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Diatomite: Its Characterization, Modifications and Applications

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Abstract: The review tackles common diatomite, its characterization, modifications and its composites, heavy metal toxicity and its immobilization techniques using diatomite, other important applications of diatomite.

INTRODUCTION

Diatomite rock is a loose, earthy or loosely cemented porous and lightweight rock of sedimentary origin, mainly formed by fragments of armor (skeletons) of diatom algae: diatomea and radiolaria. Diatomite is a microscopic diatom alga whose size ranges from 0.75 to 1500 m; sometimes this rock is called infusorial earth, kieselguhr, or mountain meal. The main components of the siliceous armor are silica hydrates of a different degree of water content (opals) SiO_2 _nH_2O. Diatomite rock belongs to the group of silica-bearing materials. Diatomite has its origin from a siliceous, sedimentary rock consisting principally of the fossilized skeletal remains of diatom, a unicellular aquatic plant related to the algae, during the tertiary and quaternary periods (Paschen, 1986; Arik, 2003).

Diatomites (or kieselguhrs) are mineral deposits of diatomaceous algae, those commercially exploited being restricted to a relatively modem age, starting from the Miocene. Older deposits have suffered tectonic processes, bringing about modifications of the texture and crystalline phase of the mineral. Amorphous silica, a constituent of the diatom frustulae, is the main component of diatomite, although variable quantities of other materials (metal oxides, clays, salts (mainly carbonates) and organic matter) may also be present, chemical precipitation and atmospheric contact, together with the prevailing environmental conditions, are determinant factors in the nature and importance of the impurity content of a deposit (Mendioroz et al., 1989).

Diatomite is a natural material formed from the remains of diatoms, which grew and were deposited in seas or lakes. Diatomite products are used in a variety of ways, such as reinforcing, stiffening and hardening of organic solids, reducing adhesion between solid surfaces, increasing adhesion, increasing viscosity, surfactant effects, hydrophobic effects, absorbent, catalysts and cloud seeding (Zhaolun et al., 2005).

Diatomite is abundant in many areas of the world and has unique physical characteristics, such as high permeability (0.1-10 mD) and porosity (35-65%) (Murer and Mobil, 2000), small particle size, low thermal conductivity and density (Hassan et al., 1999) and high surface area (Gao et al., 2005). The properties of diatomite's surface, such as hydrophobia, solubility, charge, acidity, ion exchange and adsorption capabilities, are highly governed by the presence of water, which is partially structurally connected to the crystal mesh of the diatomite, forming active hydroxyl groups on it (Yuan et al., 1997).

Diatomite ($SiO_2\_nH_2O$) or diatomaceous earth is a pale-colored, soft, lightweight sedimentary rock composed principally of silica microfossils of aquatic unicellular algae. Diatomite consists of a wide variety of shape and sized diatoms, typically 10-200 mm, in a structure containing up to 80-90% voids (Lemonas, 1997). Diatomite's highly porous structure, low density and high surface area resulted in a number of industrial applications as filtration media for various beverages and inorganic and organic chemicals as well as an adsorbent for per liter and oil spills. Although, diatomite has a unique combination of physical and chemical properties, its use as an adsorbent in wastewater treatment has not been greatly investigated (Aytas *et al*., 1999; Michell and Atkinson, 1991).

CHARACTERIZATION OF DIATOMITE

Bliznakov and Gocheva (1978) and Robertson (1980) studied diatomites by IR spectroscopy and Differential Thermal Analysis (DTA) and revealed that amorphous silicon dioxide is the main component of the diatomite. Water adsorbed on the diatomite surface and hydrated water bound to divalent cations are released at temperatures of 110-180°C and insignificant amounts of water are released at 800°C. However, the authors did not report the types of hydroxyl groups on the diatomite surface and data on the change in the band positions with a variation in the temperature for calcined samples. The dehydration of diatomites, water loss and the influence of the pore structure on the dehydration were not investigated. Castro *et al*. (1979) studied the pore structure by porosimetry; however, they did not investigate the change in the pore structure after acid treatment and calcination.

Mendioroz *et al*. (1989) made reports on a thermogravimetric study of 12 samples of different diatomite deposits from S and SE Spain. Thermogravimetric proved to be an efficient and rapid method for mineral diagnosis, the shapes of the TG curves giving the carbonate and silica contents of the diatomite samples almost quantitatively.

Structural investigation of some important Chinese diatomites done by Wang *et al*. (2009) and discussed The IR spectra exhibit bands associated with the Si-O and Al-O bonds. The acid treatment and calcination lead to a change in the size, size distribution and structure of pores. Fuya *et al*. (1995) reported that, Diatomite samples taken from the Leizhou Peninsula have been studied by chemical analysis, DTA, TG, XRD, IR, SEM and X-ray Energy Spectroscopy. The study shows that the diatomaceous genera and species and their organic contents are variable with buried depth, from Melosira to Stephanodiscus and then to Cyclotella. Various impurities in the samples, such as quartz, kaolinite and montmorilonite indicate different sedimentary environments.

Diatomaceous silica, pretreated at various temperatures between 125 and 900°C was subjected to dissolution experiments and was analyzed using X-ray diffraction and infrared spectra (Kamatani, 1974).

The IR spectrometry is a useful measure to study surface hydroxyl groups. However, it is difficult to distinguish different surface hydroxyl species of diatomite because the O-H vibration frequency (ca. 3745 cm^{-1}) of surface isolated hydroxyl groups and H-bonded hydroxyl groups are analogical. On the other hand, diatomite prefers to adsorb water for its high porosity, thereby in IR spectra the peak of strongly H-bonded hydroxyl groups is overlapped by the broad peak (with middle wave number at (ca. 3500 cm^{-1}) that assigned to the adsorbed water and then is difficult to be discerned (Yuan *et al*., 2001).

The IR spectroscopy has proved to be a powerful method to identify the isolated and H-bonded hydroxyl groups on the surface of synthetic silica (Iler, 1979; Bergna, 1994). Frost and Johansson (1998) proposed that diffuse reflectance infrared Fourier transform

spectroscopy (DRIFT) is more applicable than transmission infrared spectroscopy for powder samples because it provides a rapid technique for analyzing samples without any interference through sample preparation and the technique is particularly suitable for the study on the hydroxyl stretching region of silicate minerals. Diffuse Reflectance Infrared Fourier Transform spectroscopy (DRIFT), Raman spectroscopy of adsorbed Pyridine molecules (Py-Raman) and in situ Py-IR have been used Yuan *et al.* (1997) to investigate the hydroxyl species and acid sites on diatomite surfaces. In our study Elaboration and characterization of natural diatomite (raw material) in Aktyubinsk/Kazakhstan has been investigated including the structure, mineralogical specifics and chemical composition (Mohamedbakr and Burkitbaev, 2009a).

DIATOMITE MODIFICATIONS AND ITS COMPOSITES

There are several methods to modify the surface characteristics of diatomite for various purposes. The diatomite purification in HCl and the diatomite calcination (Goren *et al.*, 2002; Khraisheh *et al.*, 2005) have been applied to make diatomite more inert for using the treated diatomite as filter support. In these processes, the disappearance of the OH groups on the diatomite surface has a detrimental effect on the surface area. Khraisheh *et al.* (2004a) modified diatomite by NaOH treatment and manganese oxide deposition to improve the adsorption capacity of the diatomite for removal of heavy metals like Pb^{2+}, Cu^{2+} and Cd^{2+} from wastewater. Their modified diatomite has the surface area of 80 m^2 g^{-1} and the adsorption capacity of 99.00 mg Pb^{2+}/g, 55.56 mg Cu^{2+}/g and 27.86 mg Cd^{2+}/g, respectively and they explained that manganese oxide and its blockage of pores of diatomite played an important role in the adsorption on the heavy metals. Another modified diatomite with lime and aluminum sulfate is utilized to remove P from wastewater (Wu *et al.*, 2005). This modification might result in aluminum hydroxyl groups transplanted onto the surface of diatomite and elevated removal of Phosphorus primarily via chemisorption. Total Phosphorus (TP) was reduced from 5.2 mg L^{-1} in influent to 0.55 mg Lin^{-1} treated effluent and 80%TP removal efficiency was obtained by the addition of chemically modified diatomite.

Ferrihydrite-modified diatomite was developed and characterized by Xiong *et al.* (2009) and Xiong and Peng (2008) as a novel and effective P, ferrihydrite-modified diatomite has a BET specific surface area of 211 m^2 g^{-1} and has a P adsorption capacity of 37.3 mg P/g. Ferrihydrite-modified diatomite was formed through the deposition of Si-containing ferrihydrite into pores of diatomite. And they studied the effects of process parameters such as concentrations of $FeCl_2$, NaOH and drying temperature on the formation mechanism and chemical characteristics of ferrihydrite- modified diatomite are studied by using X-ray absorption near-edge structure spectroscopy. The spectra were recorded in total electron yield mode and/or fluorescence yield mode to investigate the chemical nature of Fe and Si on the surface and/or in the bulk of ferrihydrite-modified diatomite, respectively. It was found that only the surface SiO_2 was partially dissolved in the NaOH solution with stirring and heating, whereas the bulk of diatomite seemed to be preserved. The dissolved Si was incorporated into the structure of ferrihydrite to form the 2-line Si-containing ferrihydrite on the surface of diatomite. The crystalline degree of ferrihydrite increased with the increasing $FeCl_2$ concentration and the Brunauer-Emmett-Teller specific surface area of ferrihydrite-modified diatomite decreased with the increasing $FeCl_2$ concentration. The crystalline degree of ferrihydrite decreased with the increase of NaOH concentration. The high temperature calcination caused an energy shift in the Si L-edge spectra to the high energy side and a transformation of Si-containing ferrihydrite to crystallized hematite might occur when ferrihydrite-modified diatomite is calcined at 900°C. In this study, the optimal synthesis

conditions for the ferrihydrite-modified diatomite with the least crystalline Si-containing ferrihydrite and the highest surface area were found to be as the follows: 0.5 M $FeCl_2$ solution, 6 M NaOH solution and drying temperature of 50°C. Synthetic 2-line Si-containing ferrihydrite was prepared by following the procedure of Seehra *et al*. (2004) 0.025 M $Na_2SiO_3.9H_2O$ solution was added to 0.1 M $Fe(NO)_3.9H_2O$ solution to yield the molar ratio of $Si/(Si + Fe) = 0.2$. Ammonium hydroxide was then slowly added to this solution to bring the pH to 10. The precipitate was filtrated and washed by distilled water and then dried at 50°C in an oven.

New Inorganic Composite Materials (ICM) were prepared (Hadjar *et al*., 2008) by mixing an Algerian natural diatomite with a charcoal from pine. After using two consecutive necessary procedures of treatments, the ICM were characterized in order to reveal their properties with the aid of different techniques of analysis. The preliminary obtained results have clearly shown that the important quantity of calcium carbonates present in natural diatomite have disappeared from the new ICM after heating and chemical attack.

Grigoryan *et al*. (2008) synthesized calcium hydrosilicate from Armenian diatomite and $-cristobalite obtained from diatomite and calcium hydroxide under hydrothermal conditions. They established the optimal process parameters.

Ibanez and Sandoval (1998) investigated the synthesis of calcium hydromonosilicate from Spanish diatomite and calcium hydroxide. It is established that, during hydrothermal synthesis, to obtain CSH that contains no Ca $(OH)_2$, an experimental duration longer than 4 h and a temperature of 180°C are required. For Armenian diatomites, an experimental duration of 1-3 h and temperature of 90-98°C were suggested, with the use of sodium or potassium hydroxidesas mineralizers.

Grigoryan *et al*. (1997, 2007) established that the use of (-tridymite and $-cristobalite instead of $-quartz in the hydrothermal autoclave synthesis of calcium hydromonosilicate allows one to obtain calcium hydromonosilicate at comparatively low temperatures and durations of the experiment omitting the intermediate phase. And they proved that the process of cristobalization of diatomite starts at 1050°C. In investigations, they also used $ -cristobalite obtained from Armenian diatomite.

Hsien *et al*. (2009) prepared diatomite-TiO_2 composite for photo degradation of Bisphenol-A in water. and they found that the photo catalytic activity in the degradation of Bisphenol-A on diatomite-TiO_2 composites can be better than on pure TiO_2 powders possibly due to more BPA molecules adsorbed and enriched on the modified TiO_2 particles. Bazhal *et al*. (1975) showed that the surface modification of diatomite by Ca(II), Al(III) and Sn(IV) ions resulted in an increased filtration rate since these cations have a high coagulation capacity which give a marked aggregation of the particle. Hence, it can be said that the modification by manganese oxides has changed the colloid-chemical properties of diatomite and increased the aggregation of the particles, which resulted in a higher filtration rate. Moore and Reid (1973) reported an increase in filtration rates for acrylic fibers after modification with manganese oxides.

Ediz *et al*. (2010) examined the calcination and filtration characteristics of diatomite. For this purpose, diatomite ore was calcined at 1000°C in order to improve the material characteristics for use in filtration. The physical, chemical, thermal and micro-structural features of the raw and the calcined diatomites were then determined to compare them with those of the commercial filter aids currently used. In order to determine filtration efficiency of the diatomite samples, several filtration tests were carried out together with the beer samples and the commercial filter aids taken from a leading beer factory in Turkey. It is shown that the calcined diatomite could successfully be used for beer filtration after suitable arrangement of the particle size distribution, such that the highest possible flow rate and filtrate clarity are obtained.

We used FT-IR (Mohamedbakr *et al.*, 2009) spectroscopy in the regime of total internal reflection studied the reaction products of amorphous calcium phosphate, containing both mono-and diphosphate in the molar ratio of 7/3 and consisting of 80% water, with the surface of diatomite particles-a natural mineral sediment dioxide-based silicon aktobe field. It is shown that the main chemical bonds in the products of interaction as distinct from those ones in the original phosphate and minerals. When the dehydration reaction products behave like most amorphous phosphate and the chemical bonds PO alter their strength, reflecting a loss of moisture and the formation of pores in which the adsorbed carbon dioxide.

DIATOMITE AND HEAVY METALS REMOVAL AND WATER PURIFICATION

In recent decades, water pollution phenomena have become more and more frequent and acute. Petroleum hydrocarbons represent one of the most common categories of groundwater pollutants that are found at many contaminated sites, making surface water and/or groundwater unsuitable for many uses (including drinking), due to their toxic and/or carcinogenic properties.

Water is considered an important and scarce commodity in many countries around the world. In particular, the contamination of surface and ground water with heavy metals is a concern. Industries such as plating, ceramics, glass, mining and battery manufacturing are considered the main source of heavy metals, e.g., lead, in local water streams. The elevated level of lead and other heavy metals, e.g., cadmium, chromium and mercury, in the local water streams is a major concern to public health.

Inorganic pollutants, in particular heavy metal ions, constitute a major class of water contaminants. Most heavy metals are known to be toxic and carcinogenic agents and, when discharged in wastewater, represent a serious threat to the human population. Currently, many industries use heavy metals in the processing of raw materials and consequently, discharge of such metals into aquatic bodies and sources of drinking water has begun to be strictly controlled (Dantas *et al.*, 2001). Lead, cadmium and zinc are regarded as major contaminants. Lead and its compounds play an important role in industrial activities including the manufacture of paint, storage batteries and leaded gasoline. Cadmium and zinc are used as protective coatings for iron and steel. Cadmium enters the system primarily through absorption in the large intestine and is de-posited in the liver and kidneys (Holliday and Park, 1998). Most zinc compounds have no toxic properties, but zinc chloride is highly corrosive to the skin, eye and respiratory tract.

Over the last few decades, adsorption has gained importance as an effective purification and separation technique used in wastewater treatment (Lazaridis *et al.*, 2003). Adsorption systems are rapidly gaining prominence as treatment processes which produce good quality water containing a low concentration of dissolved organic and inorganic compounds (Walker and Weatherley, 1999). Sorption technologies, including physical and chemical adsorption and ion-exchange, have the potential to treat water and industrial residues.

The removal of heavy metals from industrial waste water is considered an important application of adsorption processes using a suitable adsorbent (Al-Qodah, 2000). There is growing interest in using low-cost, commercially available material for adsorption of heavy metals. Jordan has large deposits of diatomaceous earth and as a result, research is being undertaken to assess its feasibility as a low-cost alternative to activated carbon.

Within literature, many treatment processes have been proposed for the removal of heavy metals. Chemical precipitation, membrane filtration, ion exchange, alum coagulation and activated carbon adsorption are some of the most commonly used methods for the

treatment and disposal, of metal-containing wastes (Orhan and Buyukgungor, 1993; Yadava *et al.*, 1991). Adsorption is considered to be a particularly competitive and effective process for the removal of trace quantities of heavy metals (Huang and Blankenship, 1984). In principle, any solid material with a microporous structure can be used as an adsorbent, e.g., bone and coal char, clays, iron oxides, synthetic and natural zeolites, molecular sieves and activated carbon. The most important property of any adsorbent is the surface area and structure. Furthermore, the chemical nature and polarity of the adsorbent surface can influence the attractive forces between the adsorbent and adsorbate. The highly developed structure of activated carbon allows wide usage as an adsorption media for a large number of organic and inorganic materials, including trace concentrations of heavy metals. Activated carbon, however, is not suitable in developing countries due to the high costs associated with production and regeneration (Panday *et al.*, 1985). The use of alternative low cost materials for heavy metals removal is required. Materials like activated peat and clay (Brown *et al.*, 2000; Fischer, 2002), chitin and chitosan (Rae and Gibb, 2003; Bassi *et al.*, 2000) have been tested as potential sorbents for heavy metal removal. A comprehensive review has been presented by Bailey *et al.* (1999).

Karthikeyan and Chaudhuri (1986) studied the removal of Hg(II) by coal. After chemical treatment by nitric acid oxidation, H_2O_2 oxidation, CS_2 sulphurisation and impregnation with manganese oxides, the authors reported that the efficiency of the treated coal exceeded that of activated carbon. Ground husks modified with EDTA have also shown a high efficiency for removal of Cd(II) and Pb(II) (Okieimen *et al.*, 1991). Brandao and Galembeck (1990) also reported that the impregnation of cellulose acetates with manganese dioxide resulted in high removal efficiency of Cu(II), Pb(II) and Zn(II) from aqueous solutions. Sagara *et al.* (1989) prepared a selective ion-exchanger material for Li(I) and Na(I) by dispersing MnO_2 within cellulose gel beads.

The removal of BTEX (benzene, toluene, ethyl-benzene and xylenes) and MTBE (methyl tertiary butyl ether) from aqueous solution by diatomite raw (DR) and thermally modified diatomite at 550, 750 and 950°C was studied by Aivalioti *et al.* (2010).

Diatomite has already been used for the adsorption of different elements and substances from water and wastewaters, either in its natural form (raw) or modified (chemically or thermally), presenting very promising and positive results. Ridha *et al.* (1998) described first the determination of the physico-chemical characteristics and the surface properties of a natural Moroccan low density silicate from the diatomites family. Then, the adsorption of aqueous Ag^+ ions on this diatomite and the Langmuir model are studied.

We studied the removal uranium from the liquid waste by using diatomite as an adsorption medium. This is important because natural diatomite is an abundant and low-cost material when compared to other artificial chemicals. In this study, the removal of uranium from aqueous solutions by natural/modified diatomite earth from (Aktyubinsk /Kazakhstan) has been investigated. A comparison in Uranium adsorption was investigated between natural diatomite and three modified diatomite by calcinations and acidification by 0.5 N HCl (D, D_HCl, D_900 and D_900_HCl). The adsorption of uranium on the chosen diatomite sample was examined as a function of uranium concentration, contact time and type of diatomite used (Mohamedbakr and Burkitbaev, 2009b).

Naturally occurring diatomaceous earth (diatomite) has been tested by Al-Degs *et al.* (2001) as a potential sorbent for Pb(II) ions. The intrinsic exchange properties were further improved by modification with manganese oxides. Modified adsorbent (referred to as Mn-diatomite) showed a higher tendency for adsorbing lead ions from solution at pH 4. The high performance exhibited by Mn-diatomite was attributed to increased surface area and

higher negative surface charge after modification. Scanning electron microscope pictures revealed a birnessite structure of manganese oxides, which was featured by a plate-like-crystal structure. Diatomite filtration quality was improved after modification by manganese oxides. Good filtration qualities combined with high exchange capacity emphasized the potential use of Mn-diatomite in filtration.

On the spot of using an abundant and low-cost material in lead removal from the liquid waste, we studied (Mohamedbakr and Burkitbaev, 2008), lead solutions were treated using diatomite and, as a result of the treatment, its concentrations were reduced depending on the type of diatomite used and type of treatment which effect on the lead uptake capacity. The relative adsorption capacities of lead ions onto diatomite samples followed the sequence: D>D-HCl>D-900>D-900-HCl. The sorption of Pb^{2+} from aqueous solutions by a range of adsorbents.

Computerized flow injection coupled with potentiometric stripping analysis (Al-Ghouti *et al.*, 2004) (FIPSA) was employed for examination of the adsorption behavior of Pb(II), Cd(II) and Zn(II) ions onto diatomite modified with manganese oxides. Signal optimization was undertaken with respect to flow rate, deposition time, deposition potential, oxidizing agent concentration, thickness of mercury film, solution pH and metal ion concentration. Examination of the column adsorption characteristics was facilitated by introduction of an adsorption micro column, as a complementary component of the flow injection system. The resulting breakthrough curves were employed to calculate parameters including adsorption capacity and adsorption rate constant, taking into consideration initial ion concentration, flow rate, mass and particle size of adsorbent and column internal diameter. Adsorption capacities, determined using the Thomas mathematical model, showed that manganese modified Jordanian diatomite had an efficiency towards the removal of heavy metal ions from aqueous solutions; Cd(II) > Zn(II)~Pb(II). The relative adsorption rates of the ions followed the order: Pb(II) > Zn(II)~Cd(II).

Fe-Mn binary oxide has been homogeneously incorporated into diatomite and exhibited high As(III) removal efficiency (Chang *et al.*, 2009). The oxidation of As(III) can significantly enhance the As(III) removal efficiency and reduce the As(III) toxicity. Acid solution and high temperature are advantageous to oxidize and adsorb As(III). Electrostatic attraction and specific adsorption were the two major forces during the As(III) adsorption process. Being different from other coexisting anions, the presence of silicate and phosphate has negative effects on the As(III) adsorption. With the increase of pH, the negative influence of silicate was enhanced, while the competition ability of phosphate for the adsorption sites was weakened. Because of the high oxidation ability and adsorption capacity for As(III), FMBO-diatomite can be filled into fixed beds for large-scale water treatments, in order to remove As(III) with low concentration from water rapidly and effectively.

Chu *et al.* (2010) investigated the feasibility of treating micro-polluted surface water for drinking water production with a bio-diatomite dynamic membrane reactor (BDDMR) at lab-scale in continuous-flow mode. Results indicate that the BDDMR was effective in removing COD_{Mn}, DOC, UV_{254}, NH3-N and trihalomethanes' formation potential (THMFP) at a hydraulic retention time (HRT) of 3.5 h due to its high concentrations of Mixed Liquor Suspended Solids (MLSS) and Mixed Liquor Volatile Suspended Solids (MLVSS). The removal of pollutants was mainly ascribed to microbial degradation in BDDMR because the dynamic membrane alone was much less effective in pollutant removal. Though the diatomite particles (5-20 mm) were much smaller in size than the aperture of the stainless steel support mesh (74 mm), microorganisms and their extracellular polymer substances could bind these particles tightly to form bio-diatomite particles which were completely retained by the

support mesh. The analysis of Molecular Weight (MW) distribution by Gel Permeation Chromatography (GPC) shows that the BDDMR could effectively remove the hydrophilic fraction of dissolved organic materials present in the raw water.

OTHER APPLICATIONS

Processed diatomite possesses an unusual particulate structure and chemical stability that lends itself to applications not filled by any other form of silica. Foremost among these applications is its use as a filter aid, which accounts for over half of its current consumption. Its unique diatom structure, low bulk density, high absorptive capacity, high surface area and relatively low abrasion are attributes responsible for its utility as a functional filler and as an extender in paint, It is actively exploited and used as raw material for filtration of fluids, pesticides, thermal treatment, paper and rubber filling, natural water purification, among others. From the analytical point of view, this substrate has been mainly applied as chromatographic columns, Paper, rubber, an in plastics and thermal insulating material; polish, abrasive to name a few representative applications (Frederic and Kadey, 1983; Aruntas *et al*., 1998; Arik *et al*., 2002).

Diatoms are well-known for their versatility as indicators of past environments and climates (Stoermer and Smol, 1999) but their application to sediment provenance studies, although used with some success (Pokras, 1991; Abrantes *et al*., 2007) is not common worldwide. In Lake Tutira for example, diatoms have been useful for differentiating between sedimentary units derived entirely from catchment erosion and those derived predominantly from within-lake and lake margin sources (Orpin *et al*., 2006). One implication of the Lake Tutira study is that diatoms could be a useful tool to identify sediment sources in parts of the Waipaoa sedimentary system and may be an important compliment to carbon, radiochemical or biogenic marker studies. Furthermore, a quantitative measure of the diatom concentrations for background terrigenous sedimentation fluxes offshore could offer another means to identify high-delivery events caused by floods, storms or earthquakes.

Crucial to the use and accurate interpretation of diatom assemblages is an understanding of their individual ecological preferences. Surface sediments are often used to document modern diatom distribution patterns. These in turn are used to create a template in relation to present-day environmental variables so that similar patterns observed in fossil samples can be more accurately interpreted. Although much is known of the modern ecological preferences of diatoms from surface sediment and modern analogue studies around the world, only a few such studies have been undertaken in New Zealand (Cochran, 2002; Reid, 2005) and no diatom transfer functions have been developed in New Zealand's marine realm. Therefore, as a first step towards providing quantitative and locally calibrated diatom studies for source-to-sink research, we aim to document the species preserved in surface sediments offshore of New Zealand and investigate the factors determining their distribution (Cochran and Neil, 2010).

Kieselguhr sludge can be effectively utilized in the fabrication of calcium silicate bricks and to what extent the kieselguhr sludge plays a role in the reaction mechanisms of the hardening process. Furthermore, the influence of carbonation on calcium silicate bricks produced using kieselguhr sludge was investigated (Russ *et al*., 2006).

In the San Joaquin Valley, CA, diatomite is the uppermost productive member of the Monterey formation. Initial oil saturations vary from 30 to 65% and total oil accumulations in diatomite are estimated to be at least 10-12 billion barrels original oil in place (Ilderton *et al*., 1996). Oil-bearing diatomite layers are interbedded among shale and

mudstone layers (Schwartz, 1988). Individual layers vary in thickness from a few centimeters to several meters and the gross thickness of these layers can exceed 330 m_1000 ft. The interbedding of diatomaceous rock and shale resulted from cyclicrseasonal deposition of diatoms, mud and silt and the subsequent consolidation of diatom fragments and grains of mudrsilt. Thus, the quality of diatomite varies from layer to layer and field to field. In some cases, diatomite is water wet and has a matrix that is almost entirely biogenic silica with very little clay. In others, the rock might be mixed wet and clay content can be relatively high. A described later, they choose to begin with and characterize relatively clean diatomite.

We used diatomite as catalytic matrix (Mohamedbakr *et al*., 2010) that we synthesized Polyethylene glycol-400 (PEG-400) grafted in diatomite support as macromolecule ligand and the structure of the ligand was characterized by IR spectroscopy. The complex of silica-supported PEG-400 and paldium [shortened form, SiO_2-PEG-Pd (II)], radium [shortened form, SiO_2-PEG- Rh (II)], iron [shortened form, SiO_2-PEG- Fe (II)] were for the first time synthesized and characterized by infrared spectroscopy and transmission electron microscope. The possible structure of the complex was discussed. As a catalyst, complexes were used in oxidation process of cyclohexene and its catalytic activity and selectivity was also investigated. Experimental results showed that the complex possessed activity and selectivity for epoxidation of cyclohexene. The analysis oepoxycyclohexane was done by gas chromatography.

In addition to natural fractures that may be cemented or uncemented, wells in diatomite are hydraulically fractured to improve well productivity and injectivity. Induced fractures are massive with heights on the order of 100 m and total lengths of roughly the same magnitude. Such fractures are used for water (Patzek, 1992) and steam injection (Kovscek *et al*., 1996a, b), as well as production.

A systematic investigation of fluid flow characteristics within diatomite_a high porosity, low permeability and siliceous rock is reported by Akin *et al*. (2000). Using an X-ray computerized tomography_CT. scanner and a novel, CT-compatible imbibition cell, they studied spontaneous cocurrent water imbibition into diatomite samples. Air-water and oil-water systems are used and the initial water saturation is variable. Mercury porosimetry and a scanning electron microscope_SEM. are employed to describe diatomite pore structure and the rock framework. Diatomite exhibits a fine pore structure and significant pore-level roughness relative to sandstone thereby aiding the flow of imbibing water. Despite a marked difference in permeability and porosity as compared to sandstone, they found similar trends in saturation profiles and dimensionless weight gain vs. time functions. Although diatomite is roughly 100 times less permeable than sandstone, capillary forces result in a strong imbibition potential for water such that imbibition rates rival and surpass those for sandstone.

Diatomite, as an adsorbent, can effectively remove the basic dye from solution and is inexpensive (Khraisheh *et al*., 2004b). The capability of diatomite to remove reactive dyes from aqueous solution is less efficient compared to activated carbon. In addition, when diatomite is directly used in wastewater treatment, there are some limitations, especially in column studies, especially in relation to low filtration rate. Al-Ghouti *et al*. (2005) showed that MOMD is a much more effective adsorbent for the removal of basic and reactive dyes from aqueous solutions. As a result, in this study, MOMD was used as the main adsorbent. It has also been shown that MOMD has a high selectivity for dye removal. The effect of initial concentration, particle size, mass of the adsorbent, pH and agitation speed on adsorption behavior of Methylene Blue (MB) onto Jordanian diatomite has been investigated (Al-Ghouti *et al*., 2009). The maximum adsorption capacity, q, increased from 75 to 105 mg g^{-1}

when pH of the dye solution increased from 4 to 11. It is clear that the ionisable charge sites on the diatomite surface increased when pH increased from 4 to 11. When the solution pH was above the pH_{ZPC}, the diatomite surface had a negative charge, while at low pH (pH<5.4) it has a positive charge. The adsorption capacity increased from 88.6 to 143.3 mg gG^1 as the initial MB concentrations increased from 89.6 to 225.2 mg dmG^3. The experimental results were also applied to the pseudo-first and -second order kinetic models. It is noticed that the whole experimental data of MB adsorption onto diatomite did not follow the pseudo-first order model and had low correlation coefficients (R^2<0.3). The calculated adsorption capacity, qe,cal, values obtained from pseudo-first order kinetic model did not give acceptable values, qe,exp. The maximum uptake capacity seems to be independent of the particle size of the diatomite when the particle size distribution is less than 250-500 m. While at larger particle size 250-500 m, the maximum uptake capacity was dependent on the particle size. It would imply that the MB adsorption is limited by the external surface and that intra particle diffusion is reduced. The effect of the agitation speeds on the removal of MB from aqueous solution using the diatomite is quite low. The MB removal increased from 43 to 100% when mass of the diatomite increased from 0.3 to 1.7 g.

The use of diatomite as a partial replacement for cement in the production of cement mortar was investigated by Degirmenci and Yilmaz (2009). Diatomite was used at 0, 5, 10 and 15% replacement by weight for cement while sand and water quantities were kept constant. Compressive and flexural strength, freeze-thaw resistance, sulfate resistance, water absorption and dry unit weight of the mortars were determined. The compressive and flexural strength decreased with increasing diatomite content for all curing periods. However, the compressive strength of the cement mortar which was produced with 5% diatomite content complied with the minimum specified value of given in the standards. Diatomite replacement generally increased the compressive strength of the cement mortar after 25 freezing and thawing cycles. Water absorption of the mortars decreased with the increase of diatomite content except the mortar containing of 15% diatomite. Dry unit weight of the cement mortar was lower than the control mortar because of high porosity of diatomite. The expansion of the cement mortar bars immersed in 5% sodium sulfate solution decreased with increasing diatomite content and generally the sulfate resistance of the mortars was higher than that of the control mortar.

Diatomite is used as pozzolanic additives for Portland cement and mortars and grouts. Aydin and Gu (2007) studied the effect of diatomite as additive on the properties of concrete. They indicate that the increase of additive ratio results a sudden decrease in compressive strength. The pozzolanic reaction of diatomite leads to the formation of higher amounts of hydrate products, especially at the age of 28 days (Kastis *et al*., 2006). Stamatakis *et al*. (2003) demonstrated that the use of diatomite rocks as cement additives has drawbacks such as higher water demand, but compressive strength of the laboratory produced cements exhibit higher values than that of the reference Portland cement. This diatomite rock had the greatest amount of silica content reflecting its high opal-A content. Fragoulis *et al*. (2005) investigated that the addition of diatomite in cement results an increase of its specific surface (Blaine) because of their high grind ability.

The adsorption of some textile dyes by diatomite was investigated using S2f Blau BRF (SB), Everzol Brill Red 3BS (EBR) and Int Yellow 5GF (IY). Adsorption of these textile dyes onto diatomite earth samples was studied (Erdem, 2005) by batch adsorption techniques at 30°C. The adsorption behavior of textile dyes on diatomite samples was investigated using a UV_{vis} spectrophotometric technique. The effect of particle size of diatomite, diatomite concentration, the effect of initial dye concentrations and shaking time on adsorption was

investigated. Adsorption coverage over the surface of diatomite was studied using two well-known isotherm models: Langmuir's and Freundlich's. These results suggested that the dye uptake process mediated by diatomite has a potential for large-scale treatment of textile mill discharges. According to the equilibrium studies, the selectivity sequence can be given as IY>SB>EBR. Values of the removal efficiency of the dyes ranged from 28.60 to 99.23%. These results show that natural diatomite holds great potential to remove textile dyes from wastewater.

We report the formation of vertical carbon nanotubes utilizing diatomite as a substrate. This new material combines the advantages of carbon nanotubes and diatomite in one material. The SEM investigations showed that the average diameter of the carbon nanotubes was 60 nm and the growth was through the tip growth mechanism. Raman spectroscopy was also used for the carbon nanotubes characterization and showed two intensive peaks around 1350 and 1580 cmᴳ¹ and several peaks at low frequency range from 100 to 500 cmᴳ¹ which are assigned to the Radial Breathing Mode (RBM) and used as a characteristic of single wall carbon nanotubes. The photoluminescence measurements at the room temperature showed two very narrow intensive overlapping peaks near the ultraviolet range at energy of about 3 eV. And there are two peaks with lower intensity in the infrared region at 830 nm and at 940 nm (or 1.49, 1.3 eV, respectively) (Duraia *et al*., 2010).

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