



UNIVERSITI PUTRA MALAYSIA

**SYNTHESIS OF HYDROTALCITE-LIKE MATERIAL AND ITS
COMPLEXES WITH ACTIVATED CARBON FOR COLOUR REMOVAL**

YAMIN YASIN

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**MASTER OF SCIENCE
UNIVERSITI PUTRA MALAYSIA**

1999



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By

YAMIN YASIN

**Thesis submitted in fulfilment for the
Degree of Master of Science in the Faculty of Science and Environmental Studies
Universiti Putra Malaysia**

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Master of Science.

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August 1999

Chairman: Associate Professor Mohd Zobir Hussein, Ph.D.

Faculty: Science and Environmental Studies.

Hydrotalcite-like material and its complexes with activated carbon were prepared using activated carbon bought from a local manufacturer. The resulting material and its precursor were used as an adsorbent for removal of colour from natural peat water. The colour change of natural peat water was used as an indicator to measure the amount of humic substances being adsorbed.

Various parameters affecting the adsorption process were studied. These include contact time, adsorbent dosage, anions and temperature. Characterization of the resulting samples before and after treated with natural peat water was carried out to see the physicochemical changes.

X-ray diffractograms of the samples prepared showed the presence of sharp peaks which signifying high crystallinity. The basal spacing corresponding to the 003 reflection was found to be 7.9 Å. The X-ray diffractograms of humic substances-adsorbed samples were almost similar and basal spacing of around 7.9 Å was maintained. A reduction in BET and micropore surface area was observed for humic-substances-adsorbed samples. The filling of the pore with humic substances



was presumably contributed to the reduction of surface area. Adsorption kinetics showed that hydrotalcite was very effective in removing humic substances from natural peat water compared to its complexes with activated carbon and activated carbon itself.

Activated carbon was reactivated using potassium hydroxide (KOH). The resulting activated carbon was used as an adsorbent in the colour removal from methylene blue. The reactivation of activated carbon at the concentration of 30% gave optimum values of BET and Langmuir surface area, 1389 m²/g and 1836 m²/g, respectively. Various factors affecting the adsorption process were studied, which include contact time, pH and adsorbent dosage. Adsorption kinetics showed that reactivated activated carbon (ACKOH) is a better adsorbent than original activated carbon (AC) due to its high surface area. The results also showed that adsorption processes could be fitted to both Langmuir and Freundlich isotherms.

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**SINTESIS HIDROKSIDA BERLAPIS GANDA DAN KOMPLEKSNYA
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Oleh

YAMIN YASIN

Ogos 1999

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Hidroksida berlapis ganda (HBG) dan kompleksnya dengan karbon teraktif yang diperolehi dari kilang tempatan (KHBG) telah digunakan dalam kajian ini. Kesemua bahan ini telah digunakan sebagai penjerap untuk menyahwarnakan air gambut semulajadi. Perubahan warna air gambut semulajadi dijadikan sebagai penunjuk bagi keberkesanan jerapan bahan humik daripada air gambut. Sementara itu, pelbagai parameter yang mempengaruhi proses jerapan telah dikaji. Parameter ini termasuklah jangka masa jerapan, jisim sampel, anion dan suhu. Sampel-sampel yang telah terjerap bahan humik dari air gambut dianalisis dan perbandingan dengan sampel asal dilakukan.

Pembelauan sinar-X untuk sampel menunjukkan puncak yang tajam yang menggambarkan penghabluran yang baik. Jarak diantara lapisan yang diperolehi adalah 7.9 Å. Pembelauan sinar-X untuk sampel yang terjerap bahan humik memberikan jarak diantara lapisan yang sama iaitu 7.9 Å. Analisis luas permukaan menunjukkan berlaku penurunan kepada luas permukaan BET dan liangmikro untuk



sampel yang terjerap bahan humik. Penurunan ini mungkin disebabkan oleh bahan humik yang memasuki sampel liangmikro. Keputusan kajian menunjukkan HBG adalah sangat berkesan untuk menjerap bahan humik pada air gambut semulajadi jika dibandingkan dengan KHBG dan karbon teraktif.

Karbon teraktif yang dibeli dari kilang tempatan dan karbon teraktif yang dilakukan pengaktifan semula dengan menggunakan KOH digunakan sebagai penjerap dalam penyahwarnaan metilena biru. Pengaktifan semula karbon teraktif memberikan nilai maksimum untuk luas permukaan BET dan Langmuir pada kepekatan KOH 30%, dengan nilai masing-masing, 1389 m²/g dan 1836 m²/g. Pelbagai parameter yang mempengaruhi proses jerapan telah dikaji. Parameter ini termasuklah jangka masa jerapan, pH dan juga jisim penjerap. Keputusan kajian menunjukkan karbon teraktif yang dilakukan pengaktifan semula memberikan hasil yang lebih baik jika dibandingkan dengan karbon teraktif tanpa pengaktifan. Ini disebabkan oleh luas permukaan yang lebih besar hasil dari proses pengaktifan semula. Keputusan juga menunjukkan jerapan untuk kedua-dua proses mematuhi isoterma Langmuir dan juga Freundlich.

CHAPTER I

INTRODUCTION

Environmental Quality

Pollution of natural waters is usually associated with the presence of undesirable toxic substances and heavy metals resulting from man made sources (Amin and Jayson 1996).

The problems of water contamination have existed ever since man started development activities on land. With the rising outcry for more stringent control over the quality of our environment, it has become a matter of public interest to regulate all sorts of industrial effluents, rivers and streams.

Water has played an important role in human's life as well as other living organisms. Therefore, it is necessary to treat polluted water, which we consume as drinking water. The sources of water supply can be divided into two major classifications: groundwater and surface water. To these should be added rainwater and



dimineralized water. The ground water supply includes dug, bored, driven and drilled wells, rock and sand or earth springs, and infiltration galleries. The surface water supply includes lakes, reservoir, stream, pond, river and creeks supplies (Salvato, 1982).

As we know, our drinking water resources are mainly from rivers and streams. If the water from the treatment plant is contaminated with domestic discharge and industrial waste, it can create long term harmful effects to animal and human health. Consequently, awareness of carcinogenic property associated with consumption of drinking water is another matter of concern.

Layered Double Hydroxides

Clays can be divided into two broad groups, namely cationic clays, which nature prefer and anionic clays, which is less common. Clays can be prepared synthetically or chemically to enhance certain desirable properties. Clay minerals are composed of infinite layers of metal or non-metal oxides and hydroxides stacked on top of each other. For cationic clays, the charges of interlayer cations neutralize the negatively charged sheets. However, anionic clays have positively charged metal oxide or hydroxides layers with anions located at interstitial position.

Layered double hydroxides or the so-called anionic clays are rarely found in nature. Anionic clays, natural and synthetic layered mixed hydroxides contain

exchangeable anions. Hydrotalcite is a type of layered double hydroxides and can be grouped as anionic clay. The mineral consisting mainly Mg^{2+} , Al^{3+} and CO_3^{2-} , in which the metal ions forming the sheets or layers and CO_3^{2-} as interstitial anion.

Historical Background

Hydrotalcite is a mineral that can be easily crushed into a white powder was discovered in Sweden around 1842 (Cavani *et al.*, 1991). It occurs in nature in foliated and contorted plates or fibrous masses. The first reports of synthetic layered double hydroxides appeared in the 1930's when Feitknecht produced small quantities by reacting dilute aqueous metal salt solutions with base. After appropriate aging, washing and drying solids were obtained which had the distinctive X-ray powder patterns of hydrotalcite. Mannase presented the first exact formula for hydrotalcite $[Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O]$ and other isomorphous minerals (Cavani *et al.*, 1991).

Aminoff and Broome recognized the existence of two polytypes of hydrotalcite on the basis of X-ray investigations. The first one having rhombohedral symmetry and the second having the hexagonal symmetry or the so-called manasseite (Cavani *et al.*, 1991).

Structure of Hydrotalcite

The structure of hydrotalcite is similar to those of brucite-like structure, $[\text{Mg}(\text{OH}_2)]_n$, with a net positive charge on the platelets balanced by anions, which are exchangeable. In this case a proportion of the divalent metals cations were replaced by the trivalent cations. The resulting excess positive charge is balanced by anions and water incorporated in the interlayer region (Chisem *et al.*, 1994). The Mg^{2+} will occupy the octahedral sites between the sheets of closed packed anions and shares edges to form infinite sheets. These sheets are stacked on top of each other and are held together by hydrogen bonding. Figure 1 shows the basic structure of layered double hydroxides.

A positive charge is generated in the hydroxyl sheet when Mg^{2+} ions are substituted by a trivalent ion. The CO_3^{2-} anions, which lie in the interlayer region between the two brucite-like sheets, will compensate the net positive charge. Anions and water molecules maintain electrical neutrality. Therefore the main features of hydrotalcite structures are determined by the nature of the brucite-like sheet, by the position of anions and water in the interlayer region and by the type of stacking of the brucite-like sheets. In nature the anion is frequently found the carbonate anion. Figure 2 shows the structure of brucite.

The sheets containing cations, which occupy the octahedral holes in the close-packed configuration of the OH^- ions and are built as in brucite. The anions and water are randomly located in the interlayer region, being free to move by breaking their

bonds and forming new ones (as liquid water). The oxygen atoms of the water molecules and the CO_3^{2-} groups are distributed approximately closely around the symmetry axes that pass through the hydroxyl groups of the adjacent brucite-like sheet.

These hydroxyls are tied to the carbonate groups directly or via intermediate H_2O through hydrogen bridges: $\text{OH-CO}_3\text{-HO}$ or $\text{OH-H}_2\text{O-CO}_3^{2-}\text{-HO}$ (Cavani *et al.*, 1991). The CO_3^{2-} groups are located flat in the interlayer and H_2O is loosely bound. They can be eliminated without destroying the structure.

The brucite-like sheets can stack one on the other with two different symmetries, rhombohedral or hexagonal. If we call ABC the three-fold axis of the OH groups in the brucite-like sheet, the stack may have the sequence BC-CA-AB-BC, having three sheets in the unit cell, or BC-CB-BC with two sheets in the unit cell. Figure 3 shows the stacking sequences in the hydrotalcite with different symmetries.

The parameters of unit cell for hydrotalcite crystallize in rhombohedral 3R symmetry are $C=3c'$ (where c' is the thickness of one layer constitutes by a brucite-like sheet and one interlayer).

Synthetic hydrotalcite-like compounds have been extensively studied and have found many practical applications because the metal cations, size and morphology of the particles and their physical and chemical properties can be varied. The hydrotalcite have been used as such or after calcination. These applications including antacid

formulations, catalyst and oil well drilling mud. Figure 4 shows a schematic diagram of the possible applications of hydrotalcite-like compounds.

By modifying the crystal structure, the particle morphology and the composition, we can produce materials, which can absorb colours including common dyes and humic substances and toxins (mothproofs and pesticides) from aqueous systems. Absorption is rapid and capacities are high, but the most valuable feature is that these contaminants can be removed down to a level that challenge detection limits (Cockett *et al.*, 1995).

Synthetic hydrotalcite clays were found very effective in removing humic substances from upland surface water due to their anionic nature (Amin and Jayson, 1996).

Activated Carbon

Activated carbon has been named according to its properties. There are various definitions that have been defined by the researchers. Activated carbon is the collective name for a group of porous carbons (Gerhartz, 1986). According to Helena *et al.*, (1991), activated carbon is a processed carbon material with highly developed porous structure and large internal specific surface area. The inner specific area is generally greater than $400 \text{ m}^2 \text{ g}^{-1}$ but often exceeds this value, reaching to $1000 \text{ m}^2 \text{ g}^{-1}$ and it has the ability as an absorbent.

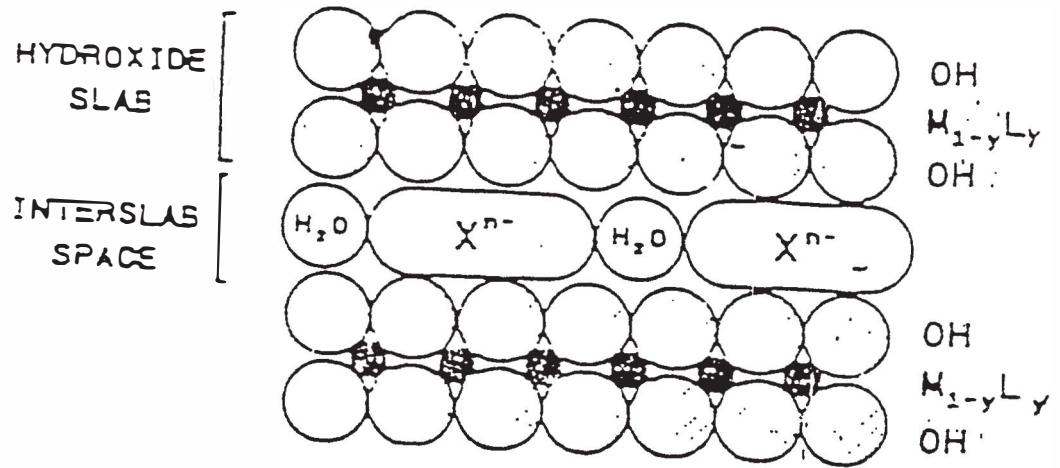


Figure 1: Hydrotalcite structure

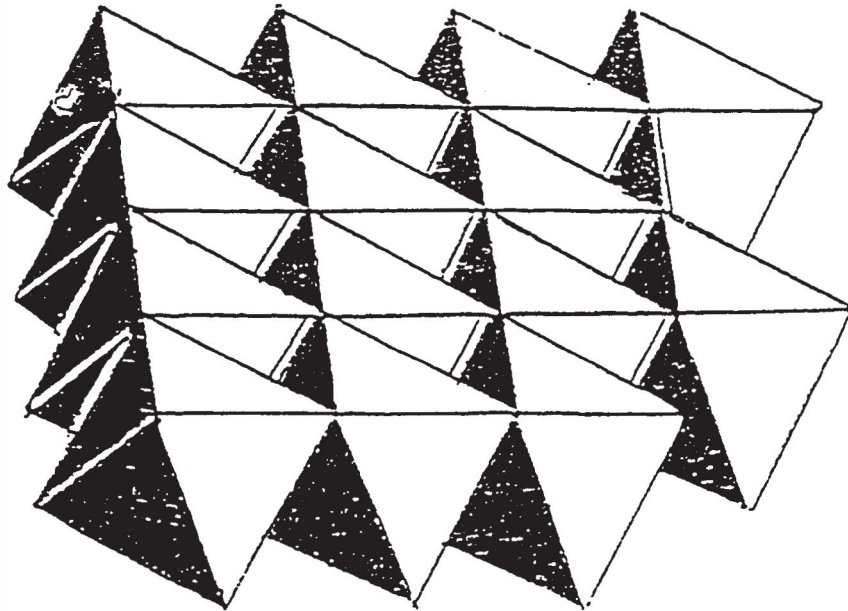
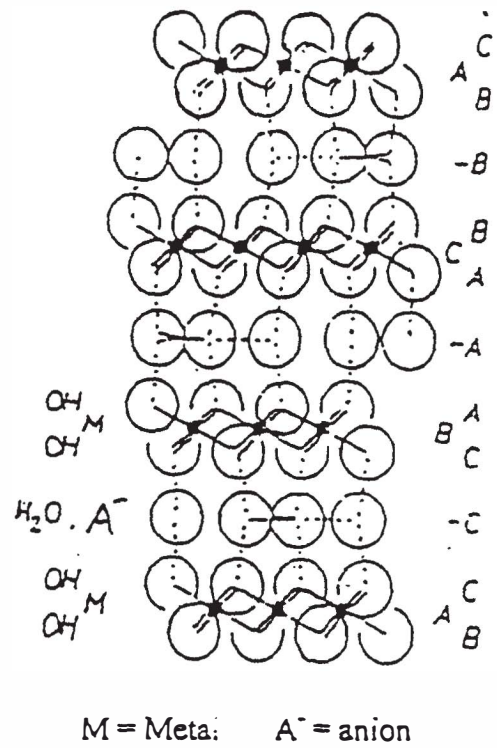
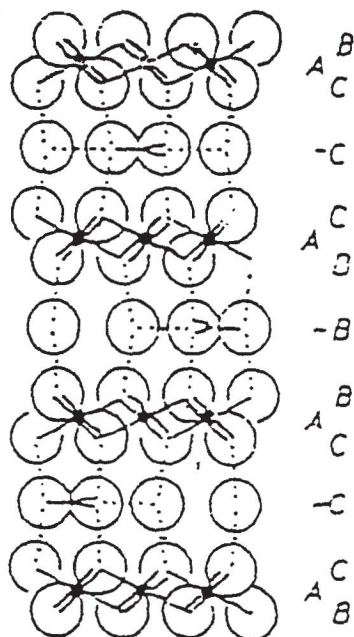


Figure 2: Brucite lattice, $Mg(OH)_2$, top view



Rhombohedral



Hexagonal

Figure 3: Stacking sequences in hydroxalcalite with different symmetries according to (Cavani *et al.*, 1991).

Possible application of hydrotalcite

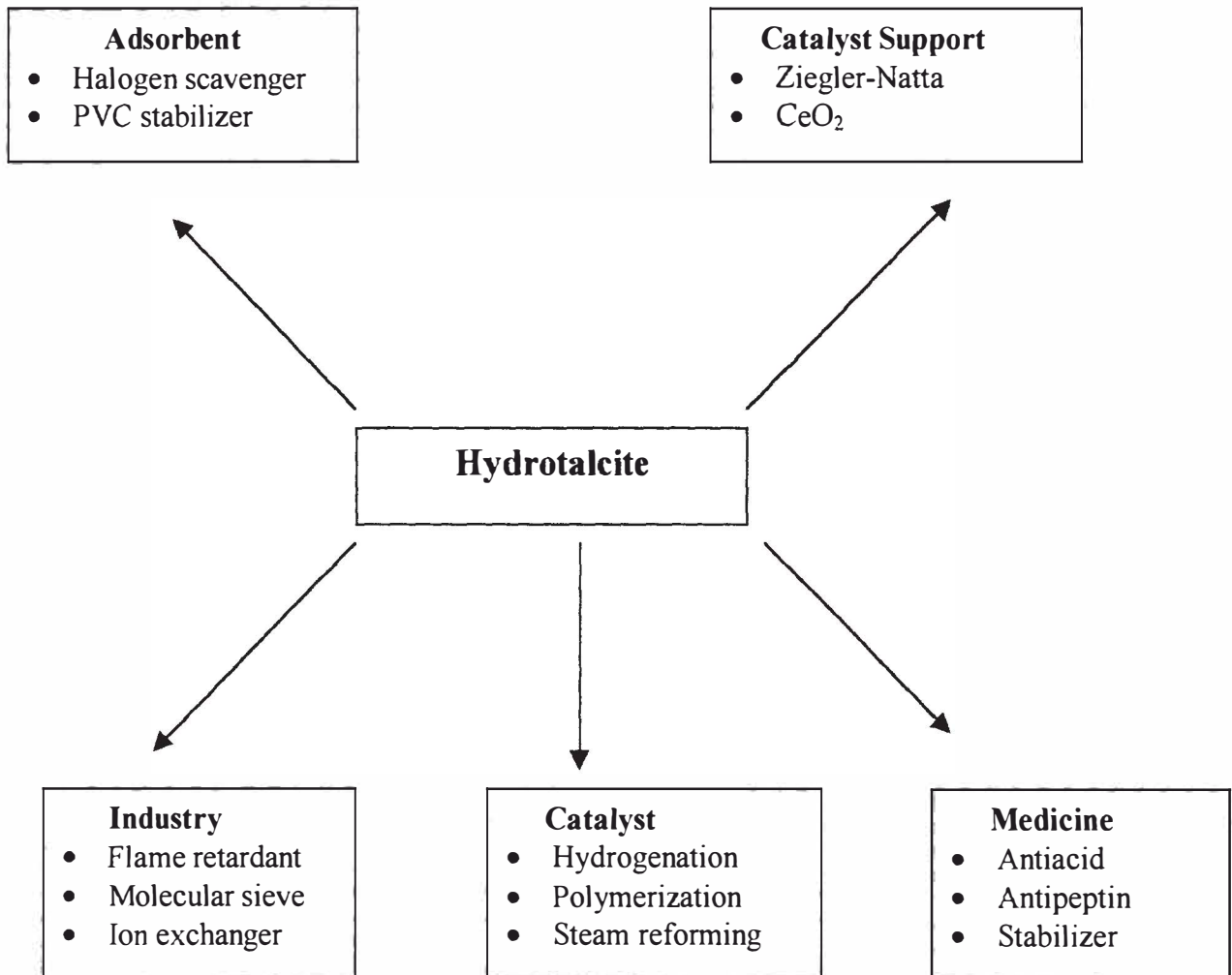


Figure 4: Possible applications of hydrotalcite