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CHARACTERIZATION OF REAL TEXTILE EFFLUENTS AND PREPARATION OF A WATER TREATMENT PROTOCOL USING HYDROTALCITE

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Abstract: *Textile wet processing generates wastewater streams with markedly different chemical profiles. This paper evaluates the use of calcined hydrotalcite as a selective adsorbent for real textile wastewater, focusing specifically on washing water and cotton reactive dyeing effluent. The adsorbent was prepared by calcining hydrotalcite at 600 °C for four hours and then cooling it in a desiccator prior to use. To link structural activation with process performance, the calcination step was interpreted using a qualitative FTIR scheme derived from a companion characterisation study. Calcination suppresses the carbonate band characteristic of hydrotalcite and enables the memory effect, favouring the reincorporation of anionic species when the solid comes into contact with water. Two industrial wastewater streams were studied and compared before and after treatment with hydrotalcite using total organic carbon (TOC), total carbon (TC), inorganic carbon (IC), total nitrogen (TN), pH, conductivity, biological oxygen demand (BOD), total suspended solids (TSS) and chemical oxygen demand (COD). The cotton dyeing wastewater exhibited the most significant response, with reductions in TOC and COD of 78.5% and 74.6%, respectively. The washing effluent showed more limited improvements, with TOC and COD reductions of 18.6% and 27.6%, respectively. This difference can be explained by the difference in pH between the two streams: a higher pH increases adsorption values. Therefore, the treatment appears promising as a selective pre-treatment for segregated dyeing streams. However, the associated increase in pH and conductivity indicates that a later neutralization or polishing step would still be required.*

Key words: *hydrotalcite; water treatment; textile effluent; cotton dyeing process; washing processes.*

1. INTRODUCTION

Textile wet processing is one of the industrial activities most strongly associated with water use and variable wastewater composition. Washing, dyeing, rinsing and finishing operations generate effluents that may contain dyes, salts, alkalis, surfactants, lubricants and other additives, meaning that the final analytical profile depends not only on the substrate, but also on the exact stage of the process [1]-[3].

This distinction is particularly important in dyehouses. Cotton reactive dyeing wastewater is typically rich in alkaline chemicals and unfixed dye-related compounds, whereas washing wastewater usually contains a lower chromatic load, but appreciable amounts of organic auxiliaries. Studies based only on model dye solutions often overlook this heterogeneity. Nevertheless, adsorption remains attractive in the textile sector because it can be applied as a selective polishing step for colour and dissolved organics using relatively simple equipment [2]-[4].

Hydrotalcite-type layered double hydroxides are particularly interesting adsorbents because their positively charged, brucite-like layers contain exchangeable interlayer anions [5, 6]. After calcination, these solids are converted into mixed oxides that can regain a layered structure when rehydrated in water. This so-called memory effect enables new anionic species to be incorporated from the treated medium [5], [7], [8]. For textile applications, this behaviour is relevant whenever the wastewater contains dye-derived anions or other species that are compatible with the reconstruction of the layered structure.

Recent papers in the Oradea textile journal show ongoing interest in adsorption and in new wastewater treatment strategies for textile processes [3], [4]. However, there is still a need for conference contributions based on real segregated industrial streams and explicitly connected to adsorbent activation. The aim of the present work was therefore to adapt the hydrotalcite calcination study to a textile-focused paper and compare the response of two real industrial streams - washing and cotton dyeing wastewater - before and after treatment with calcined hydrotalcite.

2. MATERIALS AND METHODS

2.1 Materials

2.1.1 Nanoclay and Textile Effluents used

Two types of industrial wastewater were collected from a textile company (Table 1): wastewater from washing and from cotton dyeing. The first one is a cellulose dyeing bath with reactive dye chemistry, whereas the washing water represented a more auxiliary-rich stream.

Table 1: *Selected textile streams treated with hydrotalcite*

Stream	Textile process	Main reported bath composition
W	Washing	2 g/L lubricant (polyacrylamide) + 5 g/L wetting agent (ethoxylated fatty alcohol)
C	Cotton dyeing	1 g/L wetting agent + 60 g/L sodium silicate + 6 g/L NaOH + 0.451% reactive dye

2.2 Methods

2.2.1 Treatment method

The hydrotalcite and wastewater dosages are described in

Table *2*. The hydrotalcite was previously calcinated at 600ºC for 4 hours and then cooled in a desiccator to minimize moisture uptake from the atmosphere. This step is important because if it remains exposed to humid air, calcined hydrotalcite can progressively reconstruct its layered structure. The nanoclay-wastewater dispersion was left for 1 h in maximum agitation, followed by 24 h with minimum agitation.

Table 2: *Stream and hydrotalcite quantities used.*

Sample	Stream quantity used (mL)	Stream used	[Hydrotalcite used] (g/L)
W+HT	300	W	23

C+HT	300	C	32

Finally, the dispersion was filtared for 24 hours using filter paper with a grammage of 130 g/m^{-2}, a pore size of 25–30 µm and a thickness of 430 µm. The collected water was analysed.

2.2.2 Water parameters analyzed

The streams were analysed before and after treatment using the following parameters: pH; conductivity; total suspended solids (TTS); total organic carbon (TOC); total carbon (TC); inorganic carbon (IC); total nitrogen (TN); chemical oxygen demand (COD); and biological oxygen demand (BOD). TOC, TC, IC and TN were measured using a Shimadzu TOC-VCSH analyser after filtration through 0.45 µm PTFE membranes, while pH was measured using a CRISON micropH 2002 meter and conductivity using a CRISON microCM 2101 conductimeter at 21 °C. COD was obtained by digestion and photometric measurement. BOD was measured using an OxiTop respirometric system. For the COD and BOD measurements, dilutions were selected to maintain measurable oxygen consumption without complete depletion. A total correction factor was applied based on dilution. TSS was assessed gravimetrically by filtering, drying, and weighing of the retained solids. For concentration-based parameters, the relative change caused by treatment was calculated as follows:

$Removal\ (\%) = ((C0 - Ct) / C0)\ x\ 100$

2.2.3 Hydrotalcite FTIR

FTIR analysis was conducted in ATR mode using a ZnSe prism with a Jasco FTIR 4700 IRT 5200 spectrometer with a DTGS detector. Spectra were recorded from 64 scans at aresolution of 4 cm^{-1}. The analysis was performed on hydrotalcite before and after calcination, as well as on hydrotalcite that had been calcinated and stored in the lab.

3. RESULTS AND DISCUSSION

3.1 Hydrotalcite FTIR

To connect structural activation with textile performance, FTIR analysis was conducted across the three stages we mentioned before. As shown in Fig. 1, the untreated solid displays the broad hydroxyl/water region and a characteristic carbonate absorption peak near 1365 cm^{-1} , as observed in hydrotalcite materials [8]-[10]. After calcination, this carbonate feature is strongly suppressed, which is consistent with the removal of interlayer carbonate and dehydroxylation. The partial recovery of hydrotalcite-like features after air exposure is in turn consistent with the memory effect [10].

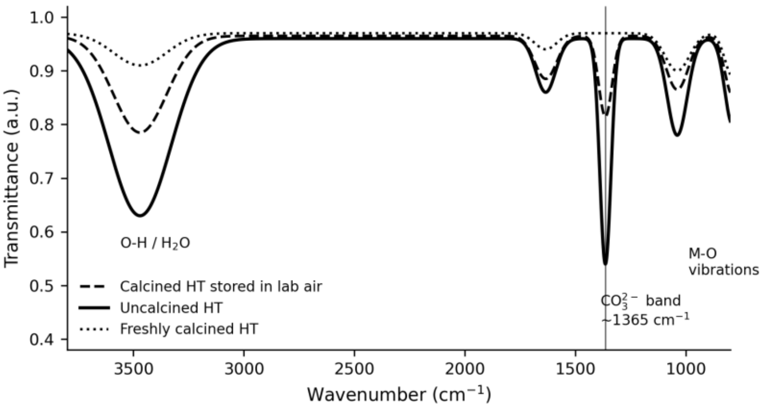

***Fig. 1**: Schematic FTIR comparison of hydrotalcite before calcination, immediately after calcination and after atmospheric exposure*

3.2 Stream characterization before and after treatment

As shown in Table 2, the response to calcined hydrotalcite depended strongly on the origin of the wastewater. The washing effluent was nearly neutral before treatment and mainly contained a lubricant and a wetting agent. In contrast, the cotton dyeing wastewater was strongly alkaline as it came from a reactive dyeing bath containing sodium silicate and sodium hydroxide. From a textile processing viewpoint, the cotton stream therefore represented dye-bearing bath chemistry, whereas the washing stream represented a more dilute auxiliary-dominated water.

The cotton dyeing effluent experienced the strongest reduction in organic load. TOC fell from 554.3mg/L to 119.1 mg/L (a 78.5% reduction), while COD fell from 1161 mg O_2/L to 295 mg O_2/L (a 74.6% reduction). These values demonstrates the ability of calcined hydrotalcite to remove a significant fraction of the carbonaceous load present in a real cotton dyeing wastewater.

***Table 3:** Carbon, oxygen-demand, pH, conductivity and TSS parameters before and after hydrotalcite treatment*

Parameter	W raw	W + HT	C raw	C + HT	Change W (%)	Change C (%)
TOC (mg/L)	437.3	355.9	554.3	119.1	18.6	78.5
TC (mg/L)	445.0	360.5	584.6	140.0	19.0	76.1
IC (mg/L)	7.664	4.61	30.3	20.9	39.8	31.0
TN (mg/L)	59.24	46.38	4.118	4.539	21.7	-10.2
COD (mg O2/L)	1329	962	1161	295	27.6	74.6
BOD (mg O2/L)	2200	0	300	30	100	90
pH	6.42	12.32	11.43	12.9	-91.9	-11.4
Conductivity at 21 °C (µS/cm)	685	1480	4620	10900	-116.1	-135.9
TSS (mg)	2.9	7.7	5	4.2	-165.5	16

The washing water showed a much more modest response. TOC decreased from 437.3 mg/L to 355.9 mg/L (a 18.6% reduction) and COD from 1329 mg O_2/L to 962 mg O_2/L (a 27.6% reduction). TN also decreased in the washing stream, from 59.24 mg/L to 46.38 mg/L. However, the cotton stream showed no reduction in nitrogen and even exhibited a slight increase within the experimental range, which may be due to an experimental error. The treatment was therefore selective rather than universal, preferentially removing dye-related or other anion-rich fractions. This can be explained by the pH, other studies have found that Hydrotalcite shows better adsorption values at higher pH values [11][12].

However, it is also due to the type of compounds the washing water contains, which are usually neutral and too large.

Regarding BOD, the reduction was above 90% in both cases, indicating that the treatment was highly successful. In the case of the cotton effluent, this decrease is consistent with the COD trend, as both parameters are expected to follow a similar pattern. However, for the washing effluent, the discrepancy observed between COD and BOD may be explained by the preferential removal of more biodegradable compounds, leaving behind less biodegradable substances that still contribute to COD but not to BOD.

Regarding TSS, we observed an increase in the W+HT and a decrease in the C+HT, which may be due to an error during filtration.

The difference between the two types of water can be explained in terms of textile chemistry and hydrotalcite reconstruction. Cotton reactive dyeing baths contain unfixed or hydrolysed dye species together with strong alkali. When calcined hydrotalcite rehydrates, its mixed oxides can recover a layered structure and capture new anions from the liquid phase [5], [7], [8]. The rationale of Fig. 1, based on FTIR, supports this mechanism: the removal of carbonate by calcination frees the interlayer environment for the incorporation of other anionic species once the solid enters water.

In contrast, the washing water was dominated by auxiliaries such as polyacrylamide lubricant and ethoxylated wetting agents. It is not expected that tese compounds will interact with calcined hydrotalcite in the same way as reactive dye-related anions. Consequently, the adsorbent only produced partial reduction in TOC and COD.

Despite the decrease in organic load, pH and conductivity increased in both waters after treatment, as summarised in Table 3. This behaviour is important for water reuse strategies because it indicates that adsorption was accompanied by the release or redistribution of alkaline species.

In the washing stream, for example, the pH rose from 6.43 to 12.32, while conductivity increased from 685 µS/cm to 1480 µS/cm. In the cotton dyeing stream, the pH increased from 11.43 to 12.90, and the conductivity increased from 4620 µS/cm to 10900 µS/cm. Therefore, calcined hydrotalcite cannot be considered a complete one-step solution for textile water reuse. Its main value lies in selective reduction of organic and probably chromophoric loads, which could simplify a subsequent biological, membrane or neutralisation stage.

This interpretation is consistent with the broader literature on textile wastewater, where combined treatment are generally considered to be more robust than a single isolated unit operation [1]-[3].

4. CONCLUSIONS

This study demonstrates the potential of using calcined hydrotalcite as an adsorbent for treating real textile wastewater, although its effectiveness is highly dependent on the type of effluent. Treatment was particularly effective for cotton reactive dyeing wastewater, achieving significant reductions in organic pollution (around 78% total organic carbon (TOC) and 75% chemical oxygen demand (COD) removal). In contrast, washing wastewater exhibited much lower removal efficiency, potentially due to the pH conditions and compounds present in the effluent.

The results confirm that the adsorption mechanism involves the “memory effect” of the reconstruction of calcined hydrotalcite, enabling the material to capture anionic species present in dyeing effluents. However, the treatment also increases pH and conductivity, meaning an additional step, such as neutralisation or polishing, is still needed before water can be reused or discharged.

This work's main contribution is evaluating hydrotalcite treatment using real segregated textile effluents rather than model dye solutions and connecting the treatment performance to the structural activation of hydrotalcite after calcination. This provides practical insight into how this material could be used as a pre-treatment step in textile wastewater treatment protocols.

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