Indigo dye waste recovery from blue denim textile effluent: a by-product synergy approach

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Received (in Montpellier, France) 11th April 2008, Accepted 9th July 2008
First published as an Advance Article on the web 12th September 2008
DOI: 10.1039/b806213g

Textile dyeing effluents present a substantial environmental problem, primarily because such effluents contain high concentrations of waste dyes, dye-products, and variable salts. The stonewashing process for the degradation of blue indigo to create a 'faded' look in blue denim results in high concentrations of indigo dye waste in the resulting effluent and because indigo is very difficult to decompose biologically, the effluent ends up in the environment, raising aesthetic concerns and damaging the integrity of the receiving streams. Wastewater containing indigo is characterized by a moderate amount of chemical oxygen demand (COD), pH, suspended solids, dissolved solids and a dark blue color. Although color and COD are some of the important parameters monitored to meet effluent discharge standards, companies are discouraged from treating or recovering the waste dye by cost implications. We report on a simple and potentially cost-effective method of recovering indigo dye waste from the effluent through adsorption with palygorskite clay and subsequent conversion of recovery by-products into Maya blue, an organic–inorganic hybrid pigment with applications in the paint and coating industry. The production of a secondary commercial product from waste stream through a by-product synergy process offers an attractive alternative to discharging the untreated effluent into municipal treatment plants or the environment.

1. Introduction

The stone-washing process to create a 'faded' look in blue denim discharges high amounts of indigo dye and uses large amounts of bleaching agents such as potassium permanganate and sodium hypochlorite, resulting in effluent characterized by large variability of chemical composition, high base content, and color.[1–3] These effluents often do not meet regulatory requirements for wastewater discharge even after undergoing treatment by conventional coagulation and activated sludge process because indigo is difficult to decompose biologically.

The discharge of such dye wastewaters into the environment raises aesthetic concerns, impedes light penetration, damages the quality of receiving streams, and may be toxic to treatment processes, to food chain organisms, and to aquatic life in general (Fig. 1). As regulations on effluent quality before discharge into municipal systems or streams become increasingly restrictive, the quality of the effluent could as well threaten permit renewal for these industries.[4] It is therefore important to recover the dye before discharge, both from an ecological as well an economic standpoint.

Current pretreatment systems are large, expensive, and have little or no payback other than the elimination of sewer charges. Companies are therefore reluctant to adopt such measures simply out of concern for the environment, but they might do so to cut costs or to generate extra revenue. Some of the physical and chemical treatment techniques effective in color removal use more energy and chemicals and could potentially create even more toxic chemicals in the effluent through degradation or alteration of the conjugated system of dyes.[5] Ultrafiltration (UF) and other membrane technologies can effectively remove indigo dye from the effluent but are prohibitively expensive. The wider application of these techniques is therefore hampered by toxicity or cost considerations.[6]

Fig. 1 Blue jeans, blue water (Tehuacan Valley, Central Mexico Credit: Maquila Solidarity Network and the Human and Labor Rights Commission of the Tehuacan Valley).

Indigo dye is extensively used by textile industries, specifically in the blue jeans industry[7] and while about 80% of the indigo dye may be fixed onto the fabric, between 5 and 20% is removed and purged in the effluent stream. Typical dye house effluent concentrations for vat dyes such as indigo reported in literature range from 0.01 to 0.1 g l^{-1}.[8–10] Since the eye can detect concentrations as low as 0.005 mg l^{-1} of reactive dye in water, concentrations exceeding this level invariably raise concern on aesthetic grounds.

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By-product synergy, a concept supported and promoted by the US Business Council for Sustainable Development (USBCSD) and the World Business Council for Sustainable Development (WBCSD), refers to production of a secondary product in the course of a manufacturing process, resulting in substantial potential savings, efficient use of materials, and contributes towards meeting regulatory guidelines.[11] The development of a commercially feasible and economical method by which indigo may be recovered from the wastewater of denim yarn dye for reuse, therefore, promises to have substantial economic and environmental impact.

We investigated the feasibility of a potentially simple, cost-effective process of waste indigo dye recovery using palygorskite (attapulgite) clay, and its incorporation in the production of a secondary product, Maya blue. Maya blue is a characteristic pigment of unparalleled stability used by the ancient Maya Indians in pottery and mural paintings. The characteristic blue-turquoise color is obtained only after heating a mixture of the clay palygorskite and organic dye indigo.[12,13]

Adsorption is the passive sequestration and separation of adsorbate from an aqueous phase onto a solid phase and depends mostly on the surface chemistry or nature of the adsorbent, adsorbate and the system conditions in between the two phases. Adsorption processes offer the most economical treatment of dye removal and can be carried out in a batch mode by adding the adsorbent to the waste, stirring the mixture for a sufficient time, allowing the adsorbent to settle, and drawing off the cleansed water.[14] The adsorbate with the adsorbed waste dye is further processed into the by-product.

Details of the synthesis of Maya-type organic–inorganic complex pigments including Maya blue are reported elsewhere.[15] Unlike many other pigments, Maya blue does not contain heavy metals and is therefore environmentally friendly and has potential applications in the paint and coating industry.

2. Experimental procedures

Palygorskite clay

Palygorskite is a hydrated magnesium silicate with partial isomorphic substitutions of magnesium and aluminium and/or iron. A two-layer clay consisting of tetrahedral SiO_4 and $Al(OH)_3$ with an octahedral $Mg(OH)_2$ layer between them, it has a fibrous texture with an internal structure of microchannels (measuring 3.7 Å × 6.4 Å in cross section) and different bonded water molecules representing almost 20% of the structure's total weight. Palygorskite has the structural formula $[Si_8O_{20}Mg_5(Al)(OH)_2](H_2O)_4{\cdot}4H_2O$, and its crystalline structure as studied by Bradley[16] is shown in Fig. 2. The clay has a fibrous texture with an internal structure of microchannels and different bonded water molecules that account for almost 20% of the structure's total weight. Besides surface water, palygorskite contains molecular or zeolitic water within the channels, water coordinated to the edge octahedral cations (also called "bound", "crystalline" or "coordinated" water) and the normal hydroxyl group of 2 : 1 layer silicate at the center of the ribbon.[17] Due to its structural morphology, considerable attention has been directed to its ability to adsorb organics on its surface.[18]

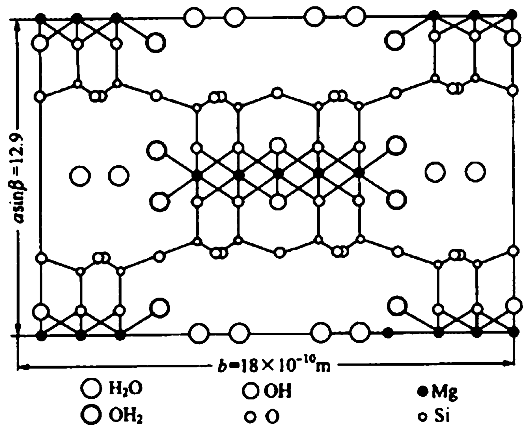

Fig. 2 Crystalline structure of palygorskite from (001) plane.[16]

2.1 Indigo and Maya blue

Indigo ($C_{16}H_{10}N_2O_2$) is an organic colorant widely used for dyeing textiles and as a colorant for artistic pigments.[19] Indigo molecules can enter the channels within the clay and form stable chemical bonds inside the clay. Heating the mixture causes the partial removal of zeolitic water[20,21] or the elimination of structural water,[22] emptying portions of the channels in which the indigo can be accommodated to form stable chemical bonds with the clay resulting in Maya blue, an organo-clay hybrid pigment with exceptional stability against chemical aggressors including acids, alkalis and chemical solvents. The pigment was originally invented and frequently used in murals, pottery and ceremonial artifacts by ancient Maya civilization in Mesoamerica during the 8th to 16th centuries.[23]

2.2 Waste indigo dye—properties and extraction from solid 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. IGP utilizes 100 mesh mechanical filters to separate by-products from the wastewater. These by-products, mainly indigo colored fibers, are removed from the denim garments during the abrading process and are stored in a landfill approximately 3120 cubic yards (2385 m^3) in capacity—at a cost of $70 000 per year. 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 for irrigation of 50 acres of alfalfa. Salinity concentrations, however, exceed the established limits of sodium adsorption ratio (SAR) of 13.20. It was envisaged that palygorskite clay could address both problems simultaneously.

The chemical characteristics of the wastewater from the IGP plant before aeration (influent) and after (effluent) 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 chemical oxygen demand (COD). While chemical oxygen demand is a measure of all chemicals in the water that can be oxidized, biological

Table 1 Chemical composition of influent-aeration and effluent-irrigation tanks

Parameter	Influent-aeration tank	Effluent-irrigation tank	Method
pH	7.5	7.4	EPA 150.1
BOD/mg l^{-1}	95	44	EPA 405.1
TSS/mg l^{-1}	2418	2548	EPA 160.1
COD/mg l^{-1}	131	125	EPA 160.1

Table 2 Elemental composition of palygorskite clay

Element	Wt%	Atom%
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

oxygen demand 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 level 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.

2.3 Simulated effluent

Indigo dye waste was reconstituted from solid waste. Solid waste was dissolved in distilled water (1 : 50 w/v) and the suspension passed through a 100 mesh screen to remove suspended solids. 1 g of palygorskite clay was added to 100 ml of the waste solution and stirred on an orbital shaker at 400 rpm for 24 h. The suspension was then allowed to settle for 2 h resulting in a clear solution. The clear supernatant was decanted and the remaining solids dried for 24 h at 100 °C and then ground in a mortar. The elemental composition of the solid indigo waste obtained from the International Garment Processors plant at El Paso is shown in Table 3 (*vide infra*).

Table 3 Elemental composition of solid indigo dye waste from IGP plant, El Paso[a]

Element	Wt%	Atom%	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				

[a] K-Ratio = X-ray intensity; *Z* = correction factor; *A* = absorption; *F* = fluorescence.

2.4 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 h. in Indigo content ranged from 1% to 8%. The resulting pigment samples were analyzed by UV-Vis.

2.5 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 1.5406 Å. 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 was obtained outside this range.

2.6 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 ESEM 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 20 kV, beam current was roughly 0.2 nA, 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.

2.7 UV-Vis

Pigment samples were prepared by grinding the appropriate ratios of clay and indigo dye in a mortar and heating the mixtures at 170 °C for 24 h. A similar set of samples was prepared using palygorskite–indigo waste as the substrate. Indigo dye in the pigments ranged from 1% to 8% by weight. Reflectance spectra were measured by a PC model 3101 spectrophotometer (Shimadzu) using $BaSO_4$ as a background.

2.8 Salt adsorption and effect on pigment properties

Wastewater effluent contains both organic and inorganic constituents both of which are adsorbed onto the palygorskite. A range of sodium chloride solutions with a concentration range of 250–2000 ppm was used as a proxy to study the salt adsorption dynamics of palygorskite, and the effect of the interaction between inorganic contaminants and palygorskite on pigment properties.

A stock solution of sodium chloride was prepared by dissolving 2 g of AnalaR grade sodium chloride salt crystals in 1 l of distilled water for a final concentration of 2000 mg l^{-1}. Standard solutions of 250, 500, 1000 and 2000 ppm were prepared by transferring the respective aliquots of the stock solution to a 100 ml volumetric flask and bringing the final volume to 100 ml. 1 g of palygorskite was added to each of the solutions and the suspension stirred for 24 h. The suspensions were then vacuum-filtered using a glass microber filter (Whatman 934-AH, 110 mm diameter). The concentration of sodium in the filtrate was the analyzed by inductively coupled plasma (ICP) (EPA Method 4.1.3/200.7). The filtered clay was dried at 100 °C for 24 h and elemental analysis done.

UV-Vis analysis was run on pigments prepared from the extract palygorskite at 4% indigo.

3. Results and discussion

3.1 X-Ray diffraction (XRD)

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 confirm the clay to be predominantly palygorskite, with traces of silica/quartz. Peaks obtained are typical for palygorskite with peaks at 2θ = 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 (Accelrys2).

3.2 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 (EDX, EDAX), the elemental analysis on microscopic sections of the material or contaminants that may be present is revealed. The elemental composition of the palygorskite clay is shown in Table 2.

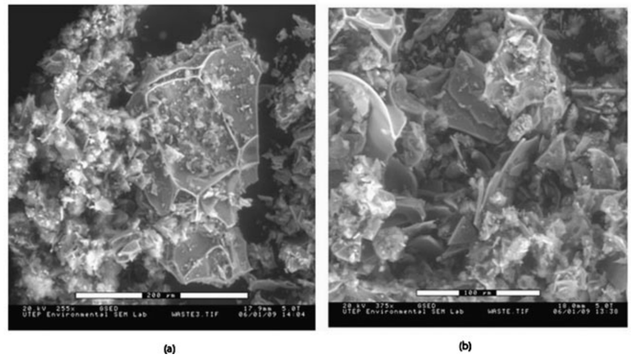

Fig. 4 ESEM micrographs of indigo dye waste showing remnants of pumice rock.

The elemental analysis of the indigo dye waste (Table 3) shares some elemental constituents with that of palygorskite, presumably from the pumice rocks used in the stonewash process.

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 and Table 3).

3.3 UV-Vis

UV-Vis spectrophotometry was used to determine and compare the absorbance of pigment samples prepared from pure indigo and palygorskite. Indigo waste was included for comparative purposes. For all pigment samples, peak absorbance occurs around 620–650 nm. Absorbance increases with the concentration of indigo in the pigment (Fig. 5).

The UV-Vis spectra of pigment samples derived from indigo waste fortified with additional indigo dye are shown in Fig. 6. Peak absorbance of the resulting pigments shifts to the left with increasing indigo dye concentration. The data also confirm the concentration of indigo dye in the waste to be well below 1%, in line with results reported in the literature.

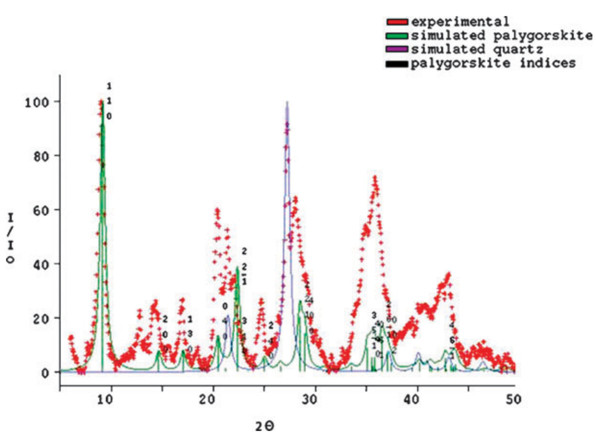

Fig. 3 Experimental and simulated X-ray diffractograms of palygorskite (λ = 1.5418 Å).

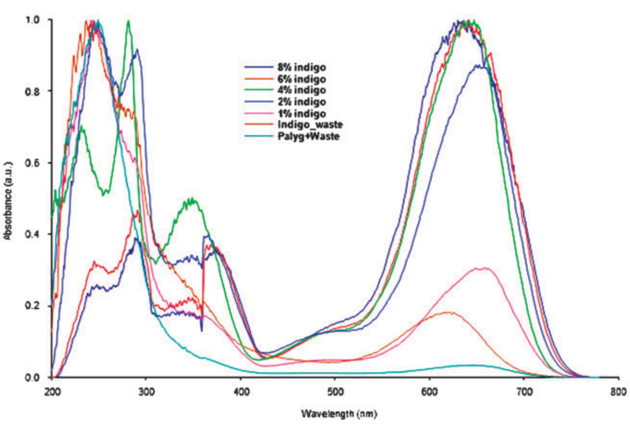

Fig. 5 UV-Vis spectra of pigment samples (pure indigo and palygorskite).

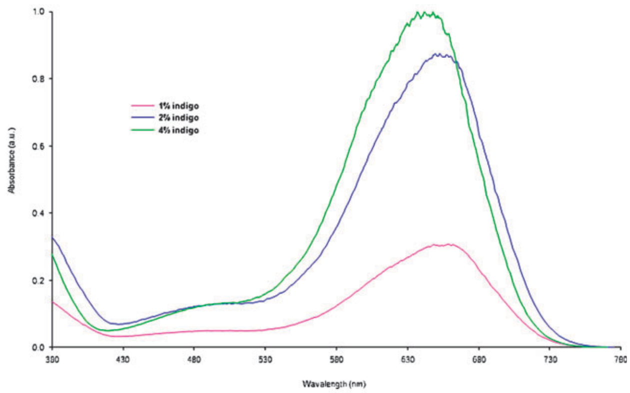

Fig. 6 UV-Vis: indigo waste with additional indigo dye (380–780 nm range shown).

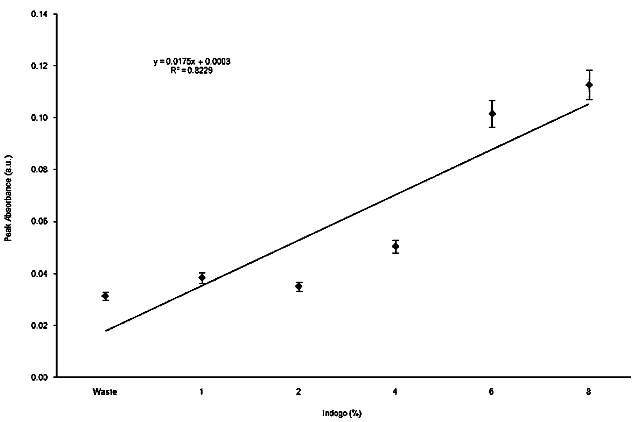

Fig. 7 Relationship between indigo concentration and peak absorbance. (Waste: no additional indigo; other samples: waste with additional indigo as shown).

A plot of the relative peak absorbance for pigments ranging from 1% to 8% indigo content shows an approximately linear relationship with increasing indigo content (Fig. 7). Waste indigo, which contains low levels of recoverable indigo dye from the textile effluent, is included for comparative purposes.

3.4 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. 8).

As expected, the color becomes darker with increasing indigo concentration for both sample lots. There is however, a perceptible color difference between them depending on the substrate. Pigments made using the 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

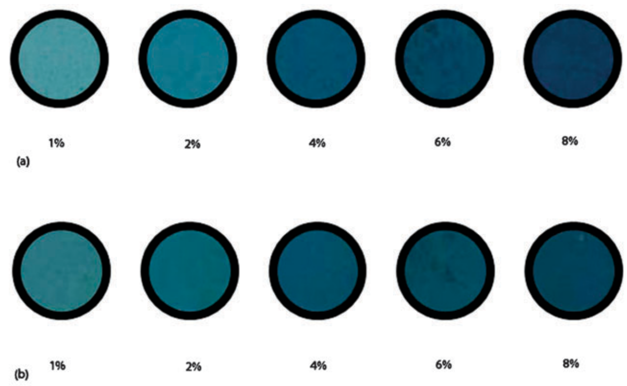

Fig. 8 Color variation with increasing concentration of indigo in (a) pure mixtures and (b) palygorskite-recovered waste. Each mixture heated at 170 °C for 24 h.

Table 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

(P, S, and Cl) found only in the solid dye waste and not in any of the pure components.

3.5 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).

The clay used in the adsorption of salts was dried at 100 °C for 24 h and used in the preparation of pigments. Pigment samples were prepared by grinding the clay and indigo and subjecting the ground mixture to 170 °C for 24 h before UV-Vis analysis (Fig. 9). All pigment samples contained 4%

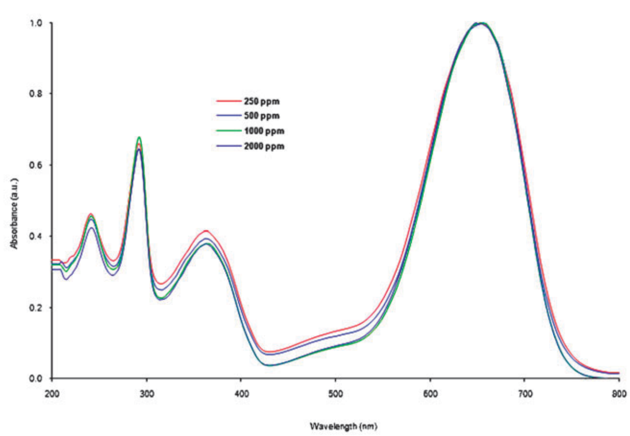

Fig. 9 UV-Vis of pigments prepared with salt-adsorbed clay (at 4% indigo).

indigo by composition. The spectral response for all pigments was uniform over the range of salt concentration tested. It is significant that the level of salt concentration does not seem to adversely affect the color properties of the resulting pigments.

4. Conclusions

The adsorption of waste indigo dye and associated salts from textile wastewater onto palygorskite clay and its conversion to a commercial by-product, Maya blue, was investigated in this study. Palygorskite clay effectively adsorbs the indigo dye from textile wastewater, significantly reducing color. The recovered by-product was used as the precursor for the synthesis of Maya blue pigment. Recovery of the indigo dye waste offers the potential for recycling or reuse of the waste indigo dye in textile effluent.

Adsorbents, mainly clays, are readily available, inexpensive, and offer a cost-effective alternative to conventional treatment of waste streams. Given the price of the palygorskite clay relative to activated carbon and polymer resins, adsorption by palygorskite appears to be a cost-effective method for the treatment of aqueous effluents both from the standpoint of color removal and revenue generation. Pigments synthesized from the recovery process and fortified with additional indigo dye produced results that compared favorably with pigments synthesized from pure components.

Salt removal levels of over between 52% and 63.5% were achieved across a test range of 250 to 2000 ppm of salt concentration, using sodium chloride as a proxy. Na^+ is probably the most common constituent of textile wastewaters due to the wide range of sodium salts used at various stages of the textile wet process. The presence of salt in palygorskite used in the recovery process does not seem to adversely affect the color properties. On the contrary the salt appears to improve the color, and therefore the quality of pigments synthesized with the clay used in the adsorption. The use of palygorskite clay in the recovery of waste indigo dye and salts from textile effluent and the synthesis of a potential commercial by-product implies significant economic as well as ecological implications.

Acknowledgements

Financial support from the Environmental Science and Engineering PhD Program/Center for Environmental Resource Management (CERM) at the University of Texas at El Paso (UTEP) is gratefully acknowledged. We thank Lola Norton for her assistance with the Environmental Scanning Electron Microscopy (ESEM) and Brenda Torres with UV-Vis analysis.

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