (the first two in a weight ratio of 1:1 to 1:9), extruding the resulting paste and then firing the honeycomb monolith in air at 450°C for 2 h. The final product had a large specific surface area and strength, and was also useful as a catalyst support. Catalysis inspite of the examples mentioned above, and excepting cordierite, the use as catalyst supports is still probably the most common fate of clay based structured materials. In this regard, several different catalytic reactions in the area of environmental pollution control have been investigated. First it is worth noting the research carried out by Bahamonde et al. (Bahamonde et al., 2001; Mohino et al., 2005) on the use of pillared clay (PILC) based monolithic catalysts for selective catalytic reduction (SCR) of nitrogen oxides (NOx) by methane. This reaction was selected as noble metals on solid acids have previously shown much higher NOx reduction rates than mixed oxides or perovskites alone. Furthermore, it is known that, like zeolites, pillared interlayer clays offer considerable Bronsted acidity, in addition to residual exchange cations which can be exchanged by metal cations from the active phases. Also, it was considered that PILCs present a tailored pore structure, perfectly tunable by exchange, which can lead to a better active phase and reactant diffusion, and finally, depending on the pillaring agent, to improvements in water vapour and SO₂ resistance. In (Mohino et al., 2005) the authors introduced pillared clays, based on Spanish bentonites, as raw material to produce square cell honeycomb monoliths with a pitch of 3.54 mm, 0.90 mm wall thickness and a cell density of 8.9 cellcm^-2.
1.7.3 Activated Carbon as Adsorbents

Though commercially available activated carbon (CAC) are usually derived from natural materials such as biomass, lignite or coal, but almost any carbonaceous materials may be used as precursor for the preparation of carbon adsorbents (El-Qada et al., 2008; Stavropoulos and Zabaniotou 2005; Bestani et al., 2008; Iqbal and Ashiq 2007; Kannan and Sundaram 2001; Fernandes et al., 2007; Raposo et al., 2009; Basava Rao et al., 2006; Marungrueng and Pavasant 2007), because of its availability and cheapness, coal is the most commonly used precursor for activated carbon production. Coal is a mixture of carbonaceous and mineral materials, resulting from the degradation of plants. The sorption properties of each individual coal are determined by the nature of the original vegetation and the extent of the physical-chemical changes occurring after deposition. Coal based adsorbents have been used by (Karaca et al., 2004; El-Qada et al., 2008; Tamai et al., 1996; McKay et al., 1986) with success for dye removal. However, since coal is not a pure material, it has a variety of surface properties and thus different sorption properties. Biomass and other waste materials may also offer an inexpensive and renewable additional source of activated carbon. These waste materials have little or non economic value and often present a disposal problem. Therefore, there is a need to valorize these low cost by-products. So, their conversion into activated carbon would add economic value, help reduce the cost of waste disposal and most importantly provide a potentially inexpensive alternative to the existing commercial activated carbons. A wide variety of carbons have been prepared from biomass and other wastes, such as date pits (Marungrueng and Pavasant 2007), olive stones (Alaya et al., 1999), furniture, sewage char and tyres (SanizDiaz and Griffiths, 2000; Lin and Teng, 2002), vermiculata plant, bamboo dust, coconut shell, groundnut shell, rice husk and straw (Hameed et al., 2007a), polyvinylidenefluoride fibers (Yamashita et al., 2001), jute fiber (Senthilkumar et al., 2005), zeolite (Yan et al., 2009), coconut husk (Tamai et al., 1996), oil palm fiber (Tan
et al., 2007; Hameed et al., 2008d), waste apricot (Basar, 2006), corncob (Tseng et al., 2006), coir pith (Kavitha and Namisivayam, 2007), Pitch (Tamai et al., 1996), oliveseed waste, fir wood, rattan sawdust (Hameed et al., 2007a), bioplant of *Euphorbia rigida* (Hameed et al., 2007b), vetiver roots (Altenor et al., 2009), durian shell (Chandra et al., 2007), oil palm shell, sugars (Legouri et al., 2005), wheat bran (Ozer and Dursun, 2007), *Hevea brasiliensis* seed coat, peach stones (Attia et al., 2008), almond shell, walnut shell, hazelnut shell and apricot stones (Aygun et al., 2003) and *Rosa canina* seeds (Gurses et al., 2006).

The excellent ability and economic promise of the activated carbons prepared from biomass (Kannan and Sundaram, 2001) reported the adsorption capacities of 472.10 mg/g of activated carbons made from straw. However, the adsorption capacities of carbons depend upon the sources of the raw materials used, the history of its preparation and treatment conditions such as pyrolysis temperature and activation time. Many other factors can also affect the adsorption capacity in the same sorption conditions such as surface chemistry (heteroatom content), surface charge and pore structure. A suitable carbon should possess not only a porous texture, but also high surface area. Recently, (Guo et al., 2003) showed that the adsorption does not always increase with surface area. Besides the physical structure, the adsorption capacity of a given carbon is strongly influenced by the chemical nature of the surface. The acid and base character of a carbon also influences the nature of the dye isotherms. The adsorption capacity depends also on the accessibility of the pollutants to the inner surface of the adsorbent, which depends on their sizes. The specific sorption mechanisms through which the adsorption of dyes takes place on these adsorbents are still not clear. This is because adsorption is a complicated process and depends on several interactions such as electrostatic and/or non electrostatic (hydrophobic) interactions. Although much has
been accomplished in terms of sorption properties and kinetics, much work is still necessary to identify the sorption mechanisms clearly.

Activated carbon has been popular choice as an adsorbent for the removal of MB from wastewater but its high cost poses an economical problem. Therefore, there is a need for the development of low cost and easily available materials, which can be used more economically on large scale. Due to the problems mentioned above, research interest into the production of alternative adsorbents to replace the costly activated carbon has intensified in recent years. Attention has focused on various natural solid materials, which are able to remove MB from the contaminated wastewater at low cost. The cost is actually an important parameter for the comparison and selection of adsorbents. An adsorbent can be considered as low cost if it requires little processing and abundant in nature (Bailey et al., 1999). It may also be defined as a by-product or waste material from the industry and needs additional disposal cost. Certain waste products from industries and agricultural operations, natural materials and bio adsorbents represent potentially economical alternative adsorbents. Many of them have been tested and proposed for MB removal.

1.7.4 Hydrous Alumino Silicates Adsorbent

The clays are hydrous alumino silicates broadly defined as those minerals that make up the colloid fraction (<2 mm) of soils, sediments, rocks and water (Pinnavaia 1983) and may be composed of mixtures of fine grained clay minerals and clay sized crystals of other minerals such as quartz, carbonate and metal oxides. The clays invariably contain exchangeable ions on their surface and play important role in the environment by acting as a natural scavenger of pollutants by taking up cations and/or anions either through ion exchange or adsorption or both. These ions can be exchanged with other ions easily without affecting the structure of clay mineral (Bhattacharyya and Gupta 2008). Natural clay minerals are well known and familiar to mankind from the earliest days of civilization. Because of

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their low cost, abundance in most continents of the world, high sorption properties and potential for ion exchange, clay materials are strong adsorbents. They possess layered structure and are considered as host materials for the adsorbates and counter ions. Vermiculite clay has the largest surface area and the highest cation exchange capacity. Its current market price (about US$ 0.04–0.12/kg) is considered to be about 20 times cheaper than that of activated carbon (Babel and Kumiawan 2003). In recent years, there has been an increasing interest in utilizing clay minerals such as bentonite, kaolinite, diatomite and Fuller’s earth for their capacity to adsorb not only inorganic ions but also organic molecules. In particular, interactions between MB and clay particles have been extensively studied (McKay and Poots 1986; Atun et al., 2003 & 2009; Gurses et al., 2004; Shawabkeh and Tutunji 2003; Gucek et al., 2005; Hajjaji et al., 2006; Almeida et al., 2009; AlFutaisi et al., 2007; Bagane and Guiza 2000; AlGhouti et al., 2003; Weng and Pan 2007; Lee et al., 1997).

The clay minerals exhibit a strong affinity for MB. The adsorption of MB on clay minerals is mainly dominated by ionexchange processes. This means that the sorption capacity can vary strongly with pH. AlGhouti et al. (2003) showed that the mechanism of adsorption of dye onto diatomite is due to physiosorption (depending on the particle size) and the presence of electrostatic interactions (depending on the pH used). Relatively good removal capabilities of clays to uptake MB has been demonstrated by many researchers. Bagane and Guiza (Bagane and Guiza 2000) reported an adsorption capacity of 300 mg/g and suggested that clay is a good adsorbent for MB removal due to its high surface area. Almeida et al. (2009) studied the removal of MB from synthetic wastewater by using as montmorillonite and described it as an efficient adsorbent where the equilibrium was attained in less than 30 min. The adsorption of dyes on kaolinite was also studied by (Ghosh and Bhattacharyya 2002) and reported that its adsorption capacity can be improved by purification and by treatment with NaOH solution. The removal performances of Fuller’s
Earth and commercial activated carbon for MB were compared by (Atun et al., 2003). They showed that the adsorption capacity is greater of Fuller’s earth than that of CAC. Moreover, Fuller’s earth is an interesting adsorbent since its average price is US$ 0.04/kg whereas CAC costs US$ 20/kg. (Shawabkeh and Tutunji 2003) studied the adsorption of MB onto diatomaceous earth (diatomite). They showed that this naturally occurring material could substitute for activated carbon as an adsorbent due to its easy availability, low cost, and good sorption properties. Further, its adsorption isotherms revealed that adsorption equilibrium was reached within 10 min. The feasibility of using diatomite for the removal of the problematic reactive dyes was also investigated by (AlGhouti et al., 2003). The siliceous materials such as perlite, glass and zeolites have been proposed for MB dye removal. The use of natural siliceous adsorbents such as silica, glass fibers and perlite for waste water is increasing because of their high abundance, easy availability and low cost. Among inorganic materials, amorphous silica deserves particular attention (Woolard et al., 2002), considering chemical reactivity of their hydrophilic surface, resulting from the presence of silanol groups. Their porous texture, high surface area and mechanical stability also make them attractive as adsorbents for decontamination applications. However, due to their low resistance toward alkaline solutions their usage is limited to media of pH less than 8 (Ahmed and Ram 1992). Moreover, the surface of siliceous materials contains acidic silanol (among other surface groups) which causes a strong and often irreversible nonspecific adsorption. Perlite is a glassy volcanic rock and has high silica content, usually greater than 70%. It is inexpensive and easily available in many countries. The use of perlite as a lowcost adsorbent for the removal of MB has been investigated by (Dogan et al., 2000; Dogan et al., 2004). It was suggested that MB is physically adsorbed onto the perlite. However, perlites of different types (expanded and unexpanded) and of different origins have different properties because of the differences in composition. (Chakrabarti and Dutta 2005) investigated the glass fiber
for the adsorption of MB. They stated that a considerable amount of the dye is adsorbed on soft glass even at ambient temperature. Zeolites are highly porous aluminosilicates with different cavity structures. They consist of a three dimensional framework, having a negatively charged lattice. The electro neutrality is maintained by exchangeable counter ions. The characteristics and applications of zeolites have been reviewed by Ghobarkar et al. (1999). High ion exchange capacity and relatively high specific surface areas, and more importantly their relatively cheap prices, make zeolites more attractive adsorbents. Their price is about US$ 0.03–0.12/kg, depending on the quality of the mineral (Babel and Kurniawan 2003). Another advantage of zeolites over resins is their ion selectivities generated by their rigid porous structures. Woolard et al. (2002), converted fly ash into zeolitic products by the hydrothermal treatment of raw ash with base. The product was found to bear significantly increased surface area and cation exchange capacity in comparison to the raw ash. This product also shows increased affinity for sorption of cationic dyes when compared to the raw ash. It is, however, that this increase in sorption capacity is merely the result of the increase in surface area, rather than a specific interaction. Although the removal efficiency of zeolites for dyes may not be as good as that of clay materials, their easy availability and low cost may compensate for the associated drawbacks.

1.7.5 Bioadsorbents

The accumulation and concentration of dyes from aqueous solutions by the use of biological materials is termed bioadsorption. In this instance, biomass used as an adsorbents in order to concentrate and to remove MB dye from solutions. The bioadsorbents are often much more selective than traditional ionexchange resins and commercial activated carbons, and can reduce dye concentration to ppb levels. Bioadsorption is a novel approach, competitive, effective and cheap. Removal of MB dye by biomass (dead or living), fungi, algae and other microbial cultures was the subject of many recent researches. It has been
found that bioadsorbents derived from suitable algal biomass can be used for the effective removal of MB from aqueous solutions. The use of biomass for wastewater is increasing because of its availability in large quantities at low cost. Biomass has a high potential as an adsorbent due to its physicochemical characteristics. Recent literature on the methods of removal of MB from wastewater focuses on MB adsorption. Yu et al (2009) studied the poly (methacrylic acid) modified biomass of baker’s yeast to improve the adsorption capacity of MB. He also studied the poly (amic acid) modified biomass of baker’s yeast to improve the adsorption capacities for removal of MB. Experimental results showed that pH and ionic strength had little effect on the capacity of the modified biomass, indicating that the modified biomass had good potential for practical use. According to the Langmuir equation, the maximum uptake capacities for MB were 869.6 mg/g for poly (methacrylic acid) modified biomass of baker’s yeast and 680.3 mg/g for poly(amic acid)modified biomass of baker’s yeast respectively, which were 17 and 13 fold than that obtained on the unmodified biomass.

Fu and Viraraghavan (2000) demonstrated that in comparison with commercial activated carbon dead fungal biomass of Aspergillus niger is a promising biosorbents for MB dye removal. Waranusantigul et al. (2003) also reported the usefulness of biomass for the removal of MB. The biosorption capacity of fungal biomass could be increased by some pretreatment (by autoclaving or by reacting with chemicals). In spite of good sorption properties and high selectivity some problems might occur. The sorption process is slow and in case of biomass of Aspergillus niger the equilibrium was reached in 42 h. Another problem is that the initial pH of the dye solution strongly influenced the bioadsorption. Marungrueng and Pivasant (2007) investigated the adsorption of MB onto green macro alga Caulerpa lentillifera. For the sorption of MB, both alga and carbon seemed to have the same sorption rate. The sorption processes were initially controlled by both film and porediffusion, and only were limited by pore diffusion in the later stage. The isotherms followed Langmuir model which suggested
that the sorption was monolayer coverage. MB adsorption on *Sargassum muticum*, an invasive macro alga in Europe, has been investigated by Rubin et al. (2005) using visible absorption spectroscopy. Different pretreatments, protonation and chemical cross linking with CaCl₂ or H₂CO₃, have been tested in order to improve the stability as well as the adsorption capacity of the algal biomass. The equilibrium binding has been described in terms of Langmuir and Freundlich isotherms, depending on the biomass pretreatment. It is remarkable that the percentage of MB removed is up to 90%, which is higher than that found for other biosorbents and it could be even compared with that of activated carbon (99.8% uptake). Bioadsorption kinetics has been described by means of the first order Lagergren equation, from which the corresponding kinetics parameters were obtained. Nacera and Aicha, (2006) investigated the biosorption of basic dye, methylene blue onto dead *Streptomyces rimosus*. The results show the percentage of dye sorption increases with the increase in quantity of the dead bacterial biomass and reaches to highest value at 20°C. The bioadsorption capacity decreased from 9.86 to 6.93 mg/g with an increase in temperature from 20 to 50 °C at the initial MB concentration of 50 mg/l. The kinetics of MB sorption by pretreated dead *S. rimosus* were fast, reaching 86% (C₀ = 50mg/L) of the total adsorption capacity in 5 min. The mechanism follows a pseudosecond order reaction model. The activation energy of sorption was evaluated as -7.18 kJ mol⁻¹ and thus the process is exothermic (ElKhaiary, 2007).

The adsorption characteristics of MB onto nitric acid treated water hyacinth (NWH). The results showed that NWH can remove MB effectively from aqueous solution. A complete removal of MB from solution was only achieved at the lower range of initial MB concentration (less than 286 mg/L). The amount of dye uptake (mg/g) was found to increase with the increase in contact time and initial MB concentration, but there is no linear relationship between the dye uptake and temperature. Laboratory investigations of the
potential of the biomass of dried roots of water hyacinth (*Eichhornia crassipes*) to remove MB from aqueous solutions were studied by Low et al. (1995).

Removal of MB by invasive marine seaweed: *Caulerpa racemosa* var. cylindracea was studied. The adsorption reached equilibrium at 90 min. for all studied concentrations (5–100 mg/L). Langmuir and Freundlich models were applied to the data related to adsorption isotherm. According to Langmuir model data, the observed maximum adsorption capacity was 5.23 mg/g at 18°C. The enthalpy of adsorption was found to be 33 kJ/mol, which was indicated a chemical adsorption between MB molecules and *C. racemosa* var. cylindracea functional groups. Bioadsorption processes are particularly suitable for the treatment of solutions containing dilute MB concentration. Biosorption is a promising potential alternative to conventional processes for the removal of MB (Fu and Viraraghavan 2000). However, these technologies are still in the developing stage and much more work is required.

### 1.7.6 Agricultural waste as Adsorbent

The waste materials and byproducts from the agriculture and other industries could be assumed to be the low cost adsorbents due to their abundance in nature and less processing requirements. The raw agricultural solid wastes such as leaves, fibers, fruits peels, seeds etc. and waste materials from forest industries such as sawdust, bark etc. have been used as adsorbents. These materials are available in large quantities and may be potential adsorbents due to their physicochemical characteristics and low cost. Sawdust is an abundant byproduct of the wood industry that is either used as solid fuel for cooking or as packing material. Sawdust is easily available at the countryside at zero or negligible price (Garg et al., 2004). It contains various organic compounds (lignin, cellulose and hemicellulose) with polyphenolic groups that might be useful for binding MB through different mechanisms. The role of sawdust materials in the removal of pollutants from aqueous solutions has been reviewed recently (Shukla et al., 2002) and some valuable guidelines can be drawn from the review.
Sawdust has proven to be a promising low cost material for the removal of MB from wastewater. Hamdaoui, (2006) studied the removal of MB, from aqueous solution (40 mg/L) onto cedar sawdust in order to explore their potential use as lowcost adsorbents for wastewater dye removal. Adsorption isotherms were determined at 20°C and the experimental data obtained were modelled with the Langmuir, Freundlich, Elovich and Temkin isotherm equations. By considering the experimental results and adsorption models applied in this study, it can be concluded that equilibrium data were represented well by a Langmuir isotherm equation with maximum adsorption capacity of 142.36 mg/g for cedar sawdust. The extent of the dye removal decreased with increase in the solution temperature and optimum pH value for dye adsorption was observed at pH 7 for both adsorbents. Ahmad et al. (2009a) investigated the scavenging behaviour of meranti sawdust in the removal of MB from aqueous solution. Batch studies were performed to evaluate and optimize the effects of various parameters such as contact time, pH, initial dye concentrations and adsorbent dosage. Langmuir, Freundlich and Temkin isotherms were used to analyze the equilibrium data at different temperatures. Equilibrium data fitted very well in the Langmuir isotherm equation, confirming the monolayer adsorption (120.48 mg/g) of MB onto meranti sawdust. Most of the studies showed that sawdust is natural form or modified form is highly efficient for the removal of MB (Chakraborty et al., 2002; Ferrero 2007; Ofomaja 2009; De and Basu 1998; Janos et al., 2009). Chemical pretreatment of sawdust has been shown to improve the adsorption capacity and to enhance the efficiency of sawdust adsorption (Garg et al., 2004; Batzias and Sidiras 2004; Batzias and Sidiras 2007a & 2007b).

Batzias and Sidiras studied that beech sawdust as low cost adsorbent for the removal of MB. Further, in order to know the effect of chemical treatment and to improve its efficiency the authors also tested the potential of the adsorbent by treating it with CaCl₂ (Batzias and Sidiras, 2004), using mild acid hydrolysis (Batzias and Sidiras 2007a) and found
it to increase the adsorption capacity. Besides this, the simulation studies for effect of pH were also carried out by (Batzias and Sidiras 2007b). The authors determined the point of zero charge (pH $zpc = 5.2$) of the sawdust and suggested that increase of the pH enhances the adsorption behaviour. The low adsorption of MB at acidic pH was suggested to be due to the presence of excess $H^+$ ions that compete with the dye cation for adsorption sites. With the increase of the pH of the system, the number of positively charged sites decreases while the number of the negatively charge sites increases that favor the adsorption of MB due to electrostatic attraction. Another waste product from the timber industry is bark, a polyphenol rich material. Bark is an abundant forest residue which has been found to be effective in removing dyes from water solutions. Because of its low cost and high availability, bark is very attractive as an adsorbent. Like sawdust, the cost of forest wastes is only associated with the transport cost from the storage place to the site where they will be utilized. Bark is an effective adsorbent because of its high tannin content used the teak wood bark as an adsorbent to remove the MB from aqueous solutions. Equilibrium isotherms were studied at 20°C using sealed flasks in a temperature controlled, agitated shaker bath. A constant fixed mass of adsorbent was shaken with 0.050 dm$^3$ dye solution using solutions varying in dye concentration from 10 to 1000 ppm. Dynamic flow studies were performed using glass columns, 0.010 m diameter and 0.150 m packed bed height, were used to determine the adsorption breakthrough curves. The dye solution flow rates through the columns were maintained at 0.120 dm$^3$ h$^{-1}$ and 0.005 dm$^3$ samples were collected for analysis out of every 0.100 dm$^3$ of solution treated. The monolayer saturation capacity for MB onto teak wood bark is 914.59 mgg$^{-1}$.

Rice husk is an agricultural waste and a byproduct of the rice milling industry to be about more than 100 million tones, 96% of which is generated in the developing countries. The utilization of this source of agricultural waste would solve both a disposal problem as
well as access to a cheaper material for adsorption in water pollutants control system (Williams and Nugranad 2000). The maximum cost of commercially available rice husk is approximately US$ 0.025/kg. Since, the main components of rice husk are carbon and silica (15–22% SiO₂ in hydrated amorphous form like silica gel) it has the potential to be used as an adsorbent. Mckay et al (1986) studied the use of rice husk in the removal of MB from aqueous solutions then after (Vadivelan and Kumar 2000) used the rice husk for the adsorption of MB. The operating variables studied were initial solution pH, initial dye concentration, adsorbent concentration, and contact time. The amount of dye adsorbed was found to vary with initial solution pH, adsorbent dose, and contact time. The monolayer sorption capacity of rice husk for MB sorption was found to be 40.58 mg/g at room temperature (32°C). The dye uptake process was found to be controlled by external mass transfer initially followed by intraparticle diffusion. Other agricultural solid wastes from cheap and readily available resources such as papaya seeds (Hameed 2009c), grass waste (Hameed 2009b), pomelo (Citrus grandis), peel (Hameed et al., 2008c), guava leaves (Ponnusami et al., 2008; Singh and Srivastava, 1999), gulmohar (Delonix regia) plant leaf powder (Ponnusami et al., 2009), jackfruit peel (Hameed, 2009c), cotton waste, banana waste (Hameed et al., 2008b; Annadurai et al., 2002), palm kernel fiber (Ofomaja, 2007), rice straw (Gong et al., 2007), broad bean peels (Hameed and ElKhaiary 2008a), rubber seed shell (Oladoja et al., 2008), castor seed shell (Oladoja et al., 2008), pumpkin seed hull (Hameed and ElKhaiary 2008b), pineapple stem (Hameed et al., 2009a), dehydrated peanut hull (Ozer et al., 2007), coconut husk (Low and Lee, 1990), coffee husks (Oliveira et al., 2008), Parthenium hysterophorus (Lata et al., 2008), garlic peel (Hameed and Ahmad 2009), fallen phoenix tree’s leaves (Han et al., 2007), raw date pits, ground hazelnut shells (Ferrero 2007; Dogan et al., 2008; Dogan et al., 2009), coconut bunch waste (Hameed et al., 2008a), peanut hull (Gong et al., 2005), Luffa cylindrica fibers (Demir et al., 2008), yellow passion
fruit waste (Pavan et al., 2008), olive pomace, *Salsola vermiculata* (SV) leaves, jute waste (Banerjee and Dastidar, 2005), cereal chaff (Han et al., 2006), orange peel, wheat shells (Bulut and Aydin, 2006), wheat straw, neem (*Azadirachta indica*) leaf powder have also been successfully employed for the removal of MB from aqueous solutions.

### 1.7.7 Industrial solid wastes as adsorbents

Industrial solid wastes such as sludge, fly ash and red mud are classified as lowcost materials because of their low cost and local availability and can be used as adsorbents for MB dye removal (Gulnaz et al., 2004; Otero et al., 2003; Lee et al., 1996; Wang et al., 2005a; Wang et al., 2008; Gupta et al., 2000; Viraraghavan and Ramakrishna 1999; Janos et al., 2003). The activated sludge biomass collected from electroplating industry of Adana Organize Sanayi, Turkey was used as an adsorbent for MB by Gulnaz et al (2004). It contains insoluble metal hydroxides and other salts and showed the highest dye uptake capacity, having the monolayer adsorption capacity 256.41 mg/g for MB, at pH value of 7.0 and 20°C (Otero et al., 2003). The adsorption equilibriums of MB by these materials have been described in terms of both Langmuir and Freundlich equations. Among the various adsorbents used for removal of MB dye the fly ash was found to be an effective adsorbent. It is a waste/byproduct of thermal power plants and generally available free of cost that may be used in construction of roads, bricks and cement etc. Owing to its high availability and problem of disposal, a number of workers have attempted to use it as an adsorbent in pollution control. Although it may contain some hazardous substances, such as heavy metals, it is widely utilized in industry in many countries (Janos et al., 2003). However, bagasse fly ash generated in the sugar industry does not contain large amounts of toxic metals and has been widely used for adsorption of dyes (Gupta et al., 2000). Fly ash has a surface area of 15.6 m²/g. Its properties are extremely variable and depend strongly on its origin (Wang et al., 2005a; Janos et al., 2003; Wang et al., 2005b) used fly ash as adsorbent for the removal of
MB from aqueous solutions and the adsorption capacity for raw fly ash was reported to be 4.47 mg/g. The effect of physical (heat) and chemical treatment was also studied on as received fly ash and the heat treatment was reported to have adverse effect on the adsorption capacity of fly ash but acid treatment (by nitric acid) resulted in an increase of adsorption capacity of fly ash (7.99 mg/g). Coal fly ash was used successfully as lowcost adsorbents for removal of MB from aqueous solution by Wang et al (2008). Viraraghavan and Ramakrishna (1999) investigated the use of coal fly ash from the Shand power plant in Canada for removal of dyes from wastewater. The negative values of free energies indicate the feasibility and spontaneous nature of the process, and the positive heats of enthalpy suggest the endothermic nature of the process. Another abundant industrial by-product/ waste material is red mud. Waste red mud is a bauxite processing residue discarded in alumina production. Red mud, an aluminum industry waste was converted into a low cost potential adsorbent and the final material has been used for the removal of MB by Wang et al. (2005a) who showed that physical and chemical treatment can significantly change its adsorption capacity.

1.7.8 Miscellaneous adsorbents

Miscellaneous adsorbents various other materials have also been put to use for preparing alternative adsorbents. An attempt to remove MB by using waste tea leaves was studied by Uddin et al. (2009) and Hameed (2009d), so as to develop a low cost methodology while having low impact on environment. Besides this various other materials have also been studied less extensively as lowcost adsorbents, such as sand (Saeed et al., 2007), stainless steel (Imamura et al., 2002), hair, crushed brick, carbinized press mud (Kumar 2002), Fe (III)/Cr (III) hydroxide (Namasivayam and Sumithra 2005), melamine–formaldehyde urea resin (Ozdemir et al., 2009), cow dung ash (Imamura et al., 2002), eggshell and egg shell membrane (Tsai et al., 2006) and polyacrylic acid bound iron oxide magnetic nanoparticles (Mak and Chen 2004) have also been explored as an adsorbents.
1.8. Properties and Characterization of Dyes

1.8.1 Malachite Green (MG)

(i) Toxicity

When malachite green is used in aquatic animals, it will be metabolized to leuco-malachite green. The non-polar LMG has been found to retain in catfish muscle for a longer period of time, 10 days for LMG compared to 2.8 in MG. It has been determined that the half lives of the retention of malachite green and leuco-malachite green catfish muscle is 2.8 days. The study of the toxicity of malachite green in fish has been hard as it is heavily influenced by the water hardness, pH, temperature and amount of dissolved oxygen in water. Detailed studies have indicated that the toxicity of the chemical increases as the temperature increases or pH decreases. The effects of malachite green on fish eggs have also been tested and it has been shown that a two fold increase in the concentration of malachite green could lead up to 20 times the mortality rate in rainbow trout eggs. This shows that it may be extremely toxic for some species of fish and especially for fish eggs. Other effects such as carcinogenesis, mutagenesis, and reduced fertility have been reported to occur in rainbow trout. Overall, although malachite green is an extremely effective weapon against fungus and parasitic infections in fish, the chemical causes serious side effects in the fish as well.

(ii) Effects on humans

Malachite green and its major metabolite, leuco-malachite green have been reported to have mutagenic and carcinogenic effects. As leuco-malachite green is the primary metabolite of malachite green and is retained in fish muscle much longer, most intake of malachite green would be in the leuco form. During the experiment, rats were fed up to 543 ppm of leuco-malachite green, an extreme amount compared to the average 5 ppb discovered in fish. After a period of two years, an increase in lung adenomas in male rats was discovered but no incidences of liver tumors. This shows that although adducts are formed, they have
“little mutagenic or carcinogenic consequence”. Therefore it could be concluded that malachite green caused carcinogenic symptoms but a direct link between malachite green and liver tumor could not be proved.

The effluents dye is a major concern due to their adverse effects to many forms of life. The discharge of dyes in the environment is a matter of concern for both toxicological and esthetical reasons (MetivierPignon et al., 2003). Industries such as textile, leather, paper, plastics, etc., use dyes in order to colour their products and also consume substantial volumes of water. As a result, they generate a considerable amount of coloured waste water (Ravi et al., 2005). It is estimated that more than 100,000 commercially available dyes with over $7 \times 10^5$ tonnes of dyestuff produced annually (McMullan et al., 2001; Pearce et al., 2003; Lee et al., 2006). It is recognized that public perception of water quality is greatly influenced by the colour. The colour is the first contaminant to be recognized in wastewater. The presence of even very small amounts of dyes in water less than 1ppm for some dyes is highly visible and undesirable (Robinson et al., 2001; Banat et al., 1996). MB is the most commonly used substance for dying cotton, wood and silk. It can cause eye burns which may be responsible for permanent injury to the eyes of human and animals. On inhalation, it can give rise to short periods of rapid or difficult breathing while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia (Ghosh and Bhattacharyya 2002; Tan et al., 2008). Therefore, the treatment of effluent containing such dye is of interest due to its harmful impacts on receiving waters. During the past three decades, several physical, chemical and biological decolorization methods have been reported; few, however, have been accepted by the paper and textile industries (Jain et al., 2003a). Amongst the numerous techniques of dye removal, adsorption is the procedure of choice and gives the best results as it can be used to remove different types of coloring materials (Ho and McKay 2003; Derbyshire et al., 2001; Sohrabi

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and Ghavami 2008). Recently, numerous approaches have been studied for the development of cheaper and effective adsorbents. Many nonconventional low cost adsorbents, including natural materials, biosorbents, and waste materials from agriculture and industry, have been proposed by several workers. These materials could be used as adsorbents for the removal of dyes from solution. Many treatment processes have been applied for the removal of dyes from wastewater such as: photocatalytic degradation (Sleiman et al., 2007; Abbasi and Asl 2008), sonochemical degradation (Zaghbani et al., 2008), micellar enhanced ultrafiltration (Wu et al., 2008), cation exchange membranes (Fan et al., 2008), electrochemical degradation (Zhu et al., 2007), adsorption/precipitation processes (Sudarjanto et al., 2006), integrated chemical–biological degradation (Sarria et al., 2003), integrated iron (III) photoassisted biological treatment (Garcia Montano et al., 2008), solar photo Fenton and biological processes (Lodha and Chaudhari 2007), Fenton on biological treatment scheme (Hameed and Daud 2008) and adsorption on activated carbon (Wu and seng 2008; Forgacs et al., 2004). As synthetic dyes in wastewater cannot be efficiently decolorized by traditional methods, the adsorption of synthetic dyes on inexpensive and efficient solid supports was considered as a simple and economical method for their removal from water and wastewater (Pokhrel and Viraraghavan 2004). Methods of dye wastewater treatment have been reviewed (Pokhrel and Viraraghavan, 2004; Robinson et al., 2001; Slokar and Marechal, 1998; Delee et al., 1998; Banat et al., 1996; Cooper 1993; Crini 2006; Gupta and Suhas 2009). Fungal and bacterial decolorization methods have been reviewed (Aksu 2005; Wesenberg et al., 2003; Pearce et al., 2001; McMullan et al., 2005; Fu and Viraraghavan 2001; Stolz 2001). Adsorption is a well known equilibrium separation process and an effective method for water decontamination applications (Dabrowski 2001; Ahmad et al., 2007; Ahmad et al., 2009b; Rafatullah et al., 2009). Adsorption has been found to be superior to other techniques for water reuse in terms of initial cost, flexibility and simplicity of design, ease of operation and
insensitivity to toxic pollutants. Adsorption also does not result in the formation of harmful substances. These deal the technical feasibility of various nonconventional low cost adsorbents for dye removal from water and wastewater.

(iii) Malachite green structure

Fig. 1 Structure of Malachite Green

Malachite green is an organic compound that is used as a dyestuff and has emerged as controversial agent in aquaculture. Malachite green is traditionally used as a dye for materials such as silk, leather, and paper. Although called malachite green, the compound is not related to the mineral malachite — the name just comes from the similarity of color. Malachite green is classified in the dyestuff industry as a triarylmethane dye. Formally, Malachite green refers to the chloride salt $[C_6H_5C(C_6H_4N(CH_3)_2)_2]Cl$, although the term Malachite green is used loosely and often just refers to the colored cation. The oxalate salt is also marketed. The chloride and oxalate anions have no effect on the color. The intense green color of the cation results from a strong absorption band at 621 nm (extinction coefficient of $10^5$ M$^{-1}$cm$^{-1}$).
1.7.2 Congo red (CR)

(i) Structure of Congo red

Congo red was first synthesized in 1883 by Paul Bottiger who was working then for the Friedrich Bayer Company in Elberfeld, Germany. He was looking for textile dyes that did not require a mordant step. The company was not interested in this bright red color, so he filed the patent under his name and sold it to the AGFA company of Berlin. AGFA marketed the dye under the name "Congo red", a catchy name in Germany at the time of the 1884 Berlin West Africa Conference, an important event in the Colonisation of Africa. The dye was a major commercial success for AGFA. In the following years, for the same reasons, other dyes were marketed using the "Congo" name: Congo rubine, Congo corinth, brilliant Congo, Congo orange, Congo brown, and Congo blue.