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# Removal of rhodamine 6G with different types of clay minerals

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#### HIGHLIGHTS

• Uptake of cationic dye rhodamine 6G (R6G) on clay minerals via cation exchange mechanism.

- Uptake of R6G on kaolinite and palygorskite on external (001) and (110) surfaces.
- Both interlayer and external spaces responsible for the uptake of R6G on montmorillonite.
- Under low and high uploading levels, R6G form monolayer and bilayer formation on montmorillonite.

• Clay minerals are effective in removal of cationic dyes for wastewater treatment.

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### ABSTRACT

With an increased use of color dye in textile industries and elevated fabrics output, more scientific studies and technology developments are needed to effectively treat wastewater containing dyes. However, better understanding of the interactions between dyes and suspended solids is a necessity to advance such developments. In this study the interactions between rhodamine 6G (R6G), a cationic dye, and different types of clays minerals, commonly found in the wastewater sludge, were elucidated. The uptake of R6G on the clay minerals was attributed to cation exchange on the external surfaces of non-swelling clays, and at both external and interlayer spaces for swelling clays. In the interlayer of montmorillonite, the R6G molecules form monolayer and bilayer configurations under low and high uptake levels. The significant amounts of R6G uptake indicate that clay minerals are good sorbents for the removal of cationic dyes from water. And the R6G could be readily removed in wastewater treatment by adding small amount of clays and flocculated the clays out.

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## 1. Introduction

With the increased amounts of textile production, use of dyes increased accordingly, resulting in more dye-containing industrial wastewater to be treated. As most of the dyes are water soluble, making their removal from water more difficult using conventional carbon based sorbents. For the removal of dyes from water, both sorptive removal and chemical degradation were studied extensively. The advantage of degradation was completely converting dye molecules into others and the final products would be less toxic (Rasheed et al., 2017). Commonly used methods include

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photocatalytic treatment of using ZnO (Lutic et al., 2012) or  $TiO_2$  (Asiri et al., 2011) as the catalysts. However, for degradation removal, reaction rate is a key limiting factor. In comparison, sorptive removal is relatively fast. Plus, settling of the flocculants in wastewater treatment is a must. Thus, selected sorbents or floc-culants could be added to increase the dye removal efficiency. For sorptive removal, correct selection of sorbents is critical. Common sorbents tested include carbons from organic sources to inorganic Earth materials. For hydrophobic organic compounds, carbon has its unique advantage, as partitioning of hydrophobic organic compounds to solid is carbon based.

Rhodamine dye is one of the synthetic dyes widely used as a colorant in manufacturing textiles and food stuffs (Shen and Gondal, 2017). A carbon adsorbent prepared from acid activated Phoenix Sylvestric leaves had an adsorption capacity of  $84-104 \text{ mmol kg}^{-1}$  for rhodamine B (RhB) (Arivoli et al., 2009). In





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comparison, the removal capacity of rhodamine 6G (R6G) by exhausted coffee ground was 17.4 mmol  $kg^{-1}$  (Shen and Gondal, 2017).

Clay minerals, on the other hand, have large specific surface area (SSA) and high cation exchange capacity (CEC). They were used extensively as sorbents for the removal of different types of contaminants (Liu and Zhang, 2014; Fida et al., 2015). Adsorption of R6G on palvgorskite increased from 70 to 90% as the solution pH increased from 2 to 12 (Bagir et al., 2013). Presence of cationic surfactants would result in a reduced uptake of RhB (Xu et al., 2015). With the initial R6G concentration equivalent to 90% of the CEC value of sepiolite, the amount of R6G adsorption was about 56% CEC (Arbeloa et al., 1997). Heat treatment of sepiolite increased adsorption of RhB slightly (Wang et al., 2013). The uptake of R6G on montmorillonite and laponite was attributed to cation exchange (Grauer et al., 1984), but the linkage between the CEC of the minerals and the R6G sorption capacity was not provided to confirm the claim. R6G uptake on a bentonite was fitted to different thermodynamic models without any units, nor mechanistic association with each model (Farhan and Sameen, 2014).

Although progressive were made for the removal of RhB and R6G from water, some discrepancies were found in the literature regarding to the their adsorption on clay minerals. For example, in one study the adsorption of RhB increased from 55% to about 95% as the solution pH increased from 2 to 10 (Khan et al., 2012). In a different study, the RhB adsorption decreased from 19 to 6 mg g<sup>-1</sup> as the solution pH increased from 2 to 12 with the highest RhB adsorption of 24 mg g<sup>-1</sup> found in pH 4 solutions (Bhattacharyya et al., 2014).





Fig. 1. R6G molecules (a) and its 3d view (b). Blue: N; Red: O; Gray: C.

As such, the purpose of this study was to understand the interactions between cationic dyes and different types of clay minerals and to elucidate the mechanism of the uptake of cationic dyes on clay minerals using R6G as an example. The uptake and removal of R6G was characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR), and molecular dynamic simulation, in addition to batch experiments.



**Fig. 2.** Kinetics of R6G uptake on kaolinite (a), palygorskite (b), and MMT (c). The lines are the pseudo-second-order fits to the observed data and the insets are linear form of the pseudo-second-order fit.

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