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# Synthesis and characterisation of novel organopalygorskites for removal of *p*-nitrophenol from aqueous solution: Isothermal studies

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## ABSTRACT

Organopalygorskites were synthesised by using dimethyldioctadecylammonium bromide (DMDOA) and cetylpyridinium chloride (CP) with surfactant loadings equivalent to 100% and 200% CEC of the palygorskite. The four organopalygorskites, thus produced, were characterised by Fourier Transform Infrared Spectroscopy (FTIR), thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and zeta potential measurement. FTIR and TGA data demonstrated that higher surfactant loadings as well as long branched chain DMDOA produced highly ordered surfactant conformation. SEM morphological results showed that the organopalygorskites had less entangled fibres than the unmodified palygorskite. The zeta potential values showed positive charge formation on the organopalygorskites surface when they were synthesised with surfactant loadings equivalent to 200% CEC of the palygorskite. The organopalygorskites were tested for adsorption of *p*-nitrophenol (PNP) with a special focus on the adsorption isotherms. The adsorption data could be fitted with multiple isothermal models indicating that the adsorption was controlled by multiple mechanisms. Sorbent loading rate, initial pH, temperature and ionic strength might all affect the adsorption process. Also, DMDOA modified organopalygorskites reduced desorption/redispersal of adsorbed PNP back into the environment to a great extent. This study will be helpful in designing palygorskite-based organoclay adsorbents for remediating organic environmental contaminants which are ionic in nature.

## 1. Introduction

Removal of toxic contaminants from the effluent of various industries is one of the most significant environmental challenges. In the recent years, several physical, chemical and biological processes have evolved for the remediation of waste effluents. Among them, contaminant immobilisation by sorption is proven to be an effective and attractive mechanism. In this context, the use of clay materials has gained considerable attention in the recent years. Clays are suitable candidates to remove organic and inorganic pollutants from waste water due to their abundance in nature, inexpensiveness, environmental stability and high adsorptive and ion exchange properties. However, the intrinsic negative surface charge of most of the natural aluminosilicate clay minerals causes them to repel anionic contaminants. Moreover, these clays are very hydrophilic and consequently show very low adsorption for hydrophobic organic pollutants. However, when the surfaces of these materials are modified by introducing long-chain organic surfactant compounds, high sorption of organic toxicants can be achieved through partitioning [1–3]. Additionally, the cationic surfactant molecules may impart a positive surface charge to the clay products that can effectively hold contaminants through electrostatic bonding.

Among the clays, bentonite has been most extensively studied material for environmental applications. Several other modified clay candidates such as pillared clay [4], acid-treated bentonite and sepiolite [5], surfactant treated sepiolite [6], layered double hydroxides [7] and spent activated clay [8] have also been used successfully. However, palygorskite and its organically modified products have been least explored for their potential use in environmental remediation. Palygorskite is a 2:1 type clay mineral which possesses moderately high structural charge due to considerable substitution of $Al^{3+}$ by $Mg^{2+}$ and $Fe^{2+}$ in the octahedral sheet. This net negative charge on palygorskite surface enables it to be modified by cationic surfactant molecules. It is also probable that the exchangeable cations, that balance the excess negative charges in the palygorskite structure, can be exchanged with surfactant cations at least on its external surfaces. In addition, this clay mineral displays fibrous particle shape, fine particle size with internal

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channels and high surface area [9]. These properties of palygorskite make it a suitable candidate for organic modification and thereby recommend its use in remediation of organic contaminants. Earlier reports suggest that palygorskite can successfully be modified with octadecyltrimethyl ammonium chloride for adsorbing organic dye compounds [10]. Also, palygorskite-based sorbent materials are likely to be more permeable than bentonite based sorbents under natural flow condition because the later has intrinsic swelling behaviour which may restrict water flow through it.

It is usually difficult to remediate ionisable organic contaminants through adsorption because these compounds are subjected to protonation or deprotonation depending on the pH of the aqueous phase. Most studies in adsorptive remediation of organic contaminants by organoclays have concentrated on non-ionic organic compounds, where the contaminants are adsorbed mainly through the partitioning mechanism. However, the removal of ionisable compounds by organoclays might be governed by multiple mechanisms, such as electrostatic attraction, partitioning, ion exchange and van der Waals forces.

In the current study, *p*-nitrophenol (PNP) has been chosen as a model ionisable organic compound to investigate its adsorption onto organically modified palygorskites. It is considerably polar in nature and has a pKa value of 7.15 at 25 °C temperature. PNP is an important member of the nitro aromatic phenol group. It is widely used in pesticides, dyes and pigments, polymer engineering, olive processing, petrochemicals and pharmaceutical industries. It is listed among the 126 priority pollutants by the US EPA. It is toxic to plant, animal and human health. In case of acute exposure, PNP is known to cause blood disorder (methenoglobinemia), liver and kidney failure, anaemia, skin and eye irritation and systemic poisoning. Because of the toxicity and environmental damage caused by PNP, it is necessary to develop an effective remediation approach for safe discharge of industrial effluents containing this compound. There are reports that organoclays have been used as adsorbent for PNP [11–15]. However, palygorskite-based organoclays have not been tested for adsorptive removal of PNP from aqueous solutions. The mechanisms of interaction between PNP and the organoclays also remains largely unknown. The goal of the present study is to demonstrate the potential of organopalygorskites for removing PNP from aqueous solutions. This paper aims to investigate the capacity and mechanisms of PNP adsorption by four different organopalygorskites synthesised from two surfactants, namely dimethyldioctadecylammonium bromide and cetylpyridinium chloride, with surfactant loading rates equivalent to 100% and 200% CEC of the palygorskite. Desorption of adsorbed PNP from the organopalygorskites is also studied.

## 2. Experimental

### 2.1. Starting clay material

The starting material in this study is an Australian palygorskite (Grade 050F) which originates in Western Australia. It was supplied by Hudson Resources Limited and was used as received without further purification. The cation exchange capacity (CEC) of this clay is 17.0 cmol ($p^+$) $kg^{-1}$ as determined by the ammonia electrode method [16] and it has a BET specific surface area of 97.3 $m^2\ g^{-1}$ as measured on a Gemini 2380 Surface Analyser.

### 2.2. Reagents

Two surfactants, namely dimethyldioctadecylammonium bromide ($C_{38}H_{80}BrN$, MW: 630.95, denoted as DMDOA) and cetylpyridinium chloride (MW: 358.00, denoted as CP), both supplied by Sigma–Aldrich, were used in this study for modifying the palygorskite. PNP ($C_6H_5NO_3$, MW: 139.11) was also obtained from Sigma–Aldrich, and all the chemicals were used without further purification.

### 2.3. Synthesis of organopalygorskites

Four palygorskite–surfactant hybrids were synthesised in a hydrothermal cation exchange reaction according to a method described previously by Frost et al. [3]. The amounts of the surfactants used for modification were equivalent to 100% and 200% of the CEC of the palygorskite.

### 2.4. Characterisation of organopalygorskites

#### 2.4.1. Fourier Transformed Infrared Spectroscopy (FTIR)

Infrared (IR) spectra were obtained using a Magna-IR™ Spectrometer 750 (Nicolet Instrument Corp. USA) equipped with a liquid nitrogen cooled mercury–cadmium–telluride (MCT) detector and Diffuse Reflectance Infrared Fourier Transform (DRIFT) accessories. Spectra over the 4000–400 $cm^{-1}$ range were obtained by the co-addition of 64 scans with a resolution of 4 $cm^{-1}$ and a mirror velocity of 0.6329 $cm\ s^{-1}$. PeakFit v4.12 software package (Hearne Scientific Software) was used for band component analysis that enabled the type of fitting function to be selected and allowed specific parameters to be fixed or varied accordingly. Gauss–Lorentz cross-product function with the minimum number of component bands was used for band fitting. The fitting was undertaken until reproducible results were obtained with squared correlations of $r^2$ greater than 0.98.

#### 2.4.2. Thermogravimetric analysis

The organoclays were characterised by thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTGA) on a TGA 2950 Thermal Analysis instrument (Thermal Analysis Inc., USA). The temperature for TGA was raised at a rate of 10 °C per minute ranging from 25 °C to 1000 °C with a resolution of 6 °C. Approximately 50 mg of finely ground sample was heated in an open platinum crucible. An inert atmosphere was maintained inside the furnace with pure $N_2$ flowing at 70 $mL\ min^{-1}$.

#### 2.4.3. Scanning electron microscopy (SEM)

Morphology of the palygorskite and its organoclays was examined by a Philips XL30 FEG scanning electron microscope (SEM). The fine ground clay products were dried at room temperature and then coated with carbon under vacuum in argon atmosphere for the SEM studies.

#### 2.4.4. Measurement of zeta potential

Zeta potential of the palygorskite and the synthesised organopalygorskites were measured by a Malvern Zetasizer Nano instrument (Malvern Instruments, USA). Clay samples were suspended in Milli-Q water (0.01% w/v) for zeta potential measurement.

### 2.5. Adsorption of p-nitrophenol on organopalygorskite

Because of the reliability and simplicity of the method, batch experiments were carried out to evaluate the adsorption capacity of the synthesised organopalygorskites for PNP. The effect of sorbent dose on the adsorption of PNP by organopalygorskites was studied for sorbent amounts varying from 0.05 g to 0.50 g in 30 mL of 3.59 mM PNP solution, providing an agitation time of 2 h. Adsorption isotherms were developed by equilibrating 0.3 g of the organopalygorskites with 30 mL of solution containing 0.72, 1.44, 2.16, 2.88, 3.59, 4.31, 5.03 and 5.75 mM PNP, respectively. An agitation time of 2 h was allowed as the kinetic experiment showed attainment of equilibration after 1 h of agitation in