

## Exploration of the Local Clay in Removing the Blue Textile Dye from the Blue Stream Commonly Known as 'Mabolou Running through Thetsane Industrial Area, Maseru

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### Abstract

As a search for affordable and efficient adsorbents for purification of textile wastewater continues, different natural materials are being investigated. Herein we report the investigation of clay obtained from Lesotho as a low cost and ecofriendly adsorbent for removal of blue textile dye from the stream running through the textile industry populated area in Ha Thetsane about 3 km South West of Maseru – the capital city of Lesotho. Batch adsorption studies were carried out for the effect of mass of adsorbent and particle size, pH, temperature and contact time on the adsorption capacity of the blue dye on the clay. The results show that the smaller the particle size of the adsorbent the higher the efficiency, although the smaller particles could also clog the pores of the filter paper; the adsorption increases under the basic media (pH  $\geq$  10) and at a low temperature (10-15°C) achieving an extraction efficiency of 88% for a 4 g clay and a 15 mL solution after 15 minutes extraction relative to the original solution. Despite the identity of the dye not being known, the clay adsorbent was found to be quite effective for the removal of this dye. The focus of the future experiments will be to obtain the information from the factories through the relevant government departments about the identity of the dye so that definitive quantitative analysis could be carried out.

**Keywords:** Clay; Batch adsorption; Textile dye; Wastewater; Environmental pollution; Maseru

### Introduction

As the world moves to improved livelihoods aspired by global conventions such as Sustainable Development Goals (SDGs) and Agenda 2063, most countries that find themselves in the Least Developed categories are still confronted with the challenges of environmental pollution – defined as any change, whether biological, chemical and or physical, in the quality of environment emanating from the human activity. Textile industry is one of the most common industries in the LDC countries due to the fact that it requires relatively lower capital investment for start-up as well as their ability to absorb a large number of unskilled manpower which provides a cushion for political instability resulting from lack of employment opportunities [1]. This situation is indeed prevailing in Lesotho where there is a huge shortage of employment opportunities due to the absence of industries [2]; as such the largest employer besides the public sector is the textile industry which employs between 40,000 and 50,000 people due to the convention between the USA and most African countries under the Africa Growth and Opportunities Act (AGOA) where products from these countries are waived from the tariffs by the former for the trade products from the latter [3]. This has increased the investment in the textile industry from the Far East, specifically China taking advantage of the AGOA opportunity. The environmental impact of this industry in Lesotho is far reaching with regards to the sludge and waste water from this industry as main source of employment [4].

Consequent of their inherent high pollution potential, textile industries contribute significantly to the international debates relating to international trans-boundary river systems [5,6]. Efforts are being made to reduce the extent of pollution such as landfilling the sludge that comes from the textile industries, which could also present a future challenge if the landfills are not properly constructed [7]. However, associated with the sludge is a release of copious amount of dyed wastewater that is used for dyeing the fabrics which is a nightmare to the sewerage authorities in places that host this industry [8]. Where law enforcement is not very effective, effluent from these factories may enter

the streams partially or untreated thereby causing a huge environmental risk due to the concoction of chemicals including dyes [9]. There are worse instances when the said investors threaten governments of closing down when being pressured by the law enforcement agencies to be environmentally friendly, thus holding governments at ransom due to the potential consequences of such closures on the employment profile of such countries [10].

Clean water has become a subject of global debates with some predicting the Third World War to be over the clean water. The World Health Organization (WHO) estimates that nearly 1.2 billion people living on earth today have no access to clean drinking water with 3.2 million people, majority being children below the age of 5, dying of infectious water-borne diseases every year [11]. Delpy and Pyke suggested that even if the UN Millennium Development Goals would be reached by 2015, poor access to water resources alluded to by WHO as well as a reported 1 in 4 ratio of 4 people in living without live without sanitation facilities in the developing economies, warrants more chemical research in water sector [12]. Sources of water pollution are either point or non-point sources with point sources comprising sources such as pipes, ditches or sewer lines that discharge contaminants or pollutants into bodies of surface water [13]. These usually include factories, sewage treatment plants, underground mines, and city storm drains. Due to their specific locations it is relatively easy to identify, monitor and regulate them.

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With the advent of the climate change, a search for the renewable resources intensifies. This has led for the search for renewable materials that adds little to no extra carbon footprint to the atmosphere. This has thus led to the exploration of naturally occurring materials for the extraction of different chemical species in the environment. These includes as natural fibres – cellulosic [14] and keratin-based materials [15] such human hair [16,17], plant materials such as pine cones [18], rice husks [19], sawdust [20], just to mention a few; as well as natural silicates – clays [21]. These materials are important since they usually do not cost much for their production except a bit of purification before use. These materials have been reported in extraction of different analytes with differing success as per a recent review [22].

Clay is abundant in Lesotho where its use has in the main been in the production of clay bricks with only recent exploration into ceramics such as pottery. This abundance makes clay a potent alternative for removal of chemical pollutants. Consequently, in this report the potential of the clay that is used by the clay brick making company was assessed for removal of the blue dye, suspected to be methylene blue as a common textile dye, from water collected from a stream running downstream of the textile factories in Ha Thetsane Industrial area South West of Maseru – the capital City of Lesotho, a tiny country wholly landlocked inside South Africa. This stream is commonly known as 'Mabolou (the blue stream) owing to its permanent blue colour. There are at least three factories that make fabric from raw cotton hence they use conspicuous amounts of dyes and release their wastewater into this stream hence a source was easily identified. One study reported that due to inefficient treatment of the waste from the concerned factories, the effluent flowing downstream in to Caledon River (< 5 km downstream) was "one of the most turbid rivers in Southern Africa" [4]; this therefore warrants efforts to reduce the extent of pollution of this important river that also acts as an international border between Lesotho and South Africa.

## Materials and Methods

### Chemicals and apparatus

Only the analytical grade purity chemicals obtained from ACE (Johannesburg South Africa), were used in this study, namely, NaCl, HNO<sub>3</sub>, NaOH and ethanol. Different concentrations of these chemicals were prepared by dissolving the appropriate amounts in distilled water prepared in-house using a laboratory water distiller.

The absorbance spectrum of the sample was measured using the Shimadzu 1201 UV-Vis Spectrophotometer (Kyoto Japan). Following this the wavelength that gave maximum absorbance was determined at which the further quantitative studies were measured. The pH was measured using a pH meter (Hanna Instruments, Romania).

### Collection and treatment of clay samples

The finely ground clay sample (about 1 kg) was obtained from the Technology Incubation Group at the University which was used for production of ceramics and clay bricks. This sample had been characterized before using X-ray diffraction technique in two different studies and produced the data shown in Table 1 [23,24]. This sample was washed with ethanol to remove all the organics that could be adsorbed on it and rinsed with copious amount of distilled deionized water before being dried in an oven at 40 °C thereafter stored in clean Schott® bottles away from organic compounds sources till further use.

### Collection and storage of the water samples

The stream water was collected in 1000 mL Schott® bottle from the stream running along the Ha Thetsane Industrial area downstream of the textile factories. However, due to their refusal for entry, the water samples were obtained several meters away from the said factories. These water samples were stored in a refrigerator at around 5°C when not in use. The samples were warmed to around room temperature (25°C) before all the experiments except those requiring specific temperature.

### Extraction procedures and optimisation of different parameters

The effect of different parameters on the adsorption of the dye was studied using batch experiments in a univariate manner. Portions of accurately weighed clay were added into a 100-mL conical flask containing 15.0 mL water sample. The mixture was stirred for 10 minutes (except where the effect of extraction time was investigated, in which case the extraction time will be specified accordingly) and then filtered to attain a clear filtrate whose absorbance was measured. The different parameters that were studied included varying the adsorbent mass, particle size, pH, temperature and contact time. The extractions were repeated three times (n=3) using three different mixtures (inter-sample variation) as it was observed that the absorbance did not vary much when the absorbance of the same sample (intra-sample variation) was measured.

## Results and Discussion

### Determination of the wavelength of maximum absorbance

Since no standard was available, the study was based entirely on the sample from the mentioned stream. The sample gave a maximum absorbance at 668 nm and yielded a similar spectrum to the one for methylene blue found in literature as opposed to the other blue dyes [25]. Therefore, further experiments were carried out using this wavelength for quantitative analyses. Other studies reported relating to this stream hypothesised that this blue compound could be methylene blue [26]. However, the authors do not want to commit to this without any confirmatory tests for the compounds in the water sample, hence they decided to refer to the analyte as a blue dye in this report.

### Effect of varying the adsorbent mass

About 15 mL sample portions were suspended in different masses of the clay samples ground and sieved at the particle size below 0.250 mm in a 100 mL conical flask. The mixture was continuously stirred for ten minutes using a stirring glass rod. Figure 1 shows the effect of varying the mass of clay used in the extraction of the blue dye following a 15 minute suspension. Despite the somewhat considerable error bars, it should be noted that these represent the % RSD ≤ 10%.

As can be seen, the removal efficiencies of different masses of adsorbent changed significantly with increasing amount of adsorbent. The decrease in absorbance as the mass is increased seems almost linear ( $R^2=0.9727$ ). This is due to the increase in availability of surface active sites resulting from the increased dose and conglomeration of the adsorbent. The adsorbent mass of 4 g was thus chosen as sufficient for adsorption of the dye achieving the lowest absorbance of 0.080 compared to the absorbance of about 0.095 obtained when using 1 g of adsorbent.

### Effect of the adsorbent particle size on the extraction efficiency

Particle size is known for improved surface area hence the effect of

Material	% Abundance			
	Reported by Nthunya L, et al. [23]	Reported by Masheane M, et al. [24]	Average	%RSD
SiO <sub>2</sub>	71.13	71.8	71.46	0.66
Al <sub>2</sub> O <sub>3</sub>	14.47	14.5	14.48	0.17
Fe <sub>2</sub> O <sub>3</sub>	4.55	4.56	4.55	0.17
K <sub>2</sub> O	2.45	2.45	2.45	0.12
CaO	0.21	0.23	0.22	6.6
MgO	0.6	0.7	0.65	11.05
Na <sub>2</sub> O	0.1	0.1	0.1	0.17
TiO <sub>2</sub>	0.95	0.97	0.96	1.64
P <sub>2</sub> O <sub>5</sub>	0.01	0.01	0.01	0.17

Table 1: Chemical composition of the clay used according to reported literature.

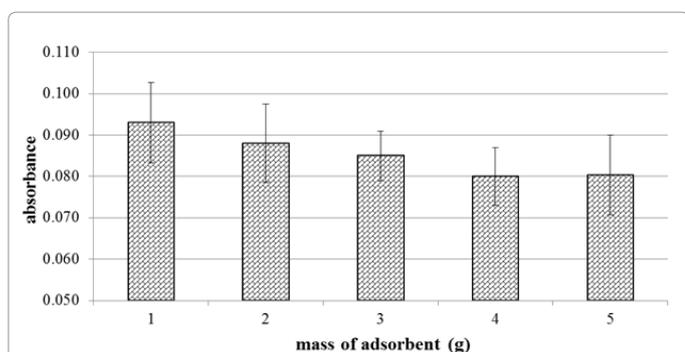


Figure 1: The effect of varying the adsorbent mass on absorbance of the water sample.

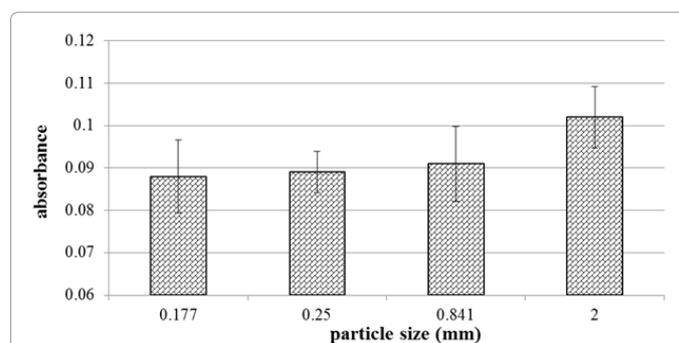


Figure 2: The effect of varying particle size of adsorbent on the uptake of the dye.

particle size is another important parameter to study. Different particle sizes were investigated using clay samples sieved through different particle sizes thus 0.841 mm, 0.250 mm, and 0.177 mm respectively. The absorbances of the filtered water samples were measured after the 15-minute suspension of the water samples in a clay adsorbent of about 4.0 g. Figure 2 shows the effect of particle size on the efficiency of the extraction.

The absorbance was found to decrease with decreasing particle size as depicted in Figure 2 this is possibly due to the larger surface area achieved by the smaller particles. The larger particles expose less surface area than smaller ones hence a loss in extraction efficiency. Despite the extraction efficiency being obtained with 0.177 mm particle size, the filter paper clogged and made filtration very difficult. Therefore the ideal particle size was chosen as 0.25 mm particle size. Grinding of adsorbent to various particle sizes does not only affect particle size but also reduced the regularity of crystalline structure of the adsorbent material, hence improving its analyte uptake.

### Effect of pH of the solution on the extraction efficiency

The activity of the H<sup>+</sup> ions commonly known as pH is known to affect adsorption studies of different compounds on different materials differently. This depends mostly on the type of interactions between the analytes and the active sites of the adsorbent. The presence of a higher concentration of H<sup>+</sup> ions (lower pH values), the H<sup>+</sup> ions reduce the electron density of the active sites hence reduce the coordinative bonding of the adsorbent to the analytes, especially if the analytes are electrophilic. The effect of pH of the sample was studied by spiking the samples with different amounts of HNO<sub>3</sub> and NaOH to a measured pH value. The pH of the original solution diluted appropriately was also measured. Figure 3 shows the effect of pH on the adsorption of

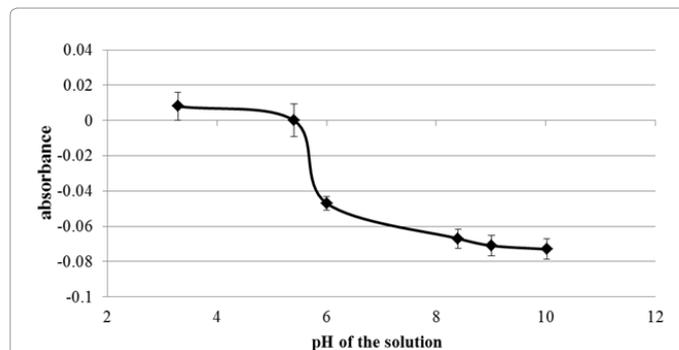


Figure 3: Effect of pH on the adsorption of the dye on clay (measured relative to the pH of the original solution -5.45).

the dye on the clay adsorbent using about 4 g of 0.25 mm particle and extraction time of 10 minutes.

As expected, absorbance decreases with decreasing H<sup>+</sup> ion activity, increasing pH values. This implies that the adsorbent becomes more efficient at alkaline conditions and less efficient at acidic conditions. This hints that the adsorption dynamics could involve some form of ion-exchange. At higher pH, surface of adsorbent particles might become negatively charged, which enhance the positively charged dye through electrostatic forces of attraction and increases adsorption efficiency. Therefore the pH of 10 was chosen as an ideal pH for the extraction of the dye.

### The effect of temperature on the adsorption efficiency

Temperature is very important in the dynamic processes since it affects the mass transfer between the two phases. However this could

also demonstrate a negative effect in that the adsorbed analytes could also be desorbed back into the solution except where such adsorption is not dynamic (equilibrium-based). The effect of temperature was investigated by equilibrating the solutions in the water bath at respective temperatures prior to the introduction of the adsorbent material and as described in the prior sections. Figure 4 shows the effect of temperature (10 - 30°C) on the efficiency of adsorption of the dye on the clay sample.

Clearly, absorbance increases with increasing temperature and this implies that the lower temperatures - 10°C and 15°C are favourable. The increase in absorbance as a result of temperature increase could be attributed to the lower binding of the dye onto the clay adsorbent, thus suggesting that the adsorption is dynamic (equilibrium-based) as the increase in temperature increases the mobility of the analytes to and fro the adsorbent material, with the reduction of the binding strength.

### The effect of contact time on the extraction efficiency

To assess the effect of extraction time on the adsorption efficiency, all the optimised conditions were employed: 4.0 g mass of clay, 0.25 mm particle size, pH of 10 and the 15°C temperature. The samples were thereafter equilibrated at different times (5-30 minutes) as per Figure 5.

As can be seen, the extraction rate increases to about 15 minutes after which it levels off. This extraction profile follows the extraction time-profile reported in many different analytes using different extraction techniques including liquid-based techniques [27]. Although the extraction efficiency at a glance seems to follow the first order kinetics, efforts to model this as a first order kinetics failed thus indicating a different kinetics order. Pseudo-second order kinetics for the uptake of Cu (II) ions using pine cones reported [18]. However the extraction

time was thus chosen to be 15 minutes where the efficiency of about 88% was realised using 4 g × 0.25 mm clay at temperature of 15°C and pH of 10 extraction conditions.

The comparison of the extraction dynamics of methylene blue using this clay (this report) and the reported activated charcoal from rice by-products [28] shows consistent behaviour with regards to most parameters such as pH effect (90% reported at pH >10), changing adsorbent mass (efficiency peaked at around 3 g of charcoal), as well as the smaller particle size demonstrating much higher efficiency. This report further put down a postulate regarding the probable adsorption mechanism attributing the reduced efficiency in the presence of H<sup>+</sup> ions (low pH values) to the protonation of the dye molecules hence reducing its binding (electron donation) to the clay particles. At a pH higher than the zero point pH of the surface, the adsorption increases due to the built-up of the negative charge on the surface. However, despite this making sense, without the positive identification of the dye and the absence of the standards, no assertions can be made towards this postulation as well as the determination of the other quantitative parameters such as loading capacity and the determination of the relevant isotherms. These will form a major part of the follow-up study in a near future with a known dye such as Methylene Blue which is suspected in this study.

### Conclusion

This piece of work demonstrated the potential of clay for use as an efficient extraction material for purification of the blue dye from the waste water from the textile industries. Although the identity of the dye was not made for quantitative analysis, the clay sample seems to extract about 88% (semi-quantitative) from the original solution. The optimum conditions for the extraction include 4 g of clay sample at 0.25 mm, at the pH of 10 (basic pH conditions) and temperature of 15°C and the extraction time of 15 minutes. One of the important aspects of this work is the simplicity of the clay and its ready availability in Lesotho making it a highly potent adsorbent material. In conclusion, it can be stated that clay offers an alternative and affordable means for an effective removal of the textile dyes from wastewater which is an environmental nightmare in countries whose economic participation relies heavily on this type of industry such as Lesotho.

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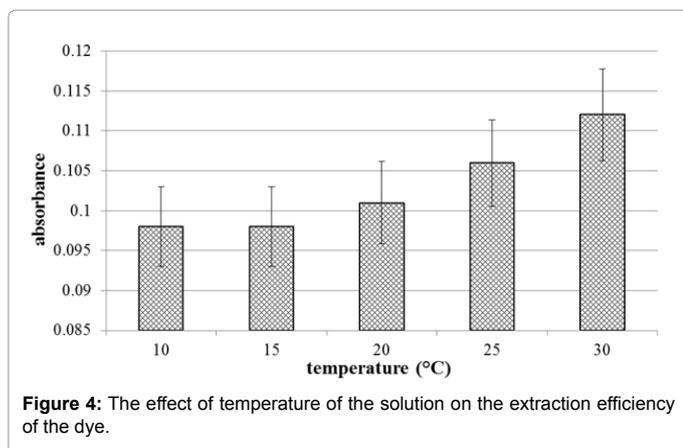


Figure 4: The effect of temperature of the solution on the extraction efficiency of the dye.

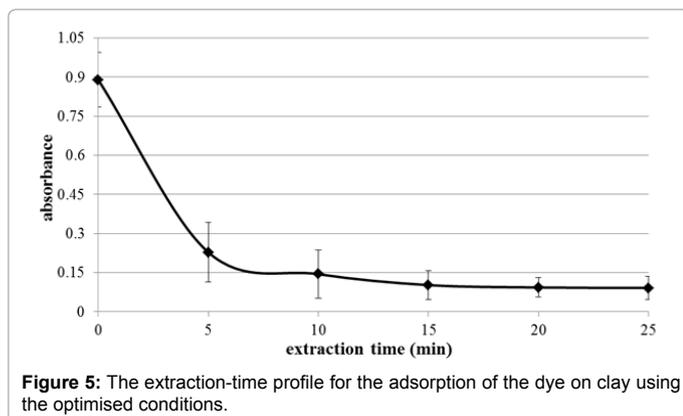


Figure 5: The extraction-time profile for the adsorption of the dye on clay using the optimised conditions.

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