

## Preparation and characterisation of organopalygorskites and their application for *p*-nitrophenol adsorption

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Organoclays are prepared by modifying clays with alkyl ammonium cations. The organoclays thus produced have wide range of environmental application for the adsorption and removal of toxic environmental contaminants in soil and water. The 2:1 swelling type clays are mostly used for organoclay preparation. However, the organoclays prepared from swelling type clays have limited applicability for environmental remediation under flow conditions. Being a non-swelling clay and having high surface area, palygorskite is a good candidate to be modified organically for environmental application under flow conditions. However, unlike 2:1 swelling type clays, palygorskite is under explored for its potential to prepare organoclays.

We prepared two organopalygorskites in cation exchange reaction (Xi et al., 2004) by modifying locally available palygorskite with dimethyldioctadecylammonium bromide (DMDOA) at organic loadings equivalent to 100% and 200% cation exchange capacity (CEC) of the palygorskite. The CEC and BET surface area of the palygorskite were 17 cmol (p<sup>+</sup>) kg<sup>-1</sup> and 97 m<sup>2</sup> g<sup>-1</sup>, respectively. The modification caused reduction in the surface area of the organopalygorskites due to pore blocking that inhibited passage of N<sub>2</sub> in the organopalygorskite structures during BET analysis. The 200% CEC equivalent organopalygorskite showed 24 m<sup>2</sup> g<sup>-1</sup> BET surface area as against 33 m<sup>2</sup> g<sup>-1</sup> by the 100% CEC equivalent organopalygorskite. The long chained DMDOA cation packed tightly on the palygorskite surface forming a well structured organic phase, which was further supported by the band shifts of '-CH<sub>2</sub>' bonds towards lower wave numbers in FTIR (Fourier Transformed Infrared spectroscopy) studies (2923 cm<sup>-1</sup> and 2852 cm<sup>-1</sup> for asymmetric and symmetric stretching respectively in 100% CEC equivalent organopalygorskite; 2921 cm<sup>-1</sup> and 2850 cm<sup>-1</sup> for asymmetric and symmetric stretching respectively in 200% CEC equivalent organopalygorskite). The unmodified palygorskite did not show any band in the above mentioned region due to absence of any organic molecule ('-CH<sub>2</sub>' bonds). Thermogravimetric analysis also indicated conformational changes of the DMDOA molecules in the organopalygorskites with incremental organic loading. DMDOA decomposition in 200% CEC equivalent organopalygorskite happened at a comparatively lower temperature (314<sup>o</sup>C) than in 100% CEC equivalent organopalygorskite (398<sup>o</sup>C). The SEM (Scanning Electron Microscopy)

examination of the organopalygorskites revealed less entangled fibrous morphology in the organopalygorskites than the unmodified palygorskite. The 200% CEC equivalent organopalygorskite had fewer cluster of fibres than 100% CEC equivalent organopalygorskite. The structural changes of palygorskite due to organic modification by DMDOA also caused alteration in the charge behaviour in the organopalygorskites. As evidenced from the measured zeta potential values, the 200% CEC equivalent organopalygorskite created 30.6 mV positive charges on its surface as against -3.45 mV for 100% CEC equivalent organopalygorskite and -19.9 mV for unmodified palygorskite.

We tested adsorption of *p*-nitrophenol (PNP) onto the palygorskite and the two organopalygorskites in batch procedures. The adsorption of PNP by the unmodified palygorskite was negligible. But, due to changes in the structural, morphological and charge properties, the prepared organopalygorskites demonstrated huge improvement in the adsorption of PNP from aqueous solution. The adsorption isotherm best fitted to Freundlich model (Freundlich, 1906) with  $r^2 > 0.99$ . The 200% CEC equivalent organopalygorskite showed ‘f value’ almost double to the magnitude of 100% CEC equivalent organopalygorskite.

Table 1: Pseudo second order kinetic parameters for adsorption of PNP onto organopalygorskites (500 mg L<sup>-1</sup> PNP, 23<sup>o</sup>C temperature, pH = 4.8)

Sample	$q_{exp}$ (mM g <sup>-1</sup> )	K (g mM <sup>-1</sup> min <sup>-1</sup> )	$q_e$ (mM g <sup>-1</sup> )	h (mM g <sup>-1</sup> min)	$r^2$
100% CEC	0.1309	4.36	0.1320	0.0759	0.9994
200% CEC	0.2320	2.92	0.2350	0.1613	0.9999

The pseudo second order kinetic model (Ho and McKay, 1998) showed almost perfect fit (with  $r^2 > 0.999$ ) in the whole range of adsorption period and had good consistency between experimental ( $q_{exp}$ ) and theoretical ( $q_e$ ) amounts of equilibrium PNP adsorption. The best fitness of pseudo second order kinetic model confirmed that not only physical adsorption, but chemical process also controlled the adsorption rate. The values of  $q_e$  increased with increasing DMDOA loadings in the palygorskite (Table 1). Contrastingly, the pseudo second order rate constants (K) decreased with increasing DMDOA doses due to the pore blocking effect; i.e. when the amount of DMDOA was more, the pore space was more densely packed, which might inhibit the migration of PNP through the pores. For this reason, 200% CEC equivalent organopalygorskite took bit longer time to reach adsorption equilibrium than 100% CEC equivalent organopalygorskite. The initial adsorption rate (h) was considerably higher for 200% CEC equivalent organopalygorskite than 100% CEC equivalent organopalygorskite. The pH and ionic strength of the solution affected PNP sorption by the organopalygorskites. The amount of PNP adsorption decreased with increasing pH and electrolyte concentrations.

So, the modification of palygorskite with DMDOA leads to successful synthesis of organopalygorskites that are highly efficient to adsorb PNP from aqueous solutions. The adsorption of PNP onto organopalygorskites is controlled by both physical and chemical processes. This study provides valuable information on the potential of organically modified palygorskites in the remediation of polar organic contaminants similar to *p*-nitrophenol from contaminated waters and soils.

### References

- Xi Y, Ding Z, He H, Frost RL (2004). Structure of organoclays—an X-ray diffraction and thermogravimetric analysis study. *Journal of Colloid and Interface Science* **277**, 116-120.
- Freundlich H (1906). Über die adsorption in lösungen. *Zeitschrift für Physikalische Chemie (Leipzig)* **57**, 385–470.
- Ho YS, McKay G (1998). A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents. *Process Safety and Environmental Protection* **76**, 332-340.

