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By-Product Synergy In The Textile Industry: Indigo Waste Recovery In The Denim Finishing Process

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BY-PRODUCT SYNERGY IN THE TEXTILE INDUSTRY: INDIGO WASTE
RECOVERY IN THE DENIM FINISHING PROCESS

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Dedication

To my beloved wife, Loise – and to our daughters - Patricia, Pamela, and Jacqueline

~ Your gracious patience over the years will forever be cherished ~

BY-PRODUCT SYNERGY IN THE TEXTILE INDUSTRY: INDIGO WASTE RECOVERY
IN THE DENIM FINISHING PROCESS

by

Dennis Wambuguh, MSc.

DISSERTATION

Presented to the Faculty of the Graduate School of
The University of Texas at El Paso
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Abstract

Textile dyeing effluents present a substantial environmental problem, primarily because such wastewaters contain high concentrations of waste dyes, dye by-products, and variable salt concentrations originating from printing or dyeing processes. Such wastewater streams often do not meet regulatory standards for wastewater discharge even after undergoing treatment by conventional means. The decolorization of textile wastewaters is a worldwide problem. Various processes have been utilized to remove the colored colloidal bodies and suspended solids and to reduce the associated high Biological Oxygen Demand (BOD).

Currently, no single treatment system is adequate to degrade the dye structures in wastewaters. A significant disadvantage of the current processes is their high capital and operating expenditures. Oxidation methods for example, are only effective in wastewater with a very low concentration of organic color while the adsorption process by active polymer resin is expensive and it is difficult to regenerate the adsorbent.

Palygorskite is a crystalloid hydrous magnesium-aluminum silicate mineral with very good colloidal properties such as specific features in dispersion high temperature endurance, salt and alkali resistance, and a high adsorbing and de-coloring capability. The structure of palygorskite was first proposed by Bradley (1940), who described a theoretical formula of $[\text{Si}_8\text{Mg}_5\text{O}_{20}(\text{OH})_2] (\text{H}_2\text{O})_4 \cdot 4\text{H}_2\text{O}$. Due to its sorptive properties, Palygorskite has been effectively applied in decolorizing and clarifying mineral oils and fats, as a carrier in pesticides, in the filtration of special products, as a sorbent on factory floors, and in the pharmaceutical industry. Its ability to adsorb indigo waste and other contaminants from textile effluents however has not been studied. Palygorskite is one of the two constituents of Maya Blue, a material of unprecedented stability with potential application in paints and coatings. The properties and quality of the pigments synthesized from the recovery products compares favorably to pigments synthesized from pure products.

The primary objective of this research was to demonstrate the ability of palygorskite to recover waste indigo dye from blue denim wastewater and to use the recovery products as a substrate for the synthesis Maya-blue pigment, a by-product with potential commercial applications. A secondary

objective was to demonstrate the simultaneous removal of salts from the wastewater without substantially compromising the quality of the synthesized pigment. Salt reductions of up to over 60 per cent were achieved. Removal of the color and salts from the wastewater essentially opens up opportunities for possible reuse of the wastewater.

We demonstrate the effectiveness of palygorskite to concurrently remove indigo dye and salts from the wastewater without significantly compromising the quality of the synthesized by-product. Given that over a billion pairs of blue jeans are manufactured every year and the inordinate quantities of indigo dye used and released as effluent in the stonewash process, the possibility to apply the process on a commercial scale would have substantial economic and environmental implications.

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Chapter 1 Introduction

1.1 THE CHARACTER OF WET PROCESSING EFFLUENT

The textile wet processing or finishing industry consumes enormous amounts of water and auxiliary chemicals (Table 1.1) primarily in the dyeing and finishing operations (Campos et al. 2001; Robinson, et al. 2001; Feitkenhauer and Meyer, 2001; Lin et al. 1997). While many of these chemicals become part of the product, some are removed from the fabric, ending up in wastewater. Approximately 12 per cent of synthetic dyes used each year during manufacture and processing operations in the textile industry are lost and 20 per cent of these lost dyes enter the environment through effluents (Hwang and Chen, 1993). Between 5 and 20 per cent of the indigo dye used in the blue jeans industry is lost to the effluent (O'Neill et al. 1999), resulting in effluent high in color, suspended solids (salts), and dissolved organics (Figure 1). Some of these constituents impart inherent toxicity to the effluent, are aesthetically displeasing, damage the quality of receiving streams and may be toxic to treatment processes, to food chain organisms and to aquatic life. They may also place at risk permit renewal for the concerned industries (Marmagne and Coste, 1996; Woerner, undated). In essence, dealing with the removal or recovery of dyes and salts from textile effluent is a worldwide problem.



Figure 1.1 Blue jeans, blue water (Tehuacan Valley, Central Mexico)

Credit: Maquila Solidarity Network and the Human and Labor Rights Commission of the Tehuacan Valley

It is difficult to find figures relating to actual concentration of dyes in textile wastewater as most authors discuss color in terms of absorbance or the American Dye Manufacturers Institute (ADMI) values. Dye concentrations in dye house effluents cited in literature range from 0.01 g dm^{-3} - 0.25 g dm^{-3} , depending on the dyes and the processes used (O'Neill et al. 1999, Laing, 1991). For vat dyes such as indigo, concentrations ranging from 0.05 g dm^{-3} - 0.1 g dm^{-3} have been reported (Jia et al. 1999, Li and Zang, 1996). The typical concentration of indigo dye in the wash water is 0.02 g dm^{-3} . Since the eye can detect concentrations of 0.005 mg L^{-1} of reactive dye in water, concentrations exceeding this level raise concern on aesthetic grounds.

Traditionally, the stone-washed look in denim fabric or jeans involves washing the fabrics in the presence of pumice to generate the desired localized erosion of the fabrics, followed by a partial bleaching treatment with sodium hypochlorite and a neutralizing and rinsing step. The 'stonewashing' process for the degradation of blue indigo to create a 'faded' look consequently results in excessive amounts of indigo being removed from the fabrics into discharged wastewater. Color is highly visible even in concentrations as low as 1ppm for most dyes, eliciting complaints from an increasingly environmentally aware public and often failing to meet regulatory requirements for wastewater discharge.

While this work will undoubtedly add to the body of knowledge to the field of textile waste management, the purpose of this research is to present and describe a process of waste indigo dye recovery from the blue denim effluent originating from the stonewash process, and reconstitute it into a product with potential commercial applications, a process termed by-product synergy.

Resulting from this work, a patent is pending which will be licensed to an existing company dealing in a line of products akin to the product synthesized under this recovery process.

Table 1.1 Auxiliary chemicals used in textile wet processing (Correia, 1994)

Description	Composition	Function	Processing step
Salts	Sodium chloride	Neutralize zeta potential of fiber, Retarder	Dyeing
Acids	Acetic acid, sulfuric acid	pH control	Preparation, dyeing, finishing
Bases	Sodium hydroxide, Sodium carbonate	pH control	As above
Buffers	Phosphate	pH control, dyeing	
Sequestering agents, Chelates	EDTA	Complex hardness, Retarder	
Surface active agents	Anionic, cationic, and nonionic	Softeners, disperse dyes, regular dye application, Wetting agents, Emulsifiers	As above
Oxidizing agents	Hydrogen peroxide, Sodium nitrite	Insolubilize dyes	Dyeing
Reducing agents	Sodium hydrosulfite, Sodium sulfide	Solubilize dyes, remove unreacted dyes	Dyeing
Carriers	Phenyl phenols, Chlorinated benzenes	Enhance absorption	Dyeing

Since conventional wastewater treatment plants rely on sorption and aerobic biodegradation which have low removal efficiency, the discharge of such dye waste into the environment raises aesthetic concerns, impedes light penetration and damages the quality of receiving streams, and may be toxic to treatment processes, to food chain organisms, and to aquatic life in general.

1.2 TREATMENT METHODS FOR COLOR REMOVAL

Consistent with the high variability of the characteristics of textile wastewaters, many different physical, chemical, and biological treatment methods have been employed for its treatment (Table 1.2). The physical and chemical methods include the use of anion exchange resins (Karcher et al. 2002), flotation (Lin and Lo, 1996), electroflotation, electrochemical destruction, irradiation (Shen et al. 2002), ozonation (Zang et al. 2002), adsorption (Nasser and El-Geundi 1991), and the use of activated carbon (Pala et al. 2002). McKay et al. (1999) studied the feasibility and effectiveness of low-cost adsorbents including rice husk, cotton, bark, hair, and coal to remove dye colors from solution using Safranin and Methylene Blue dyes. Of these carbonaceous and cellulosic materials, bark, rice husk, and cotton had high adsorption capacity for Safranin and Methylene Blue dyes.

Activated carbon and polymer resins are effective adsorbents in removing waste chemicals from relatively concentrated wastewater, but these are prohibitively expensive and necessitate regeneration (McKay, 1981; Blum et al. 1993; Meshko et al. 2001). Some of the physical and chemical treatment techniques are effective for color removal but use more energy and chemicals than biological pre-processes. They also tend to concentrate the pollution into solid or liquid sidestreams requiring additional treatment or disposal.

Oxidation and adsorption are two major technologies for wastewater treatment in the textile industry. The use of ultraviolet light and ultraviolet/hydrogen peroxide treatments is very effective in eliminating organic carbons in wastewater (Huang and Shu 1995). Adsorption on the other hand is rapidly becoming a prominent method of treating aqueous effluents and has been extensively used in industrial processes for a variety of separation and purification purposes, especially in the removal of colored and colorless organic pollutants from industrial wastewater (Al-Qodah 2000).

Table 1.2 Wastewater treatment technologies (Robinson 2001; Mattioli 2002)

Treatment Method	Color Removal	Disadvantage
Biological	Ineffective	Little biodegradation of dyes
Physical/Chemical (ferric salts, alum)	Uncompleted dye removal	Increased salt concentration, high sludge production
Oxidation (hydrogen peroxide)	Effective on many dyes	Acid/alkali addition, residual iron, high sludge production
Photocatalysis (UV)	Effective	-
Ozonation	Very effective	Toxic/carcinogenic by-products, short half-life of ozone
Adsorption (activated carbon)	Effective on a wide range of dyes	Expensive
Membrane technology		
Ultrafiltration (UF)	Effective in recovery of chemicals	Fouling of membranes, disposal of concentrate
Reverse Osmosis (RO) and Nanofiltration (NF)	Effective in removal of salts	Expensive
Other physical and chemical methods		
Ion exchange	Effective for cationic/anionic dyes	Ineffective for disperse dyes
Electrokinetic coagulation	Effective for direct dyes	Poorly effective with acid dyes, residual ferrous sulfate and ferric chloride

Oxidants may potentially create even more toxic chemicals in the effluent through degradation or alteration of the conjugated system of dyes (Yang et al. 1998). The wider application of physical and

chemical treatments techniques in the industry is therefore hampered by either toxicity and/or cost considerations (Edwards, 2000; Lin and Chen, 1997).

Biologically, enzymatic degradation of indigo with purified laccases secreted by a great number of white-rot fungi including *Trametes hirsuta* and *Sclerotium rolfsi* has shown some potential both in the stone-wash process and for color removal in dyeing effluents. Campos et al. (2001) suggested a possible pathway by which laccases oxidize indigo to isatin (indole-2,3-dione), which is further decomposed to anthranilic acid (2-aminobenzoic acid) (Figure 1.2). Laccase treatment of textile dyes such as indigo allows selective removal of the color from effluent and thus presents a possibility of reuse of the water and dyeing auxiliaries in the dyeing process.

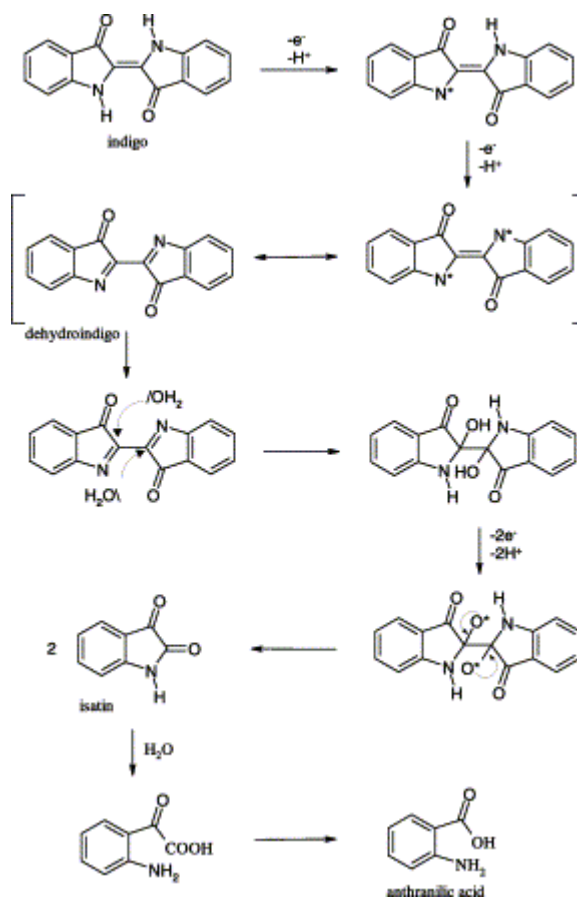


Figure 1.2 A possible mechanism for laccase catalyzed degradation of indigo dye.

As regulations on effluent quality before discharge into municipal systems or streams become increasingly restrictive, it is critical to minimize pollution and implement an appropriate treatment process. Pretreatment systems to control the pollution however, are large and expensive, and have little or no payback other than the elimination of sewer charges. The development of a simple, cost-effective method by which indigo may be recovered from the wastewater of denim yarn dye for reuse would, therefore, have significant economic and environmental implications.

1.3 THE 'STONEWASH' PROCESS IN THE DENIM INDUSTRY

Undyed denim is nearly white in color. For production of blue jeans, it is dyed with an indigo-based dye, coloring the fabric dark blue. Traditionally, the stone-washed look in denim fabric or jeans involves washing the fabrics in the presence of pumice stones or enzymes (cellulase-laccase cocktails) to generate the desired localized erosion of the fabrics, followed by a partial bleaching treatment with sodium hypochlorite and a neutralizing and several rinsing steps.

A more recent process of stonewashing uses Perlite, a form of naturally occurring silicon rock in place of pumice. Perlite treatment has recently gained ground ostensibly because it reduces the rate of harm caused to large washing machines by pumice stones and gives the denim better supple and softer finish. Whatever the process used, the 'stonewashing' process for the degradation of blue indigo to create a faded look in effect results in excessive amounts of indigo being removed from the fabrics and discharged in the wastewater. The abrasion of the fabric also reduces the life of the garment, which contributes to maintaining consumer demand for the denim products

Furthermore, high amounts of bleaching agents such as potassium permanganate and sodium hypochlorite) are also discharged (Campos et al. 2001), resulting in effluent characterized by large variability of chemical composition (Kobya et al. 2003), high salt base content (Kim et al. 2003) and color. Color, usually the first contaminant to be recognized in wastewater even in very small quantities ($10\text{-}50\text{ mg L}^{-1}$), is highly visible and aesthetically displeasing, impedes light penetration, damages the quality of receiving streams and may be toxic to treatment processes, food chain organisms, and aquatic life. Effluent standards however, require wastewater quality to meet certain standards before discharge into public water bodies or to meet requirements for reuse.

1.4 BY-PRODUCT SYNERGY AND WASTE INDIGO RECOVERY

By-product synergy (BPS) refers to the production of a secondary or additional product, generated in the course of a manufacturing process, in addition to the principal product, a concept currently being promoted by the U.S. Business Council for Sustainable Development (BCSD) and a conglomeration of 125 companies from 30 countries under the Geneva-based World Business Council for Sustainable Development (WBCSD).

The decolorization of textile industry wastewater is a worldwide problem. Consequently there is a growing interest in using commercially available low-cost materials, including clays, for the adsorption and recovery of such waste dyes. Subsequent conversion of the indigo dye waste to Mayan-based pigments would offer potential savings in converting waste to a secondary commercial product, result in more efficient material use, generate revenue or savings, and reduce liability inherent in failing to meet regulatory guidelines. Maya blue, the flagship of a range of complex organic/inorganic hybrid pigments with potential applications in the paint and coating industry is made from indigo and natural clay, palygorskite (a.k.a. attapulgite). The pigment is reputed to have high stability and is resistant to chemical attack by acids, alkalis, chemical solvents, oxidizing and reducing agents, as well as biodegradation (Fois et al. 2003).

Some reports point to potential savings of up to \$500,000 per year worth of indigo dye per year in a typical dye house as a result of waste indigo recovery while the cost savings from color removal at wastewater treatment plants may be worth an additional \$500,000 per year. Concurrent adsorption and removal of salt would be an added advantage, particularly if the product quality were not adversely affected. A system to remove color and recover salt from fiber reactive dyeing for example, has a two-year payback if the water price including purchase, sewer charges and fines is \$4.50/1000 gallons (Woerner, undated).

1.5 CLAYS AND ADSORPTION

Clays are perhaps the oldest materials from which humans have manufactured various artifacts and have found uses as drilling mud, as absorbents, in waterproofing and sealing, in refining and clarifying, as catalysts, and as carriers in the pharmaceutical industry. Adsorption of contaminants in aqueous effluents with industrial clays such as palygorskite is rapidly becoming a prominent treatment method.

Palygorskite is a crystalloid hydrous magnesium silicate mineral with very good colloidal properties such as specific features in dispersion, high temperature endurance, salt and alkali resistance and a high absorbing and decoloring capability (Figure 1.3). Palygorskite clay has a high surface area, a high cation exchange capacity, and its sorptive and bleaching qualities have been applied in the purification and decolorization of fats and oils since antiquity (Galan, 1996) and as an absorbent for water, chemicals, and even wastes (Murray, 2000). Palygorskite and indigo are the two constituents of Maya blue.

1.5.1 Palygorskite clay

Palygorskite (a.k.a. attapulgite, fullers earth) clay is a hydrated magnesium silicate with partial isomorphic substitutions of magnesium by aluminum and/or iron. Palygorskite is fibrous clay with average fiber dimensions ranging from 0.1-2 microns (Figures 1.3 and 1.4). Natural palygorskite exists in two space groups/forms with different symmetries, orthorhombic *Pbmm* and the more ordered monoclinic *C2/m*. A two-layer clay consisting of two silica (SiO_4) tetrahedral sheets linked by an octahedral (MO_6) sheet with M mainly magnesium and aluminium ions (Figure 1). The clay has a fibrous texture with an internal structure of microchannels (measuring $3.7 \text{ \AA} \times 6.4 \text{ \AA}$ in cross section) and different bonded water molecules representing almost 20% of the structure's total weight (Barrios et al. 1995). The composition of the unit cell is $\text{Si}_8(\text{Mg},\text{Al})_4[\text{O}_{20}(\text{OH})_2(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$; when the same amount of Mg and Al in the octahedral sheet is present, a neutral cell results. Its ideal structure as studied by Bradley (1940) is shown in Fig. 1.4. The palygorskite clay molecule has two types of water

present in its formula; magnesium coordinated water and adsorbed water. The structure of the clay results in zeolite-like channels that may be filled with water or organic molecules (Figure 1.5).

Like other industrial clays, Palygorskite is characterized by high surface area, high porosity, high surface charge, and high cation exchange capacity conferring excellent sorptive, colloidal, and gelling properties. Its sorptive and bleaching qualities have been applied in purification and decolorization of fats and oils since antiquity (Galan 1996), to absorb water, chemicals, and even toxic wastes (Murray, 2000). Its adsorption behavior in textile effluents (salts and color) however, has been less studied.

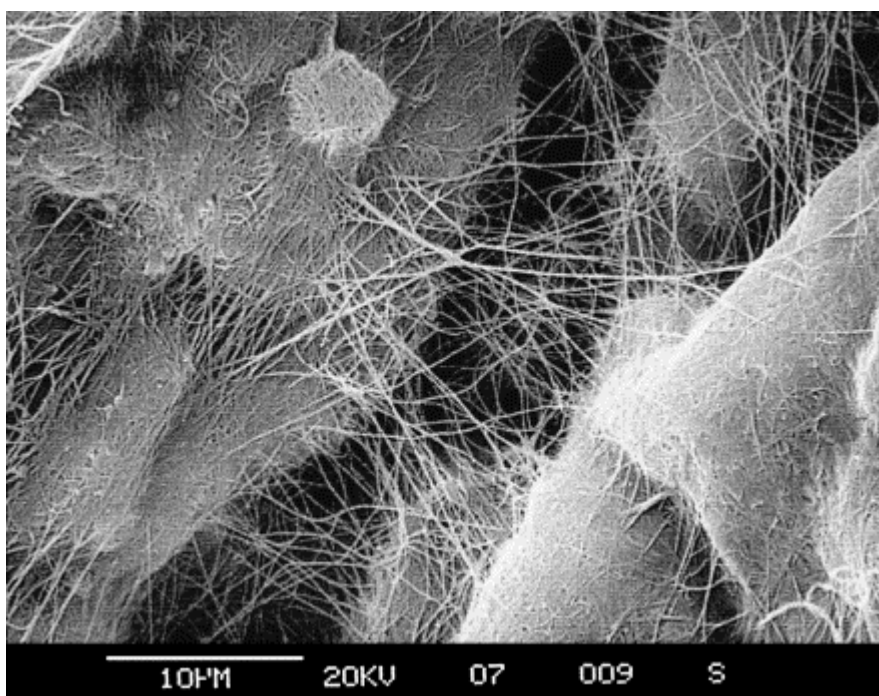


Figure 1.3 SEM of palygorskite showing elongate particle shape (Murray 2000)

The surface characteristics of palygorskite can be modified by treatment with acids or cationic surfactants such as hexadecyltrimethylammonium (HDTMA) and octadecyltrimethylammonium bromide (ODTMA), making them more adsorbent and more efficient in color removal. Acid treatment leaches cations from the octahedral and tetrahedral sheets (which are replaced by hydrogen ions), removes impurities such as calcite and dolomite, and opens the edges of platelets. The net effect of these changes is to increase the surface area, porosity, and thermal stability of the modified clay (Araujo Melo et al.

2000). The decolorizing ability of acid treated palygorskite increases with the intensity of the acid treatment up to a point and then decreases as crystallinity decreases with the destruction of the octahedral structure into amorphous silica (Barrios et al. 1995).

SEM Image of Palygorskite

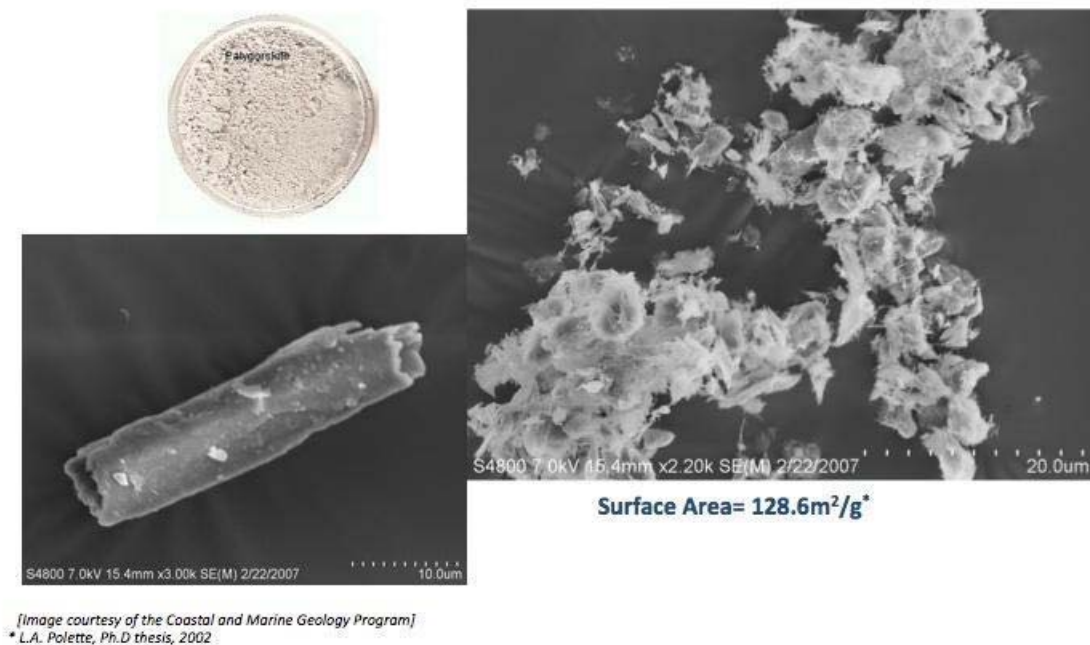


Figure 1.4 Scanning Electron Micrograph of palygorskite

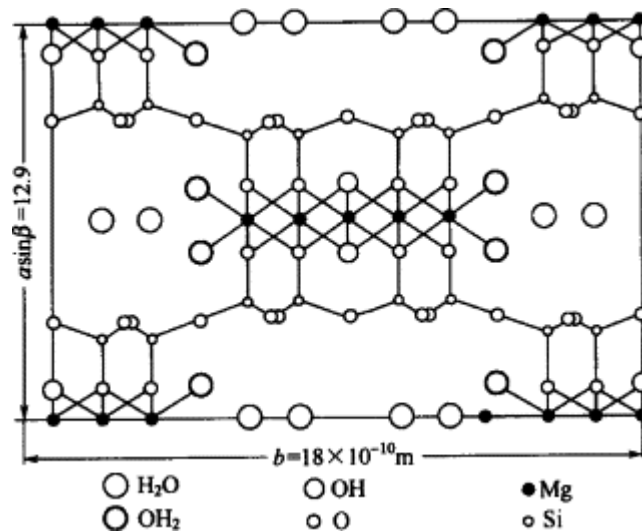


Figure 1.5 Crystalline structure of attapulgite from (001) plane

Source: Bradley 1940

Cationic surfactant-modified clays have been shown to have enhanced ability to sorb non-ionic organic compounds and different anions such as chromate, nitrate and sulfate (Li et al. 2003).

1.5.2 Indigo

Many of the dyes are primarily based on complex substituted aromatic and heterocyclic groups such as aromatic amine, phenyl, and naphthyle groups. Indigo, a vat dye is a highly structured compound, practically insoluble in any solvent, and very difficult to degrade by biological treatment methods. For its application on cotton denim, it is first solubilized by reducing it with sodium sulfite, and then exhausting it on fiber where it is re-oxidized. The dye, a dark blue crystalline powder with the chemical formula corresponding to $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2$ (Figure 1.5) has a melting point of $390^\circ\text{C} - 392^\circ\text{C}$. It is extensively used for dyeing textiles particularly in the blue jeans industry (Manu and Chaudhari, 2003) and as a colorant for artistic pigments (Sanchez Del Rio et al. 2006). In the United States, indigo is primarily used as a dye for cotton work clothes and blue jeans. Worldwide, approximately one billion pairs of jeans are dyed blue with indigo every year, a demand that can only be met by synthetic indigo from BASF.

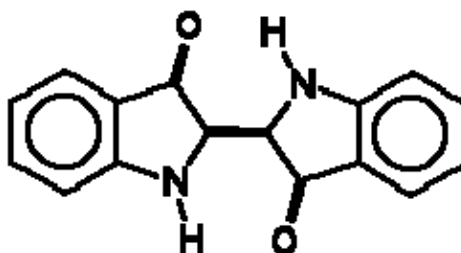


Figure 1.6 Molecular structure of indigo

Indigo does not bond strongly to the fiber, and wear and repeated washing may slowly remove the dye. In actual practice, only about 80 per cent of the dye is fixed onto the fabric, while the remainder is washed away (Woerner, undated). Between 5 and 20 per cent of the dye is therefore essentially lost to the effluent (O'Neill et al. 1999). The dye reportedly can be removed from the wastewater by coagulation and flocculation (Manu and Chaudhari, 2002) but the method does not appear to be practical.

1.5.3 Maya Blue

Maya blue is a synthetic an unusual pigment consisting of a mixture of the clay mineral palygorskite (or sepiolite) and the organic dye indigo ($C_6H_{10}N_2O_2$). The pigment is reputed for its unprecedented stability and was used by the ancient Maya Indians in murals, pottery, and artifacts. The pigment is famed for its resistance to attack by dilute mineral acids, alkalis, chemical solvents, oxidants, reducing agents, moderate heating and even biocorrosion (Jose-Yacaman et al. 1996). Because of these properties, the pigment has potential applications in paint and coating industries, among other uses.

The stability of Maya Blue arises from the almost perfect fit of indigo in the channels, controlled by steric (van der Waals) interactions (Tilocca et al. 2003). The desorption of some structural water molecules during synthesis leads to some uncoordinated Mg ions exposed on the inner surface of the channels, making these 'defect' sites very reactive towards adsorption. The carbonyl group of indigo is then coordinated to the exposed Mg ions, forming very stable bonds. The trapping of indigo inside the palygorskite channels determines the high stability of the Maya blue. Indigo molecules can also be locked in channel 'side pockets' formed by the sorption of structural water molecules.

Maya Blue is now produced synthetically by treating indigo with palygorskite clay. Heating the mixture causes partial removal of zeolitic water (Kleber et al. 1967; Chiari et al., 2003) or the elimination of structural water (Fois et al., 2003) from clay structure, emptying portions of the channels in which the indigo can be accommodated to form stable chemical bonds with the clay. Heating induces a strong bond formation between surface cations on the clay and the carbonyl and nitrogen in indigo resulting in the complex organic-inorganic hybrid of the Maya blue pigment. The characteristic turquoise-blue color is obtained only after the heating.

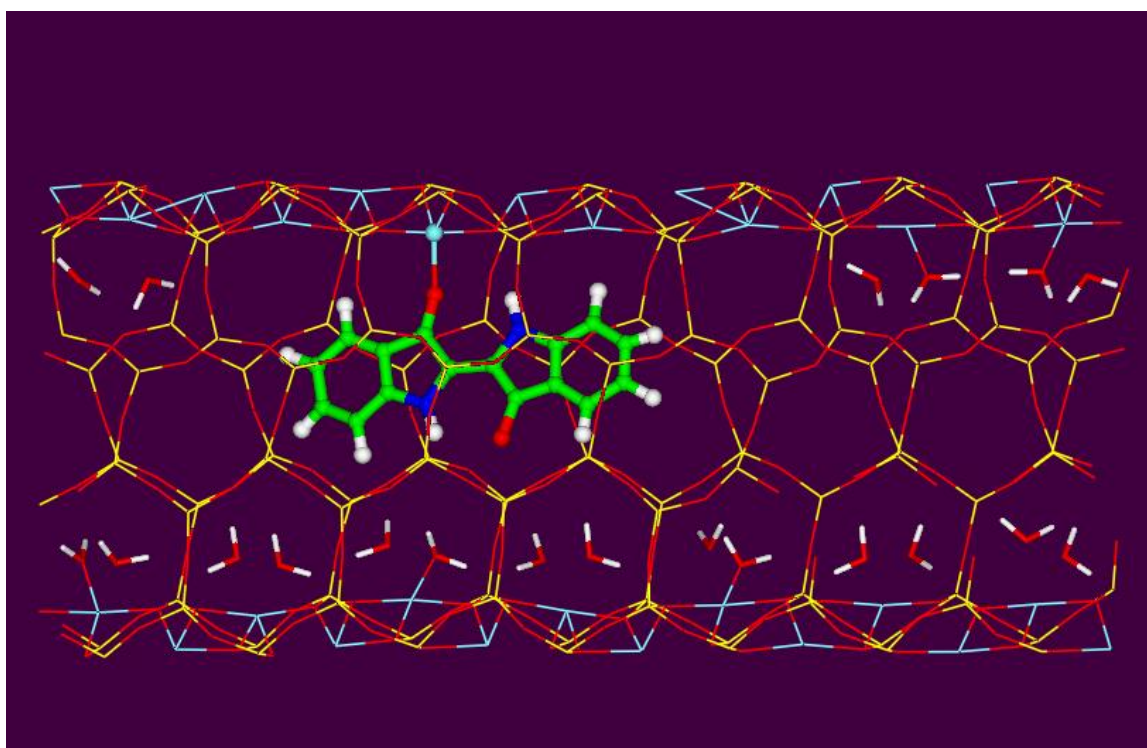


Figure 1.7 MD simulation showing indigo-mg interaction at top of channel

Source: Fois, 2003

Chapter 2 Research Objectives

The textile industry consumes enormous amounts of water and chemicals in the wet process of textile finishing. A diverse range of chemical reagents and dyes are used, ranging from inorganic compounds to polymers and organic products (Mishra and Tripathy, 1993; Banat et al., 1996 and Juang et al., 1997). While the release of dyes into the environment constitutes only a small proportion of water pollution, the presence of very low concentrations of dyes in effluent is highly visible and undesirable (Nigam, P., Armour, G., Banat, I.M., Singh, D. and Marchant, R., 2000). More than 100,000 commercially available dyes with over 7×10^5 tons of dye-stuff are produced annually (Meyer, 1981; Zollinger, 1987). Due to their complex chemical structure and synthetic origin, many of the dyes are resistant to fading on exposure to light, water and many chemicals (Baughman and Perenich 1988; Poots and McKay, 1976; McKay, 1979) and are therefore not easily removed from solution by conventional municipal aerobic treatment systems, dependent on biological activity (Moran et al., 1997). There are many structural varieties, such as, acidic, basic, disperse, azo, diazo, anthroquinone based and metal complex dyes.

But as regulations on effluent quality before discharge into municipal systems or into receiving streams become increasingly restrictive, the quality of the effluent could as well threaten permit renewal for these industries. It is therefore important both from an ecological as well as an economic standpoint to reduce the dye concentration in the wastewater before discharge or recover the dye for recycling/reuse.

Among the treatment options for color removal from industrial effluents (biological treatment, coagulation, flotation, adsorption, oxidation and hyperinfiltration), adsorption appears to have considerable potential due to its simplicity and cost-effectiveness. It is rapidly becoming a prominent method of treating aqueous effluents and has been extensively used in industrial processes for a variety of separation and purification purposes especially for the removal of colored and colorless organic pollutants from industrial wastewater (Al-Qodah 2000).

Adsorption is a rapid phenomenon of passive sequestration of adsorbate from an aqueous phase onto a solid phase, adsorption of the dye molecules on the surface of the adsorbent through molecule

interactions and diffusion of dye molecules from the surface into the interior of the adsorbent (Ardizzone et al. 1993). The process depends mostly on the surface chemistry or nature of the adsorbent, the adsorbate, and the system conditions between the two phases. Due to their enormous surface area per unit weight, the most common industrial adsorbents include activated carbon, silica gel, and alumina.

Activated carbon and polymer resins appear to have considerable potential for the removal of chemical contaminants in wastewater, but their wider applications is hampered by cost considerations since they eventually become exhausted and have to be replaced (Sanghi and Bhattacharya 2002). Reports of cost-effective adsorbent systems include the use of natural clay for basic and acid dyes (El-Geundi 1991), chitosan for reactive dyes (Juang et al. 1997), sunflower stalk for basic dyes (Sun and Xu 1997), sepiolite for Rhodamine (Arbeloa et al. 1997), shale oil ash for azo dyes (Al-Qodah 2000), montmorillonite and sepiolite for Methyl Green (Rytwo et al. 2000), and natural zeolite for basic dyes (Meshko et al. 2001). Sanghi and Bhattacharya (2002) give a summary of previously reported work on the various low cost adsorbents from agricultural, commercial, and industrial waste sources, and their adsorbent capacities for the decolorization of colored effluents. Most of these processes are designed to remove the dye from solution in an attempt simply to clarify the water for reuse and not for any other purpose. Indigo dye can effectively be removed from the effluent by ultra-filtration and other membrane technologies but the wider application of these technologies is hampered by cost considerations.

Adsorbents, mainly clays are readily available, inexpensive, and offer a cost-effective alternative to conventional treatment of waste streams. The ability of clay to decolorize and refine oils, fats and waxes is well known. Fuller's earth, a generic term for montmorillonite-rich clay material, has been used for the purpose since 1880 (Murray 1990). Decolorization of textile wastewaters with palygorskite clay results from adsorption and is subject to many physico-chemical factors including dye-sorbent interaction, sorbent surface area, particle size, pH, and interaction time (Robinson et al. 2001). The process is often carried out in batch mode by adding adsorbent to a vessel containing the colored wastewater, stirring the mixture for a sufficient time, then letting the adsorbent settle, and drawing off the cleansed water. Properties of the wastewater itself such as COD, BOD, color, temperature, conductivity, and hydraulic retention times are important parameters. However, a major advantage of palygorskite is its insensitivity to salts and other electrolytes (Murray, 2000) that are major constituents

in textile wastewaters. Heat activation, chemical treatment or both have been reported to further enhance the sorbent properties of the palygorskite.

The objective of this research was two-fold; first determine the feasibility and effectiveness of using palygorskite clay to remove waste indigo dye and salts from denim effluent, and secondly, to evaluate and characterize the quality of the synthesized Maya-blue type pigment synthesized using recovery products rate as the substrate in the process. Methodologies and instrumentation used to characterize the materials used and/or synthesized in this research include Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM/EDS), Ultraviolet-visible spectroscopy (UV/VIS), and X-Ray Powder Diffractometry (XRD).

SEM permits the observation of materials in macro and submicron ranges and generates three-dimensional images for analysis of topographic features. An Energy Dispersive X-ray Spectrometer (EDS) attachment allows for elemental analysis on microscopic sections of the material. When the electron beam of the SEM bombards the specimen, electrons are ejected from the atoms on the surface of the specimen. An electron from a higher shell fills the resulting electron vacancy and an x-ray is emitted to balance the energy difference between the two electrons. The EDS detector measures the number of emitted x-rays versus energy, which is characteristic of the element from which the energy was emitted. A spectrum of the energy versus relative counts of the detected x-rays is obtained and evaluated for quantitative and qualitative determinations of the elements.

UV-Vis spectroscopy is routinely used in the quantitative determination of solutions of transition metal ions and highly conjugated organic compounds. In the visible and adjacent near ultraviolet (UV) and near infrared (NIR) energy space, molecules undergo electronic transitions. UV-Vis was used in this research to compare determine the concentration of dye in the solid waste and in color comparisons for pigments synthesized and no analysis was carried out on liquid media.

The XRD technique takes a sample of the material and places a powdered sample in a holder, then the sample is illuminated with x-rays of a fixed wavelength and the intensity of the reflected radiation is recorded using a goniometer. This data is then analyzed for the reflection angle to calculate the inter-atomic spacing (d value in Angstrom units - 10^{-8} cm). The intensity (I) is used to discriminate

the various d spacings using I ratios, and the results are used to identify possible matches. X-ray crystallography provides a powerful and accurate method for determining single-crystal structures.

2.1 CLAY MINERAL CHARACTERIZATION

Palygorskite is sold as an extremely fine powder, light cream in color having an average particle size of about 0.1 micron in diameter, free moisture content of 12% (%weight loss at 105°C), pH (ASTM 1208) of 7.5-9.5, and having a bulk density of 30-35 kg/m³ (Barr, 1997).

The clay mineral, Mintech 325A (MinTech International, Inc.) was characterized by both X-ray diffraction for phase purity (Figure 1) and Scanning Electron Microscope (SEM) fitted with an energy-dispersive X-ray (EDX) analysis system for compositional analysis (Table 1). EDX analysis is useful in the identification of materials and contaminants, and their relative concentrations on the surface of the specimen.

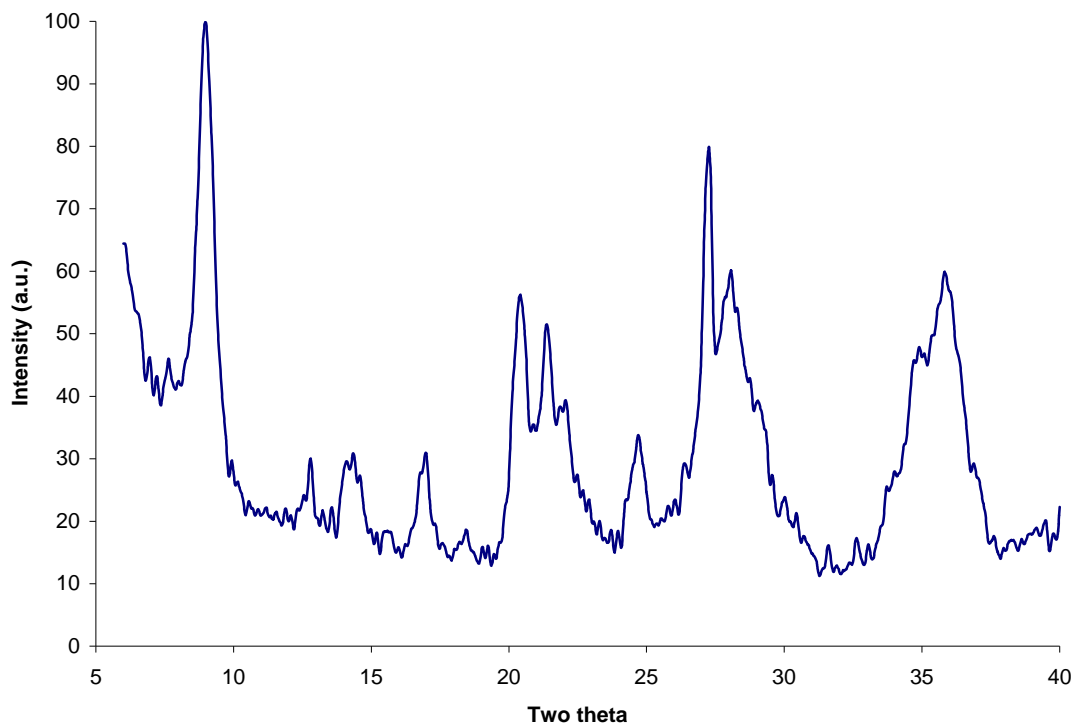


Figure 2.1 X-ray diffraction pattern of palygorskite (Mintech 325A)

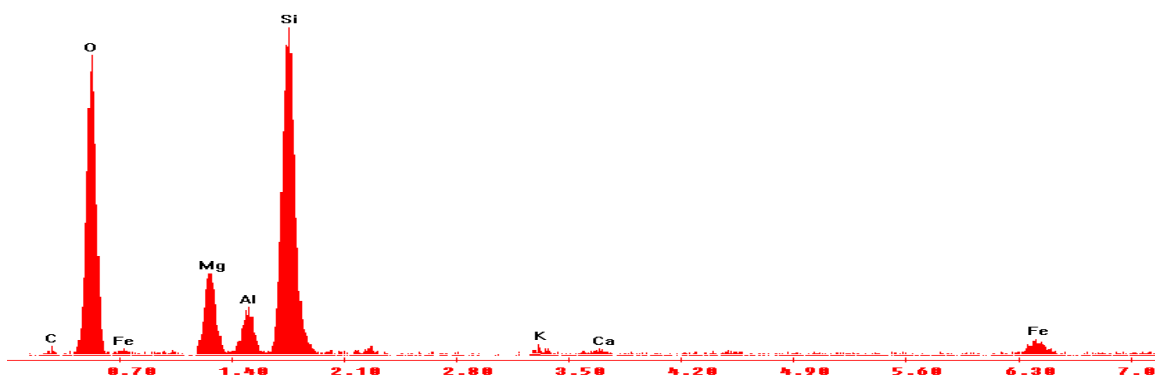


Figure 2.2 Typical EDS spectrum of palygorskite (MinTech 325A)

2.2 SALT ADSORPTION CHARACTERISTICS OF PALYGORSKITE

While the main objective of this research was recovery of waste dye in the stonewash effluent and its subsequent conversion into commercial product, a request was received from the International Garment Processors to look at the possibility of simultaneously cleaning up of salts as the “treated” water was being used for irrigation purposes. Even after undergoing filtration and aeration, the water still retained a high content.

The salt adsorption characteristics of palygorskite clay were studied using a range of sodium chloride concentrations. A stock solution was prepared by dissolving 2g of analar grade sodium chloride salt in 1L of distilled water for a final concentration of 2000 mg/L. Standard solutions of 250, 500, 1000 and 2000 ppm were prepared by transferring the respective aliquots of the stock solution to a 100ml volumetric flasks and bringing the final volume to 100ml. 1g of acid-treated or untreated palygorskite clay was then added to each of the standard solutions and mixed under a magnetic stirrer for 24 hours. The clay was acid-treated with 0.5M, 1M, and 3M hydrochloric acid (HCl).

The suspensions were then vacuum-filtered using glass microber filter (Whatman 934-AH, 110mm diameter). The concentration of sodium in the filtrate was then assayed by Inductively Coupled Plasma-Optical Emission Spectrophotometry (ICP-OES) (EPA Method 4.1.3/200.7) at Assaigai

Analytical Laboratories, Inc. (Albuquerque, NM). The reduction of salts from solution by palygorskite is presented in Appendix I and Appendix II.

2.3 WASTE INDIGO DYE EXTRACTION FROM TEXTILE WASTE

Solid indigo dye waste used in this work was obtained from the International Garment Processors (IGP) plant located outside the city limits of El Paso. The plant utilizes 100-mesh mechanical screens to filter out the by-product from the wastewater. The by-product, consisting mainly of indigo colored fibers removed from the denim garments during the abrading process is stored in a landfill approximately 3,120 cubic yards in capacity - at a cost of \$70,000 per annum. Approximately one million gallons of wastewater generated from the finishing process per day are then treated in large aerated lagoons. The treated water is utilized to irrigate 50 acres of alfalfa, which yields about \$350,000 per year in revenue. Salinity concentrations however, exceed established limits of sodium adsorption ratio (SAR) of 13.20. The SAR is an expression of the relative proportion of sodium ions concentration to calcium and magnesium ions concentration in water. It was envisaged that palygorskite clay could address both problems simultaneously.

The composition before aeration (influent) and after (effluent) presented in Table 2.1 and Table 2.2 respectively. While the biological oxygen demand (BOD) is reduced by more than half at the effluent tank, the chemical oxygen demand and the total dissolved solids (TSS) are not affected to any appreciable degree. This component would likely include a significant portion of the waste indigo dye which is virtually insoluble and difficult to degrade.

Table 2.1. Chemical composition of influent-aeration tank

Parameter	Result	Analytical method
pH	7.5	EPA 150.1
BOD (mg/l)	95	EPA 405.1
TSS (mg/l)	2418	EPA 160.1
COD (mg/l)	131	EPA 160.1

Source: International Garment Processors, El Paso

Table 2.2. Chemical composition of effluent-irrigation tank

Parameter	Result	Analytical method
pH	7.40	EPA 150.1
BOD (mg/l)	44	EPA 405.1
TSS (mg/l)	2548	EPA 160.1
COD (mg/l)	125	EPA 160.1

Source: International Garment Processors, El Paso

Chapter 3 Experimental Procedures

3.1 COLLECTION AND EXTRACTION OF INDIGO DYE WASTE SAMPLES

Textile effluent was reconstituted from solid indigo waste obtained from a landfill at the International Garment Processors (IGP), a local denim finishing plant located outside the city limits of El Paso. Reconstituting artificial textile wastes allows research to be carried out in the absence of a local source of effluents and gives better control of treatment conditions. At its peak, the plant was processing some 25,000 units per week with an average water consumption of 14 gallons per unit.

The current wastewater treatment includes mechanical separation of solids by filters to a level less than 100 microns. The filtration process yields slightly blue-colored water. The wastewater is then sent to an aeration (stabilization) pond for biological decomposition and natural purification. Mechanical aerators oxygenate the effluent for 45 days before passing through polishing diffusion aerators in order to oxidize and settle suspended solids and organics. The effluent is then pumped to a larger polishing pond where it undergoes further aeration. The treated water is used for irrigation of 50 acres of alfalfa. Despite the treatment, salinity concentration of the irrigation water exceeds the established limits with a sodium adsorption ratio (SAR) of 13.20. IGP requested we look at the possibility of salt reduction after removal of color from the wastewater stream. It was envisaged that adsorption using palygorskite clay could address the twin problems of color removal and salinity reduction.

The chemical characteristics of the waste before (influent-aeration tank) and after (effluent-aeration tank) aeration are presented in Table 1. Aeration significantly reduces the Biological Oxygen Demand (BOD), but it does not appreciably affect pH, Total Suspended Solids (TSS), or the Combined Oxygen Demand (COD). While COD is a measure of all chemicals in the water that can be oxidized, BOD measures the amount of organic carbon that bacteria can oxidize. Indigo dye, in the quinone form is highly insoluble in water and extremely

recalcitrant to biological degradation, which largely explains the high presence of the non-destructible COD in the effluent-irrigation tank. The level of total suspended solids, which includes the indigo waste dye, remains virtually unchanged both at the influent and effluent end.

Table 3.1 Chemical composition of influent-aeration and effluent-irrigation tanks

<i>Parameter</i>	<i>Influent-aeration tank</i>	<i>Effluent-irrigation tank</i>	<i>Method</i>
pH	7.5	7.4	EPA 150.1
BOD (mg/l)	95	44	EPA 405.1
TSS (mg/l)	2418	2548	EPA 160.1
COD (mg/l)	131	125	EPA 160.1

3.2 SIMULATED EFFLUENT

Although it is difficult to simulate textile effluent for experimental processes due to the variability in composition and dye concentrations in the effluent, the artificial textile effluent used in this investigation significantly resembles the effluent produced in the stonewashing process. Indigo waste effluent was reconstituted from solid indigo dye waste collected from a dye waste landfill. The solid waste as collected from the landfill was run through UV-Vis analysis (see graph labeled indigo_waste in Figure 4.4).

The extraction of the waste indigo dye from the solid waste starts by dissolving the solid waste in distilled water in a ratio of one part solid waste to 50 parts of distilled water (i.e. 1:50 w/v) to form a suspension. The suspension was passed through a 100-mesh screen to remove suspended solids. 1 g of palygorskite clay was added to 100 ml of the filtered waste supernatant solution and stirred on an orbital shaker at 400 rpm for 24 hours. The suspension was then allowed to settle for 2 hours resulting in a clear solution. The clear supernatant was decanted and the solids dried for 24 h at 100°C. The lightly colored solids were analyzed through UV-Vis (Palyg+Waste in Figure 4.4). The solids, with the adsorbed indigo dye, were ground in a mortar and formed the substrate for further pigment synthesis through addition of progressive fractions of indigo dye. These pigments are labeled as 1% to 8% indigo in Figure 4.4. A simplified flow diagram showing the procedure used in reconstituting the simulated effluent and subsequent pigment synthesis is shown in Figure 3.1

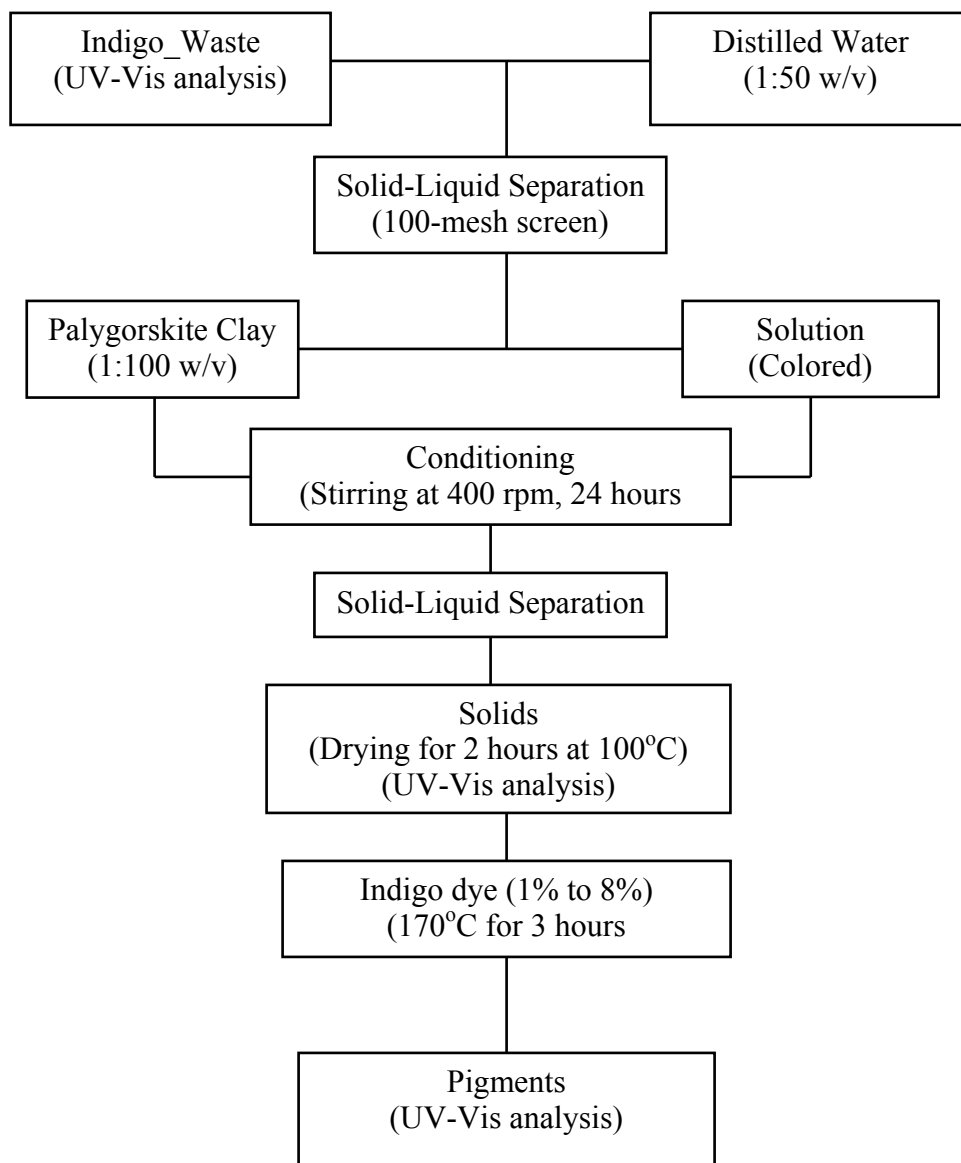


Figure 3.1 Pigment preparation from solid waste

Solid waste obtained from the International Garment Processors plant, El Paso, was analyzed for elemental composition (Table 3). The organic component is presumed to be mainly from cotton fluff (carbon) and from chemical constituents used during the stonewashing process. Pumice rocks largely contribute to the inorganic component of the analysis.

Table 3.2 Elemental composition of solid indigo dye waste from IGP plant, El Paso

Element	Wt %	At %	K-Ratio	Z	A	F
C	15.51	24.21	0.0258	1.0388	0.1598	1.0004
O	43.69	51.18	0.0853	1.0214	0.1911	1.0003
Na	0.03	0.02	0.0001	0.956	0.2462	1.0027
Mg	2.14	1.65	0.0076	0.98	0.3585	1.0049
Al	3.95	2.74	0.0179	0.9513	0.4738	1.0077
Si	20.93	13.97	0.1161	0.979	0.5655	1.0015
P	0.59	0.36	0.0026	0.9426	0.4584	1.0021
S	0.53	0.31	0.0029	0.9629	0.5726	1.0032
Cl	0.54	0.29	0.0034	0.921	0.6786	1.005
K	4.02	1.93	0.0317	0.928	0.8441	1.007
Ca	4.89	2.29	0.0402	0.95	0.8644	1.0012
Fe	3.17	1.06	0.0273	0.8628	0.9968	1.0000
Total	100	100				

3.3 CLAY MINERAL AND PIGMENT CHARACTERIZATION

Palygorskite clay (Mintech 325A, Mintech International, Inc.) was characterized to determine its mineralogical composition (XRD), its surface topography and microanalysis by an environmental scanning electron microscope (ESEM) equipped with an EDAX system. Pigment samples were prepared by mixing, grinding, and then heating the mixtures to 170°C for 24 hours using the extracted dry indigo waste substrate as the starting material or alternatively using pure components of palygorskite and indigo dye for comparison purposes. Indigo content ranged from 1% to 8% in both sets of pigments. The resulting pigments were then analyzed by UV/Vis.

3.4 X-RAY DIFFRACTION (XRD)

Wide-angle X-ray spectra were recorded with a Scintag model XDS2000 (Scintag, Inc.) diffractometer fitted with a copper anode X-ray source generating a wavelength of 1.5406Å. The X-ray source was operated at 40 mA and 45 kV in step mode with a scan rate of 0.04° min⁻¹ and step width of 0.02°. The typical angle diffractometer range was set from 5 to 80°. For our purposes, a range of 5° to 40° is shown as no useful information is obtained beyond this range.

3.5 MICROSCOPIC EXAMINATION (ESEM)

The morphology of the samples was inspected in an environmental scanning electron microscope (ESEM). One advantage of ESEM over conventional scanning electron microscopy (SEM) is that it allows the imaging of systems with no prior specimen preparation and does not require that materials be coated by gold–palladium, thus preserving the original characteristics of the sample. An FEI-Electroscan ESEM 2020 (Hillsboro, OR) with a cerium hexaboride electron source, long working distance gaseous secondary electron detector, and an EDAX DX Prime EDS detector (Mahwah, NJ) was used to characterize the clay for compositional analysis. The accelerating voltage was 20kV, beam current was roughly 0.2nA, and water vapor was used as the chamber gas. Samples were fixed to the aluminium sample stub with double-sided conductive copper tape. Images were collected using a 30 s integration period.

Chapter 4 Results and Discussion

4.1 X-RAY DIFFRACTION

Fig. 3 shows the experimental and simulated x-ray pattern of the clay used in this work. The simulated x-ray pattern is based on an idealized crystal structure of palygorskite. Our data confirms the clay to be predominantly palygorskite, with traces of silica/quartz. Peaks obtained are typical for palygorskite with peaks at $2\theta=8.3$, 13.6 , 19.7 , and 26.6° corresponding to the primary diffraction of the (110), (200), (040), and (400) planes of the clay respectively as reported by other authors^{24,25} and confirmed by simulation with Cerius2 Molecular Modeling (Accelrys).

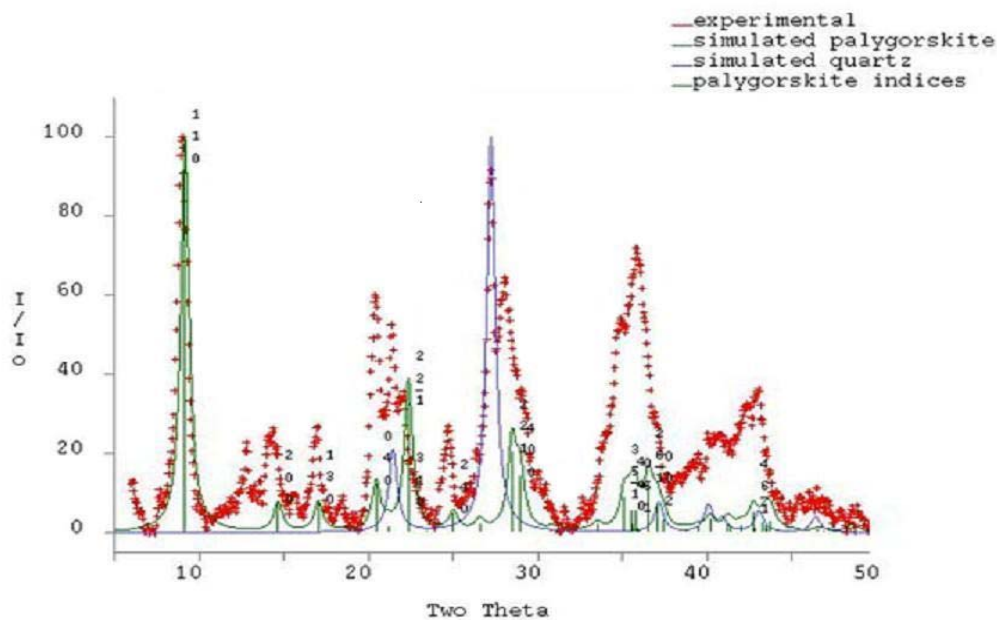


Figure 4.1 Experimental and simulated x-ray diffractograms of palygorskite.

4.2 MICROSCOPIC EXAMINATION (ESEM)

The scanning electro microscope permits the observation of materials in macro and submicron ranges and is capable of generating three-dimensional images for analysis of topographic features. When used in conjunction with EDS (a.k.a. EDX, EDAX), the elemental analysis on microscopic sections of the material or contaminants that may be present is revealed.

When the sample is bombarded by the electron beam of the SEM, electrons are ejected from the atoms comprising the sample's surface. A resulting electron vacancy is filled by an electron from a higher shell, and an x-ray is emitted to balance the energy difference between the two electrons.

The EDS x-ray detector measures the number of emitted x-rays versus their energy. The energy of the x-ray is characteristic of the element from which the x-ray was emitted. A spectrum of the energy versus relative counts of the detected x-rays is obtained and evaluated for qualitative and quantitative determinations of the elements present in the sampled volume. Energy Dispersive Spectroscopy (EDS) is a standard procedure for identifying and quantifying elemental composition of sample areas as small as a few cubic micrometers. The characteristic X-rays are produced when a material is bombarded with electrons in an electron beam instrument, such as a scanning electron microscope (SEM). Detection of these x-rays can be accomplished by an energy dispersive spectrometer, which is a solid-state device that discriminates among X-ray energies. The elemental composition of the palygorskite clay is shown in Table 4.1.

Table 4.1 Elemental composition of palygorskite clay

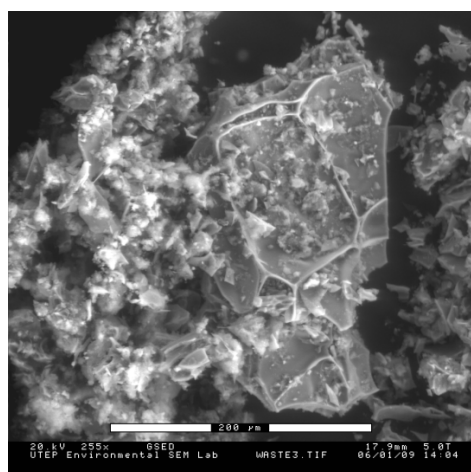
Element	Wt %	At %
C	3.86	6.17
O	55.56	66.64
Na	0.58	0.49
Mg	6.38	5.03
Al	4.25	3.02
Si	24.45	16.71
K	0.87	0.42
Ca	0.94	0.45
Fe	3.12	1.07
Total	100	100

The elemental analysis of the indigo dye waste (Table 4.2) shares some chemical constituents with palygorskite, presumably derived from the pumice rocks used in the stonewash process. Pumice, which is closely related to granite, is nominally composed of various oxides including silica (SiO_2), alumina (Al_2O_3), along with other various minerals with varying percentages.

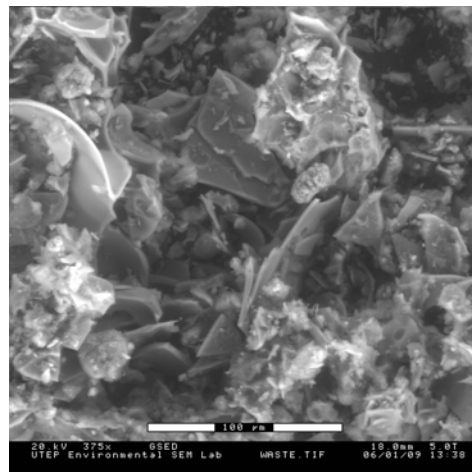
Table 4.2 Elemental composition of solid indigo dye waste from IGP plant, El Paso

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C	15.51	24.21	0.0258	1.0388	0.1598	1.0004
O	43.69	51.18	0.0853	1.0214	0.1911	1.0003
Na	0.03	0.02	0.0001	0.956	0.2462	1.0027
Mg	2.14	1.65	0.0076	0.98	0.3585	1.0049
Al	3.95	2.74	0.0179	0.9513	0.4738	1.0077
Si	20.93	13.97	0.1161	0.979	0.5655	1.0015
P	0.59	0.36	0.0026	0.9426	0.4584	1.0021
S	0.53	0.31	0.0029	0.9629	0.5726	1.0032
Cl	0.54	0.29	0.0034	0.921	0.6786	1.005
K	4.02	1.93	0.0317	0.928	0.8441	1.007
Ca	4.89	2.29	0.0402	0.95	0.8644	1.0012
Fe	3.17	1.06	0.0273	0.8628	0.9968	1.0000
Total	100	100				

Environmental Scanning Electron Microscopy (ESEM) combined with energy dispersive X-ray analysis (EDX) of the indigo dye waste confirms a clay with organic colloids/tissue properties as evidenced by the presence of phosphorus, sulfur, and chlorine (Fig. 4.2 and Table 4.2).



(a)



(b)

Figure 4.2 ESEM micrographs of indigo dye waste showing remnants of pumice rock.

The elemental composition and EDS of untreated and acid-modified palygorskite after treatment with sodium salts is shown in Appendix 3.

4.3 UV-VIS

UV-Vis spectrophotometry was used to determine the absorption spectra of various samples including indigo, pigments prepared from indigo and palygorskite with increasing ratio of indigo, solid indigo waste recovered from the effluent, and indigo dye waste recovered from the effluent using palygorskite as an adsorbent (Figure 4.3 and Figure 4.4). UV-Vis was recorded by dual-beam UV-NIR spectrometer designed for absorbance and transmittance measurements in the wavelength range of 300 to 3000 nm (UV-3101 Spectronic PC, Shimadzu).

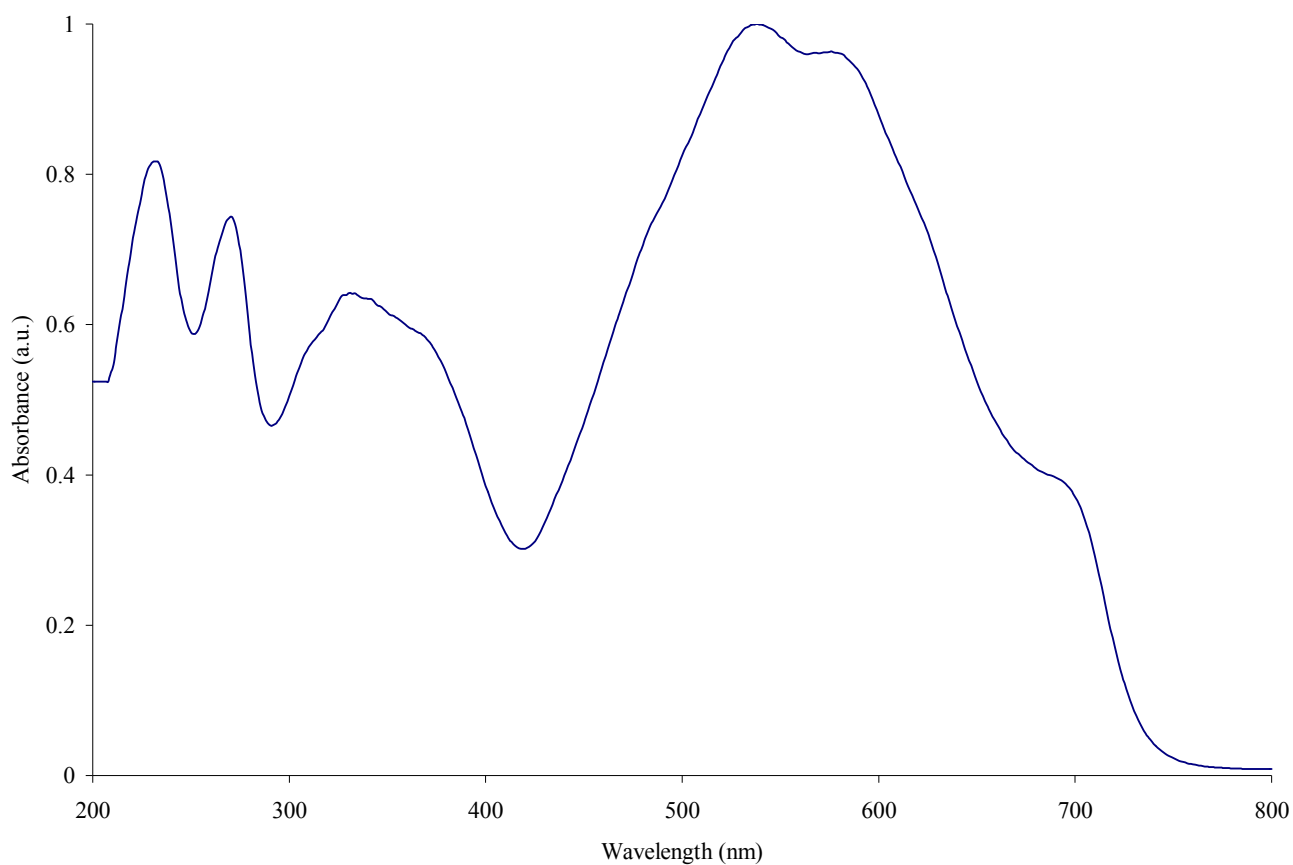


Figure 4.3 UV-vis of indigo

Indigo waste was included for comparative purposes. For all pigment samples, peak absorbance occurs around 620-650 nm. Peak absorbance increases with increasing concentration of indigo in the pigment (Figure 4.4).

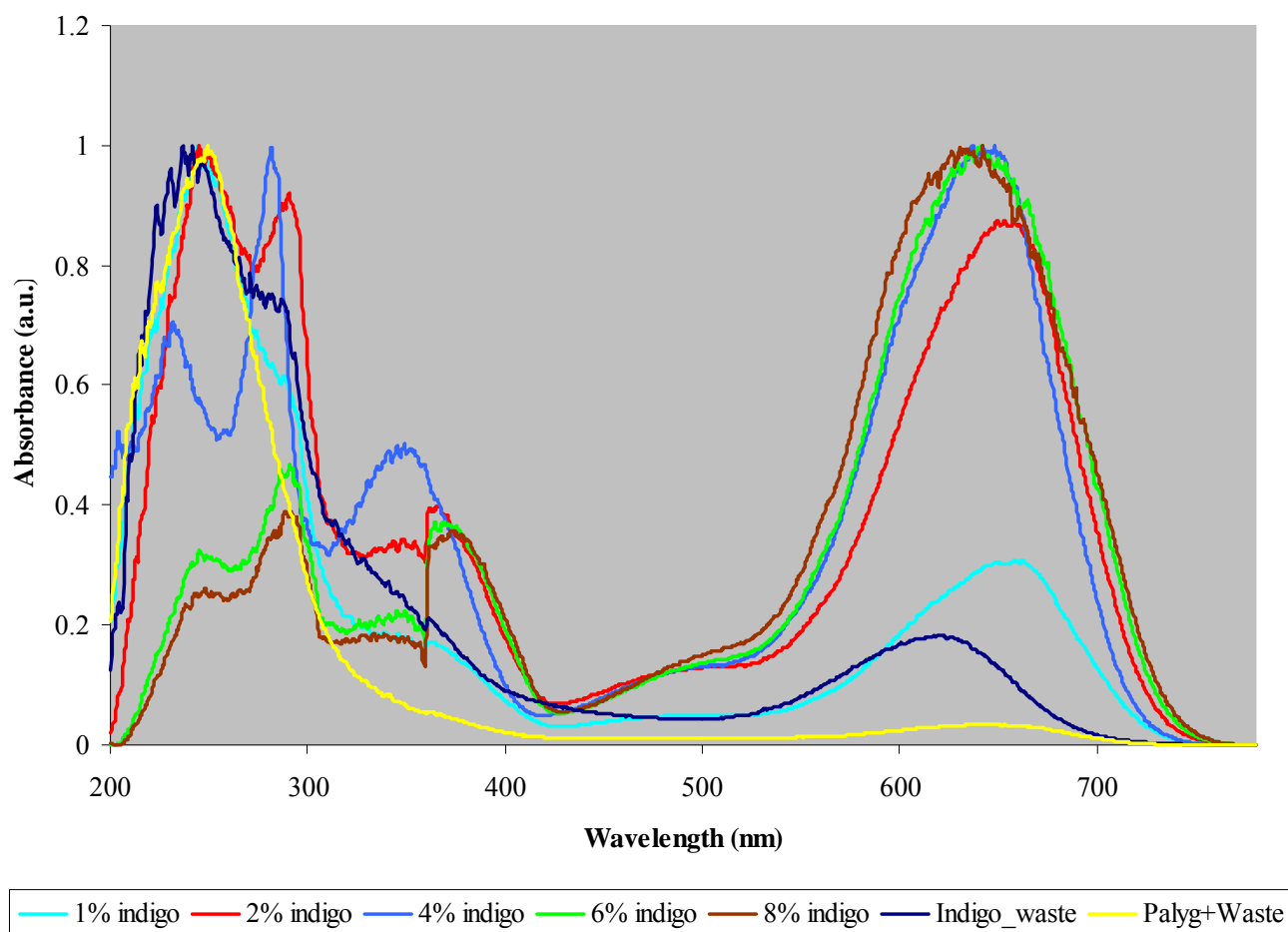


Figure 4.4 UV-vis spectra of pigment samples.

The UV-Vis spectra of pigment samples derived from indigo waste fortified with additional indigo dye is shown in Fig. 4.4. Peak absorbance of the resulting pigments shifts to the left once the indigo is locked in. The color intensity also increases with increasing fraction of the dye. The data also confirms the concentration of indigo dye in the waste to be well below 1%, in line with results reported in literature.

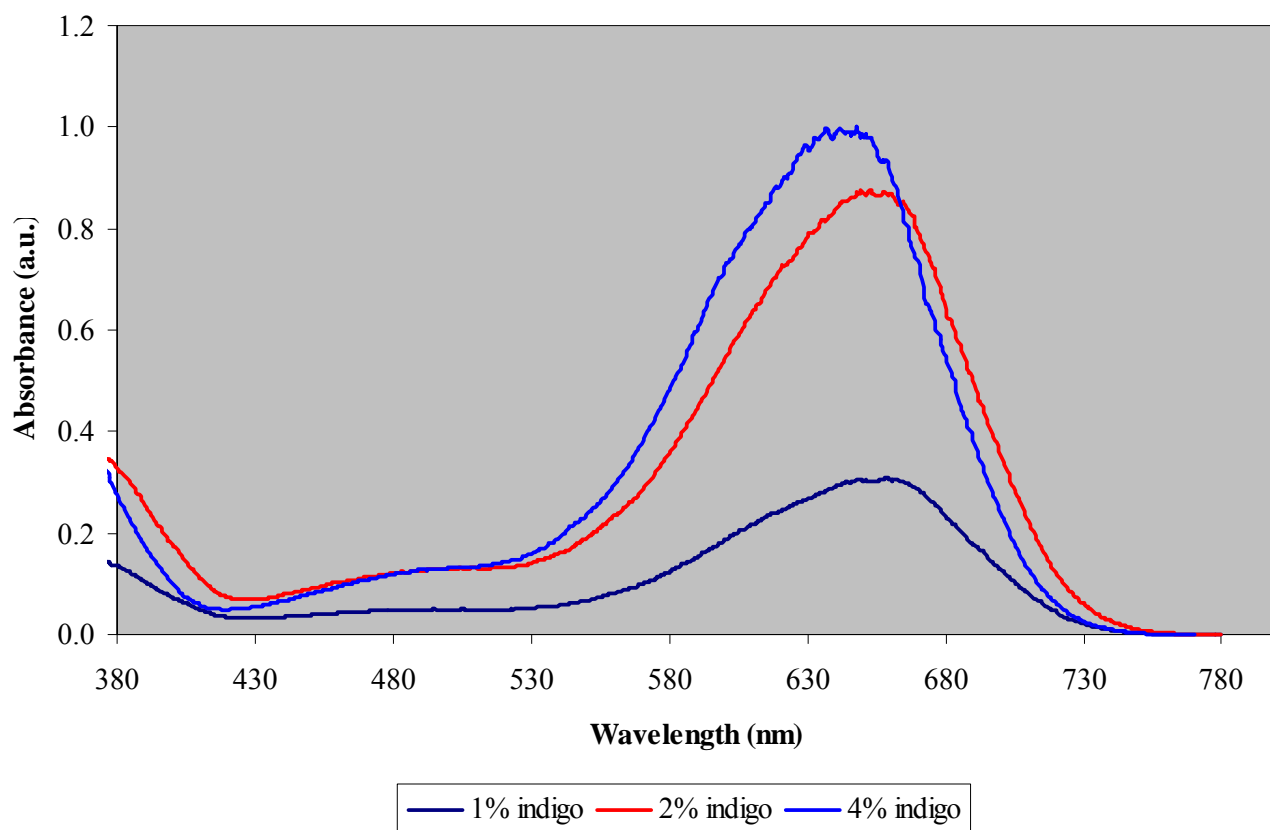


Figure 4.5 UV-vis: indigo waste with additional indigo dye (380-780nm range shown).

A plot of the relative peak absorbance for pigments ranging from 1% to 8% indigo content shows an approximate linear relationship with increasing indigo content in the pigment added to the waste indigo (Fig. 4.6). Indigo dye waste from textile effluent contains low levels of recoverable indigo dye and is shown for comparative purposes.

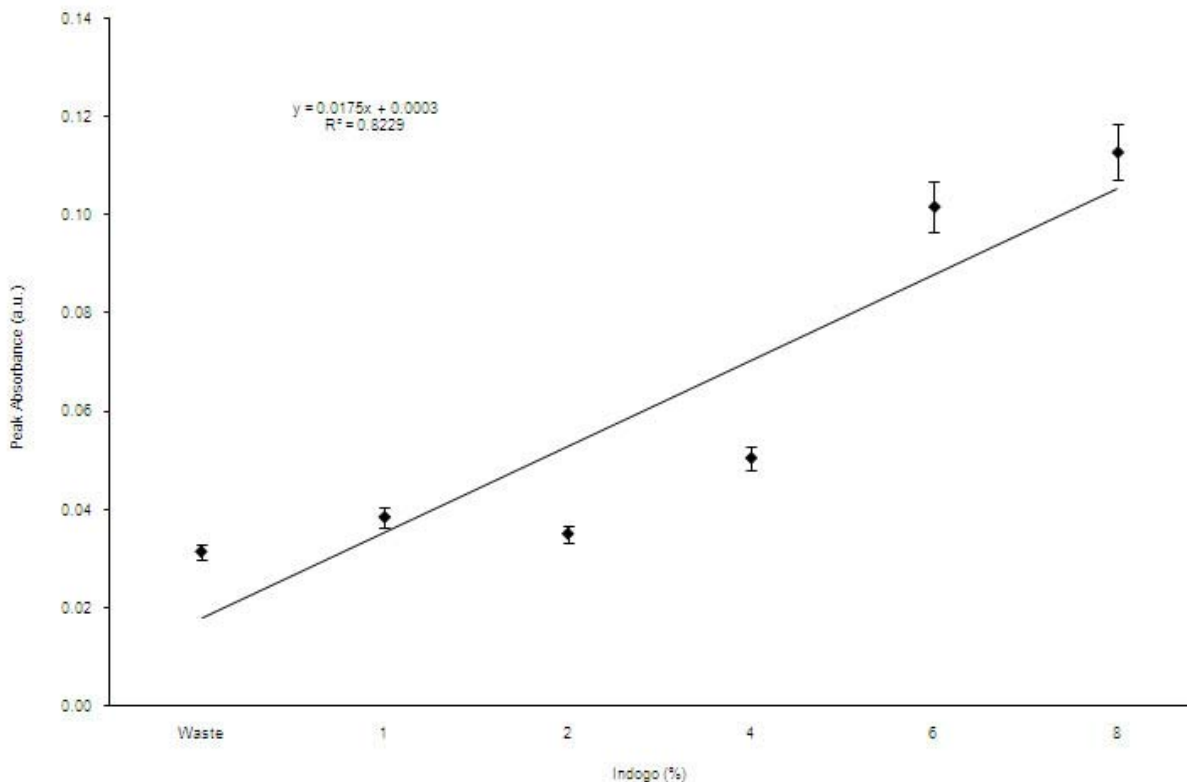


Figure 4.6 Relationship between indigo concentration and relative peak absorbance.

4.4 COLOR VARIATION: PURE MIXTURES VERSUS SAMPLES FROM WASTE

Pigment samples were prepared using palygorskite and indigo in incremental amounts or indigo waste as the substrate with additional indigo dye amounts added incrementally. The pigment samples were prepared by grinding and mixing the appropriate fractions of palygorskite/indigo and/or indigo waste/indigo mixtures, which were then placed in an oven at 170°C for 24 h. The pigments were then scanned for color for comparison (Fig. 4.7).

4.5 COLOR ATTRIBUTES

The CIE $L^*a^*b^*$ values for the various pigments are shown in Table 4.3. The $L^*a^*b^*$ scale, commissioned by the Commission Internationale de l'Eclairage (International Commission on Illumination) identifies colors numerically. Under the system, L^* defines lightness, a^* denotes the

red/green value, and b^* the yellow/blue value. Note the gradual diminution of the lightness (L^*) and the red/green (a^*) component with increasing fraction of the indigo dye, and a concomitant increase of the yellow/blue component.

Table 4.3 $L^*a^*b^*$ values for various pigments

Pigment component	L^*	a^*	b^*
Indigo waste	78.4	-11.85	-7.83
1% indigo	73.42	-14.2	-12.49
2% indigo	62.34	-15.52	-18.74
4% indigo	49.4	-13.01	-27.41
6% indigo	44.96	-10.78	-28.79
8% indigo	41.72	-7.99	-30.96

As expected, the color variation becomes darker with increasing indigo concentration for both sample lots (Fig. 4.7). There is however, a perceptible color difference depending on the substrate. Pigments synthesized with indigo waste as the substrate have discernible vibrancy in color, relative to those synthesized from pure palygorskite and indigo, which could probably be ascribed to the presence of organic constituents (P, S, and Cl) found only in the solid dye waste and not in any of the pure components.

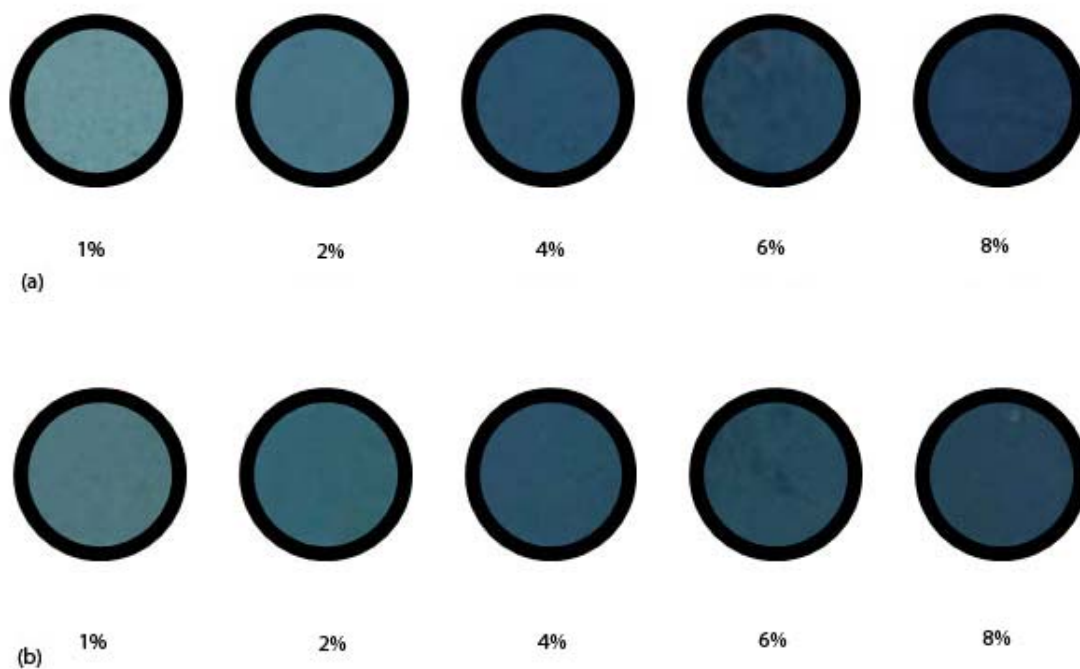


Figure 4.7 Color variations with increasing indigo fractions

- (a) Pure indigo-palygorskite components
 - (b) With palygorskite-recovered waste as substrate
- All mixtures were heated at 170°C for 24 h.

4.6 ADSORPTION CHARACTERISTICS OF PALYGORSKITE

The use of large amounts of bleaching agents such as potassium permanganate and sodium hypochlorite results in effluent with a large variability of chemical composition and a high base content. Palygorskite clay shows significant potential for removing salts from solution (Table 4.4).

Table 4.4 Sodium adsorption by palygorskite in aqueous solution

Initial Na ⁺ concentration (ppm)	Final Na ⁺ concentration (ppm)	% Removal
250	120	52
500	221	55.8
1000	365	63.5
2000	796	60.2

Some clays have been reported to undergo changes in their superficial topology and in the number of active sites under acid treatment, making the material more amenable to different applications including as adsorbent and as a color remover (Ruiz et al. 2002; Barrios et al 1995).

A comparison between untreated and acid-treated (1M HCl) is shown in Fig. 4.8). Both untreated and acid-treated palygorskite exhibit salt adsorption capacities above 50 per cent across the concentrations evaluated with untreated palygorskite peaking at almost 64 per cent at 1000 ppm salt concentration.

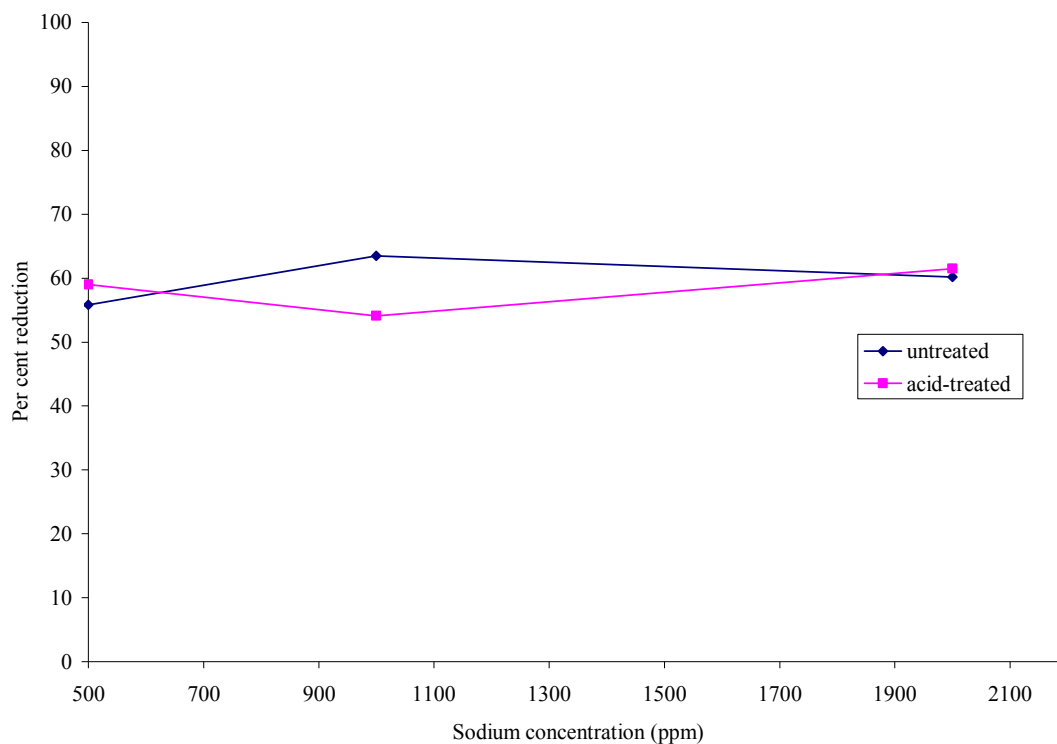


Figure 4.8 Adsorption of sodium by palygorskite clay

The clays used in the adsorption of salts were filtered and then dried at 100°C for 24h. Each of the dried clay was used in the preparation of pigments. Pigment samples were prepared thoroughly mixing and then grinding the clay/indigo mixture before heating the mixture at 170°C for 24hours. The pigments were then evaluated under UV-vis analysis (Fig. 4.9). Each pigment sample contained 4 per cent indigo by weight. The spectral response for all pigments was uniform over the range of salt concentration tested. Significantly, the level of salt concentration does not seem to adversely affect the color properties of the resulting pigments to any appreciable degree as the color properties across the various salt concentrations remained constant. It seems like palygorskite is capable of substantially removing salts from solution without reducing the quality of the resulting pigment.

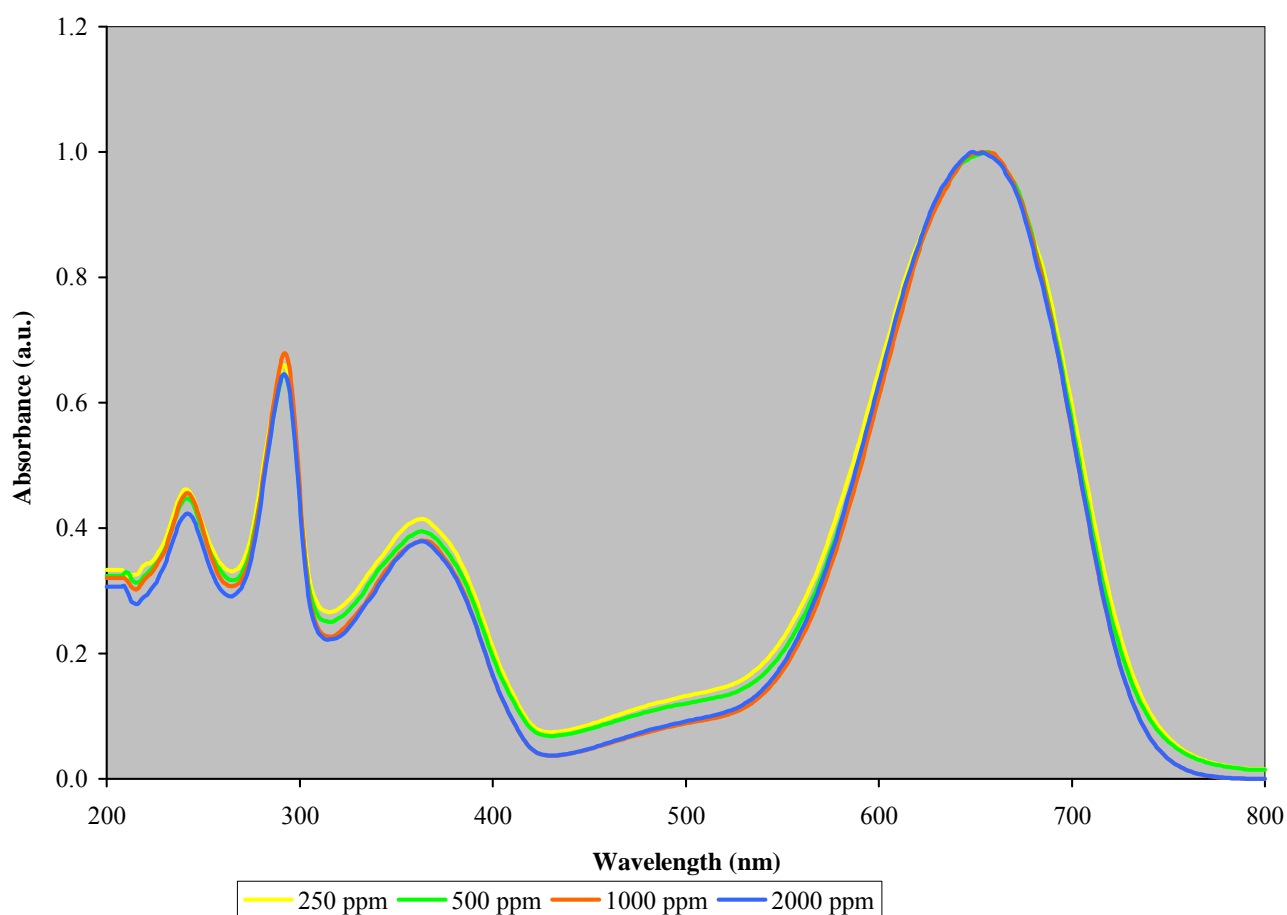


Figure 4.9 UV-vis of pigments prepared with salt-adsorbed clay (at 4% indigo)

Chapter 5 Summary and Conclusions

Dyeing effluents constitute a major economic and environmental issue in the textile industry and in recent years, the color of the effluent discharged into receiving waters has become a serious environmental problem. More than 10,000 different textile dyes with an estimated annual production of 7×10^5 metric tonnes are commercially available worldwide (McMullan et al. 2001). 2% of these dyes are directly discharged as aqueous effluents and 10% are subsequently lost during textile coloration process (Pearce et al. 2003). Worldwide, approximately 10^6 kg/yr of dyes are discharged into waste streams by the textile industry each year (Chandran et al. 2002).

El Paso, Texas, was once considered the denim stonewashing capital of North America. Its abundant relatively unskilled and low-wage workforce attracted labor-intensive industries, especially the apparel industry. As stonewashed denim clothing gained popularity in the 1980s, El Paso's apparel industry diversified to include stonewashing as part of the garment finishing process. But the textile industry has undergone profound changes, partly as a result of globalization and partly due to changes in water and wastewater regulations. No matter where the stonewashing industry is located, it remains highly intensive. Imposition of water reuse requirements in El Paso played a part in the eventual relocation of many firms.

To meet wastewater discharge requirements, finishers were required to install onsite pretreatment systems for wastewater before releasing it into El Paso's wastewater system. The primary discharge violations among stonewashing operations included color discharge and discharge of stones and pumice material into the municipal wastewater. Industrial pretreatment was by trial and error and included filter systems for removing pumice, lint, dyes, and chemicals from the wastewater.

The stonewashing industry was unprepared to meet wastewater discharge requirements and therefore, many of the industries relocated south to Mexico where an apparent lack of industrial pretreatment regulatory enforcement is an area of concern. At the time, Mexico may not yet have developed rigorous pretreatment enforcement and compliance procedures. Violations by the stonewashing industry in Mexico included total suspended solids, chlorides, color, solids, and toxic corrosive substances. As a pretreatment process before discharge into wastewater stream or reuse, using

palygorskite for the purpose adds to the arsenal of techniques that have the potential to address increased pollution from inadequate industrial wastewater pretreatment.

Because many dyes used in the textile industry are particularly difficult to remove by conventional waste treatment methods and are resistant to aerobic digestion, the impact of color on the esthetics of receiving streams is of primary concern (McKay et al. 1980). Such effluents produce a strongly colored dye bath highly loaded in organic compounds and highly concentrated in mineral salts (Allegre et al. 2004). Dyed cotton is the leading dyed fiber and over a billion pairs of denim are dyed every year.

A great number of feasibility studies have been carried out in an effort to find a solution to this intractable problem. Among the standard methods used are biological degradation, coagulation-flocculation-decantation treatments, and absorption on activated carbon.

Ozone attacks the double bonds responsible for the coloration, but is not always accompanied by a significant decrease of the COD and may add extra costs. Membrane processes (reverse osmosis, nanofiltration, ultrafiltration and microfiltration) are efficient in the separation of dyes and salts from solution, but their widespread use is hampered by cost consideration and the handling of permeates.

Physical removal of dyes from effluent through adsorption using low cost adsorbents for waste and wastewater treatment is reviewed in Pollard et al. 1992; Mall et al. 1996; and Bailey et al. 1999. What had not been examined to an appreciable degree is not only the incorporation of water saving processes, but the recovery of the dye waste in the effluent, both of which constitute beneficial economic and environmental impacts relative to previous practices. This study examined the feasibility of using palygorskite in the recovery of indigo dye waste and salts in the blue denim industry, and through a process of by-product synergy, synthesize Maya blue - a potential commercial product. The process has the added advantage of making the reuse/recycling of the wastewater possible.

Utilizing various methods to evaluate the characteristics of pigments synthesized using the recovered waste dye and those synthesized from component indigo/palygorskite, we have demonstrated that pigments synthesized using the recovered waste dye is of the same quality or exceeds that synthesized from the component products.

Chapter 6 Future Work

This work investigated the potential feasibility of using palygorskite clay in the recovery of waste indigo and salts from textile effluent and subsequently using the recovery products as a substrate for synthesis of new materials. This process of by-product/waste valorization is the treatment of waste for beneficial use as raw material and has significant potential environmental and sustainability implications.

Our research has provided the “proof of concept”. We have been able to show adsorption as a process can be used to recover not only the waste indigo dye from the blue denim effluent arising from the stonewash process, but salts as well. Of greater significance is the use of the recovery products as substrate for further processing to synthesize Maya blue, a hybrid organic-inorganic pigment with applications in the paint and coating industries.

Indigo is also the more expensive of the two components and its recovery from the effluent and its reuse would effectively reduce the quantity of additional indigo that goes into the preparation of such pigments resulting in substantial cost savings. The removal of color from the textile effluent has the additional benefit of making it possible to reuse/recycle the wastewater. This by-product synergy process has enormous potential for reducing waste volumes, cutting operating costs, additional revenue, and reducing environmental pollution – thus promoting sustainability.

This research has shown that palygorskite, inexpensive and readily available industrial clay can be used to recover waste indigo dye from blue denim effluent. We have shown the process is feasible in batch mode and future research should be geared towards the possibility of up-grading the process to continuous mode.

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Appendix 1

Sodium adsorption by palygorskite

Clay treatment	Initial concentration	Final concentration	Dilution factor
Untreated*	250	120	5
Acidified**	250	112	5
Untreated*	500	221	5
Acidified**	500	205	5
Untreated*	1000	459	10
Acidified**	1000	365	10
Untreated*	2000	770	20
Acidified**	2000	796	20

Concentration values in mg/L = parts per million (ppm)

Untreated* = palygorskite clay

Acidified** = treated with 0.5 M HCl

Method: EPA 4.1.3/200.7 ICP; Method Detection Limit (MDL) 0.5 mg/L

Analysis by Assaigai Analytical Laboratories, Inc., Albuquerque, NM

Appendix 2

Sodium adsorption by palygorskite

Clay treatment	Initial concentration	Final concentration	Dilution factor
Acidified**	250	92.3	1
Acidified**	500	204	10
Acidified**	1000	406	10
Acidified**	2000	772	20

Concentration values in mg/L = parts per million (ppm)

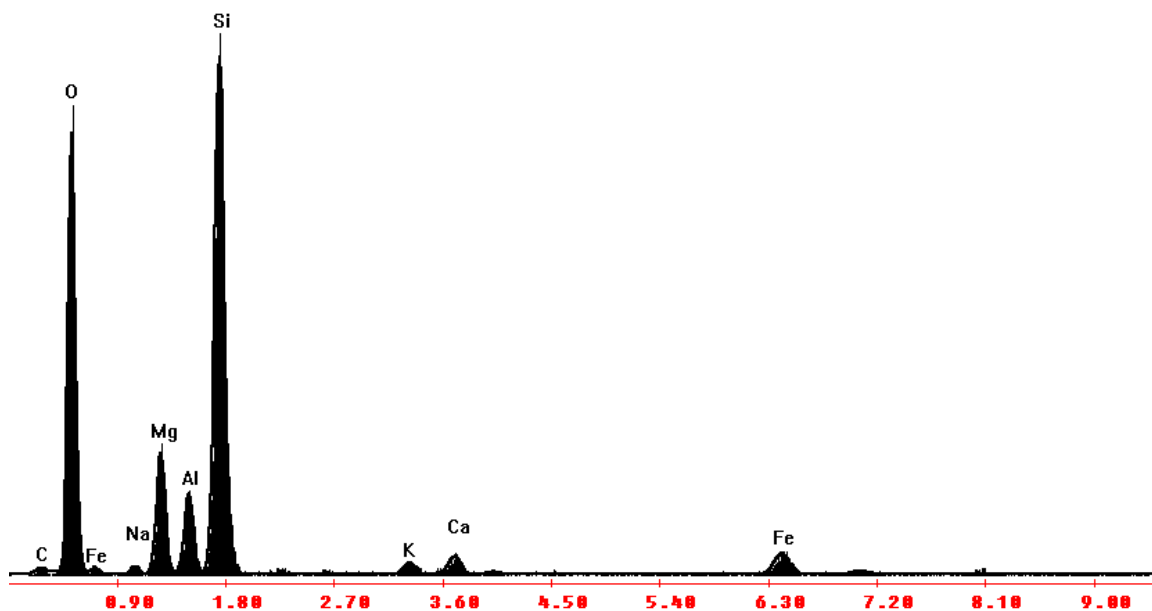
Acidified** = treated palygorskite (3M HCl)

Method: EPA 4.1.3/200.7 ICP; Method Detection Limit (MDL) 0.5 mg/L

Analysis by Assaigai Analytical Laboratories, Inc., Albuquerque, NM

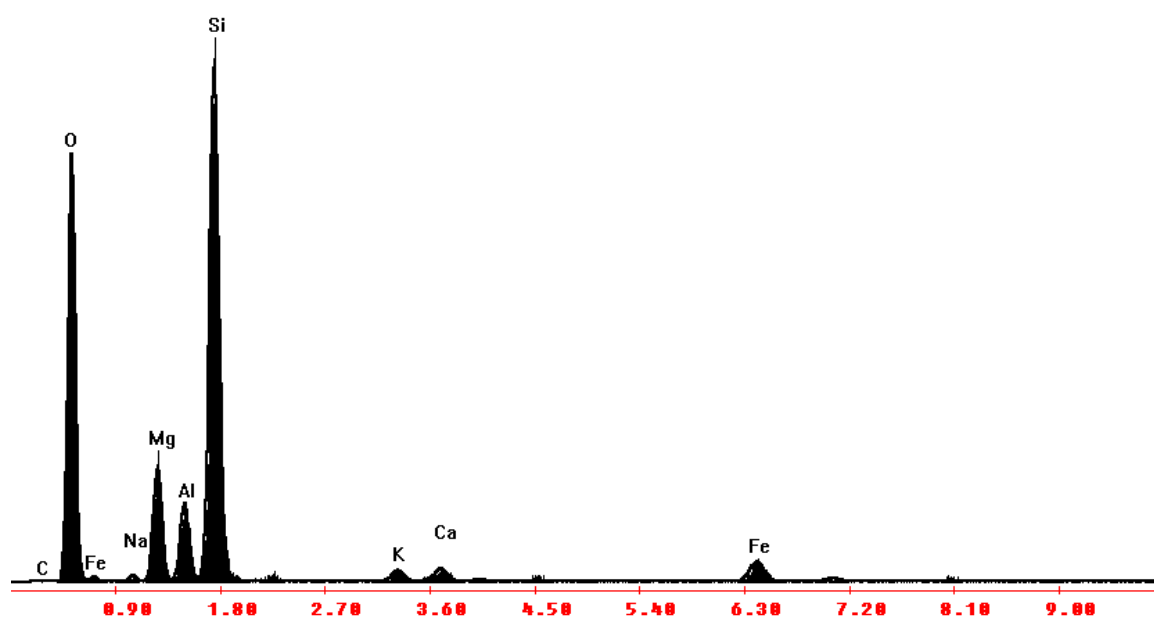
Appendix 3

EDS spectrum and elemental composition of palygorskite treated with 2000 ppm Na⁺



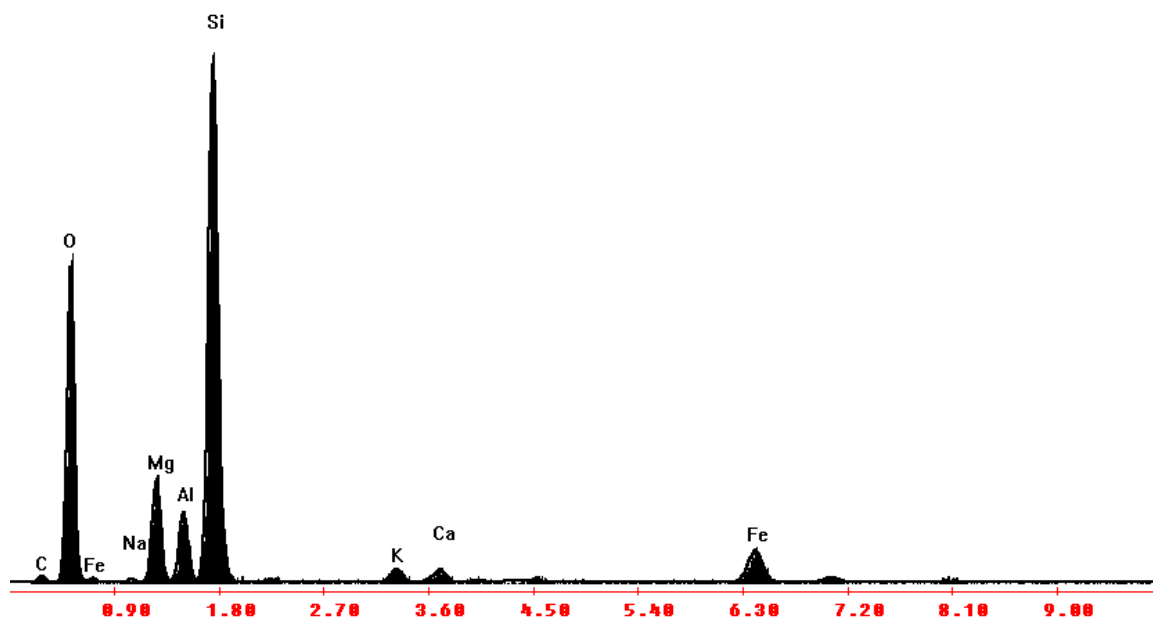
Element	Wt %	At %	K-Ratio	Z	A	F
C	0.75	1.24	0.001	1.0402	0.1333	1.0006
O	55	67.84	0.1738	1.0228	0.3088	1.0004
Na	0.72	0.62	0.0017	0.9572	0.2497	1.0037
Mg	7.8	6.33	0.0275	0.9813	0.3571	1.0052
Al	4.8	3.51	0.0189	0.9525	0.4104	1.0078
Si	26.64	18.72	0.1289	0.9803	0.4936	1.0002
K	0.62	0.31	0.0046	0.9292	0.7959	1.0018
Ca	0.97	0.48	0.0079	0.9512	0.8567	1.001
Fe	2.71	0.96	0.0236	0.8638	1.0073	1
Total	100	100				

EDS spectrum and elemental composition of palygorskite treated with 1000 ppm Na+



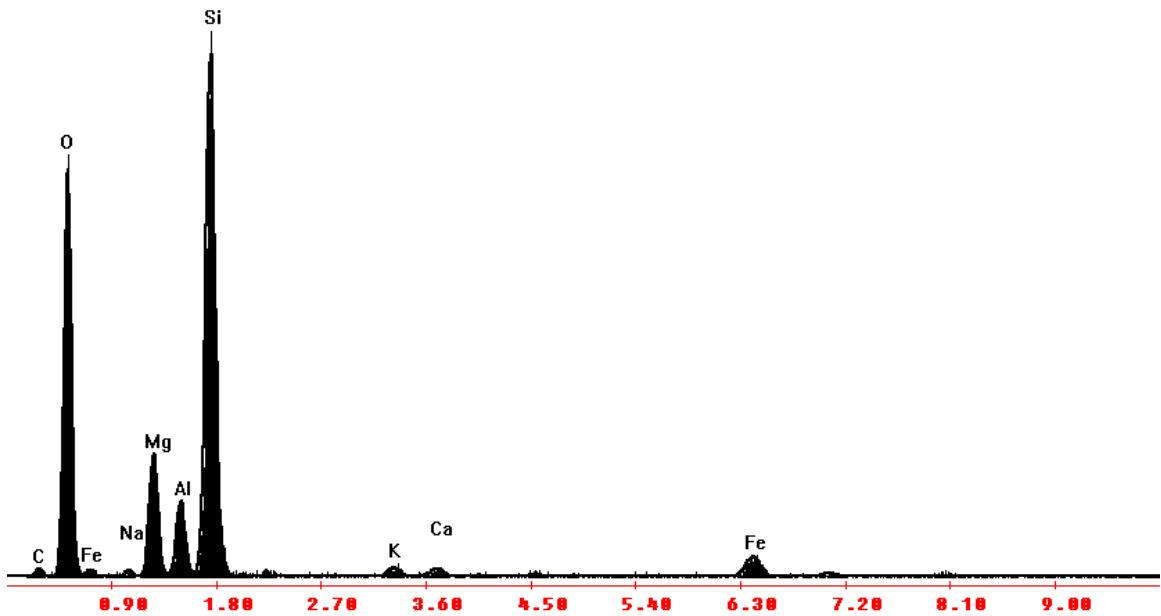
Element	Wt %	At %	K-Ratio	Z	A	F
C	0.12	0.2	0.0002	1.0405	0.1304	1.0006
O	54.92	68.14	0.1757	1.023	0.3126	1.0004
Na	0.52	0.45	0.0013	0.9575	0.2512	1.0038
Mg	7.81	6.37	0.0278	0.9816	0.3608	1.0054
Al	4.91	3.61	0.0195	0.9528	0.4137	1.0082
Si	27.79	19.64	0.135	0.9806	0.4954	1.0002
K	0.59	0.3	0.0043	0.9295	0.79	1.0014
Ca	0.7	0.35	0.0057	0.9515	0.8521	1.001
Fe	2.64	0.94	0.023	0.8641	1.0069	1
Total	100	100				

EDS spectrum and elemental composition of palygorskite treated with 500 ppm Na+



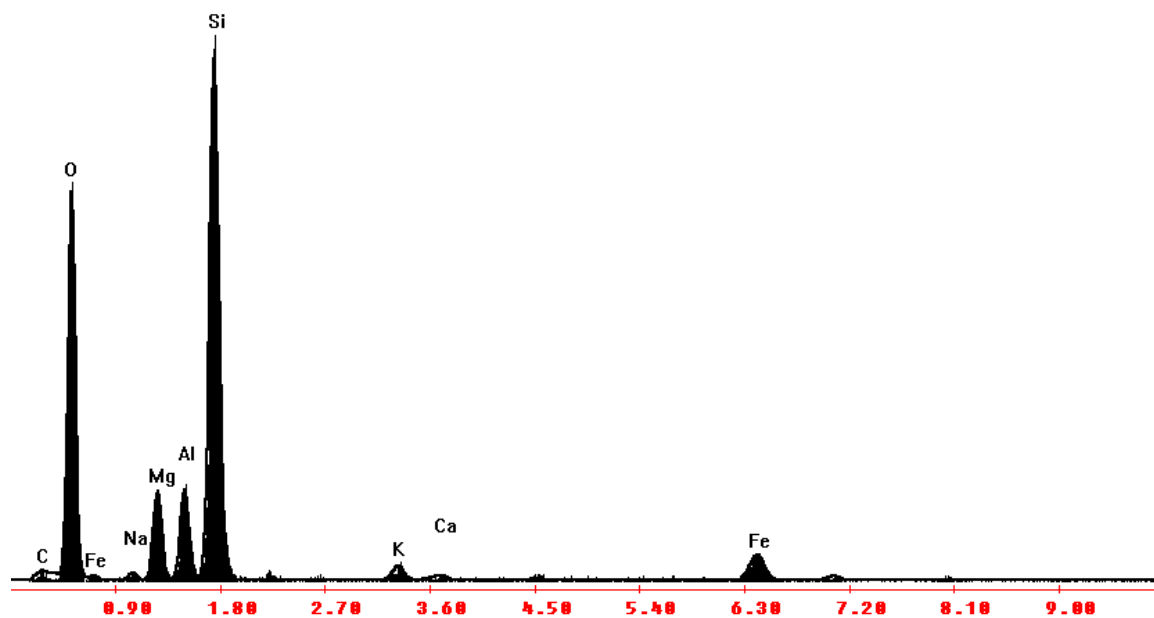
Element	Wt %	At %	K-Ratio	Z	A	F
C	2.51	4.22	0.0033	1.0435	0.1263	1.0005
O	48.88	61.73	0.1406	1.026	0.2803	1.0005
Na	0.32	0.28	0.0008	0.9602	0.2519	1.0039
Mg	7.54	6.27	0.0271	0.9844	0.363	1.0058
Al	4.69	3.51	0.0189	0.9555	0.4178	1.0089
Si	29.98	21.57	0.1479	0.9833	0.5014	1.0002
K	0.77	0.4	0.0056	0.9324	0.7797	1.0019
Ca	0.75	0.38	0.006	0.9545	0.8419	1.0017
Fe	4.55	1.65	0.0396	0.8669	1.004	1
Total	100	100				

EDS spectrum and elemental composition of palygorskite treated with 250 ppm Na+



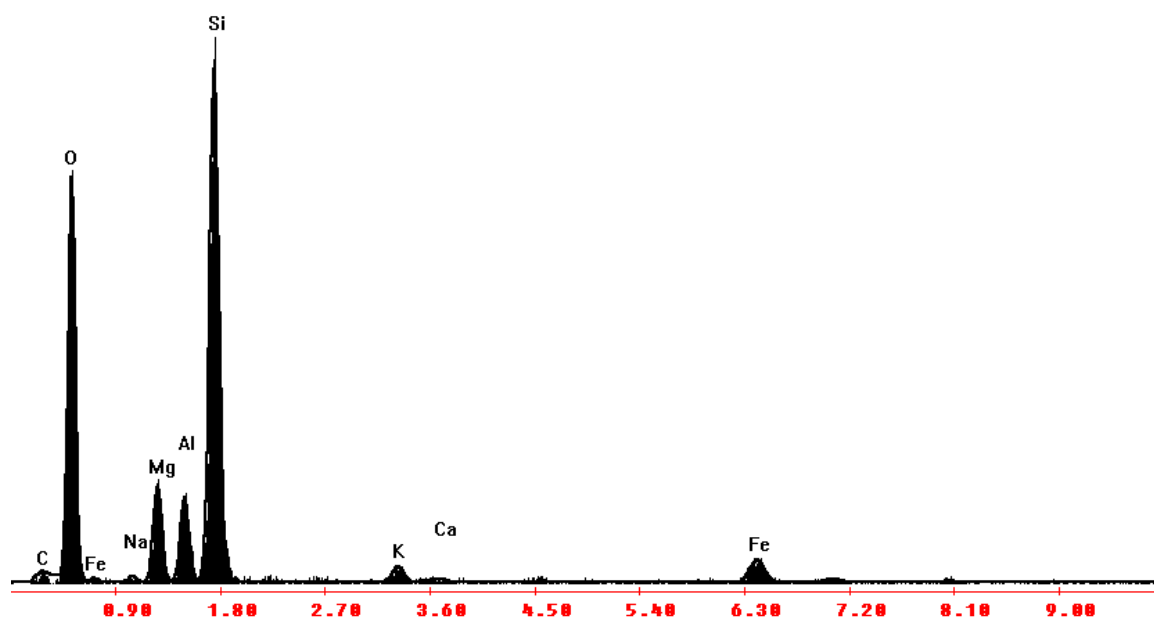
Element	Wt %	At %	K-Ratio	Z	A	F
C	2.85	4.63	0.0039	1.0392	0.1329	1.0006
O	53.29	64.93	0.1639	1.0218	0.3009	1.0004
Na	0.5	0.42	0.0012	0.9564	0.2547	1.0038
Mg	8.09	6.49	0.0292	0.9804	0.3661	1.0053
Al	4.56	3.29	0.0182	0.9516	0.4155	1.0081
Si	27.19	18.87	0.1334	0.9794	0.501	1.0001
K	0.49	0.25	0.0037	0.9282	0.7957	1.0011
Ca	0.41	0.2	0.0033	0.9503	0.8576	1.001
Fe	2.62	0.92	0.0228	0.8629	1.0091	1
Total	100	100				

EDS spectrum and elemental composition of acid-modified (1M HCl) palygorskite after 2000 ppm Na⁺



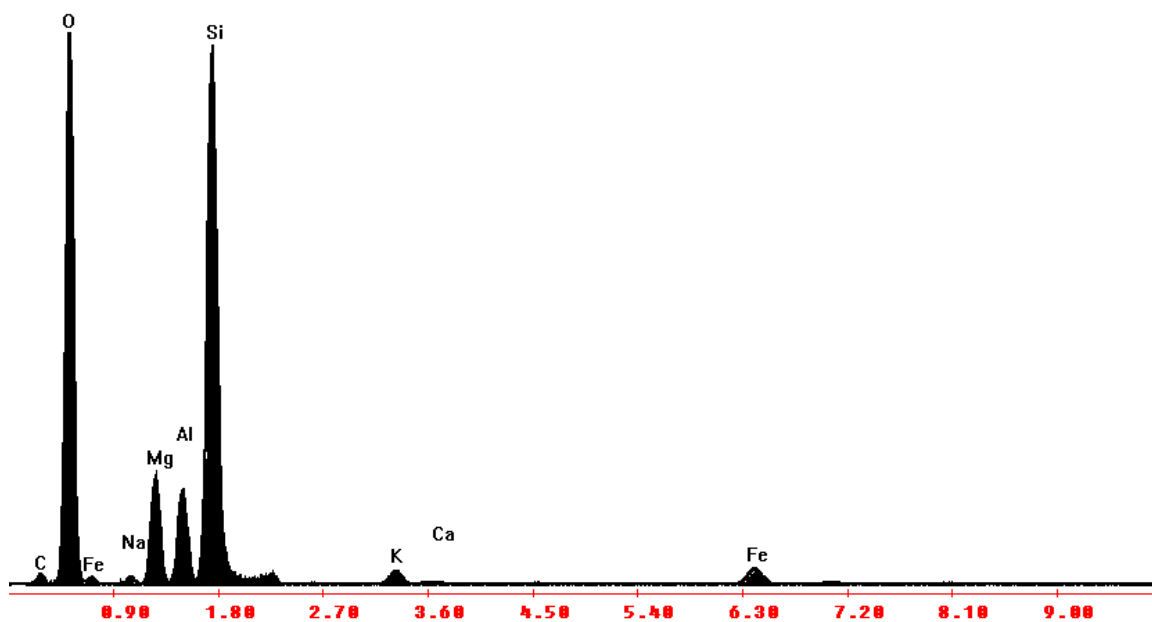
Element	Wt %	At %	K-Ratio	Z	A	F
C	0	0	0	1.0428	0.126	1.0006
O	52.77	66.58	0.1663	1.0253	0.3071	1.0005
Na	0.75	0.66	0.0018	0.9596	0.2505	1.0038
Mg	6.41	5.32	0.0227	0.9838	0.3576	1.0059
Al	5.75	4.3	0.0235	0.9548	0.4242	1.0088
Si	29.62	21.29	0.1444	0.9827	0.4961	1.0002
K	0.79	0.41	0.0057	0.9317	0.7797	1.0011
Ca	0.23	0.12	0.0019	0.9538	0.8418	1.0014
Fe	3.68	1.33	0.032	0.8662	1.0055	1
Total	100	100				

EDS spectrum and elemental composition for acid-modified (1M HCl) palygorskite after 1000 ppm Na+



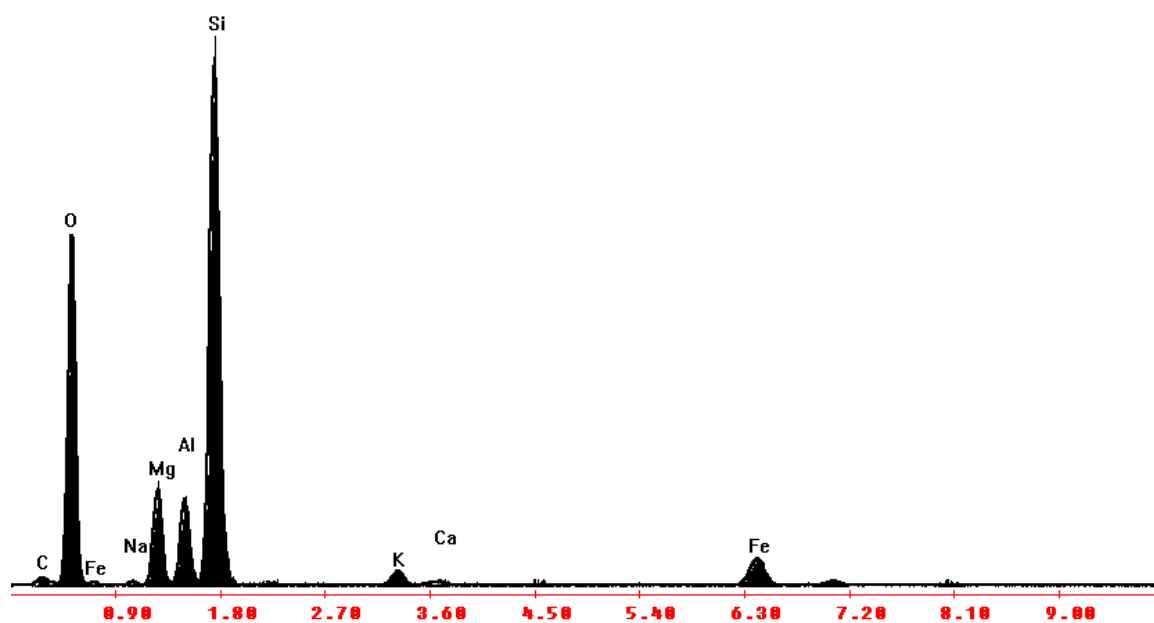
Element	Wt %	At %	K-Ratio	Z	A	F
C	0	0	0	1.0417	0.128	1.0006
O	53.96	67.51	0.1724	1.0242	0.3118	1.0004
Na	0.62	0.54	0.0015	0.9586	0.2508	1.0038
Mg	6.93	5.7	0.0246	0.9827	0.3592	1.0057
Al	5.39	4	0.0218	0.9538	0.4207	1.0086
Si	28.85	20.56	0.1407	0.9817	0.4968	1.0002
K	0.89	0.46	0.0065	0.9306	0.7844	1.0009
Ca	0.17	0.09	0.0014	0.9527	0.8448	1.0012
Fe	3.18	1.14	0.0277	0.8652	1.0064	1
Total	100	100				

EDS spectrum and elemental composition for acid-modified (1MHCl) palygorskite after 500 ppm Na⁺



Element	Wt %	At %	K-Ratio	Z	A	F
C	3.3	5.19	0.0049	1.0359	0.1433	1.0007
O	58.48	68.97	0.1929	1.0186	0.3238	1.0004
Na	0.58	0.47	0.0014	0.9534	0.2479	1.0033
Mg	6.33	4.91	0.0222	0.9774	0.3563	1.0049
Al	4.93	3.45	0.02	0.9487	0.4247	1.0072
Si	23.99	16.11	0.1186	0.9764	0.5063	1.0001
K	0.59	0.29	0.0045	0.925	0.8169	1.0005
Ca	0.06	0.03	0.0005	0.9471	0.8744	1.0007
Fe	1.74	0.59	0.0152	0.8598	1.0142	1
Total	100	100				

EDS spectrum and elemental composition for acid-modified (HCl) palygorskite after 250 ppm Na⁺



Element	Wt %	At %	K-Ratio	Z	A	F
C	1.92	3.21	0.0025	1.0425	0.1264	1.0005
O	50.72	63.56	0.1522	1.025	0.2926	1.0005
Na	0.39	0.34	0.001	0.9594	0.2534	1.0039
Mg	6.87	5.66	0.0248	0.9835	0.3646	1.0059
Al	5.62	4.17	0.023	0.9546	0.4262	1.0088
Si	29.64	21.16	0.1454	0.9825	0.4993	1.0002
K	0.81	0.41	0.0059	0.9314	0.7807	1.0011
Ca	0.19	0.1	0.0016	0.9535	0.8424	1.0014
Fe	3.84	1.38	0.0335	0.866	1.0057	1
Total	100	100				

Curriculum Vita

Dennis Wambuguh was born in the Central Region of Kenya. He graduated from Njiri's High School in 1972 before joining the premier Alliance High School for pre-university/higher education. Dennis received his Bachelors degree in agriculture from the University of Nairobi, Kenya, in 1978. He progressively worked as a Research Scientist with Kenya's Ministry of Agriculture, a Research Officer with the World Agroforestry Center (formerly ICRAF), Nairobi, Kenya before being awarded the prestigious Overseas Development Association Shared Scholarship (ODASS) to pursue a Masters degree in Forestry in Relation to Land Use at the Oxford Forestry Institute of the University of Oxford, United Kingdom. He rejoined ICRAF after his studies for a while before joining the Policy Research Group as a director and consultant. He consulted for various development agencies on environmental natural resource management, and economic development issues. He has also previously worked as a Senior Research Technician at the University of Missouri-Columbia where he was involved with the implementation of the Missouri Soil Fertility and Fertilizers Research Program, and the Soybean Research Project. Dennis is currently working as an Environmental Specialist with the Bureau of Environmental Epidemiology, Department of Health and Senior Services, State of Missouri, where he specializes in risk assessment reviews for technical/regulatory compliance with State/Federal laws, regulations and guidance. He is also responsible for recommending modifications to standardize exposure and fate/transport models based on site-specific conditions at CERCLA, RCRA, and other hazardous waste sites as well as reviewing the technical accuracy and impacts of proposals, rules, and various documents relating to human exposure to hazardous waste via air, water, and soil media.

A paper based on his dissertation research was published in the December 2008 issue of the *New Journal of Chemistry*.

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