



Adsorption of phenols on reduced-charge montmorillonites modified by bispyridinium dibromides: Mechanism, kinetics and thermodynamics studies



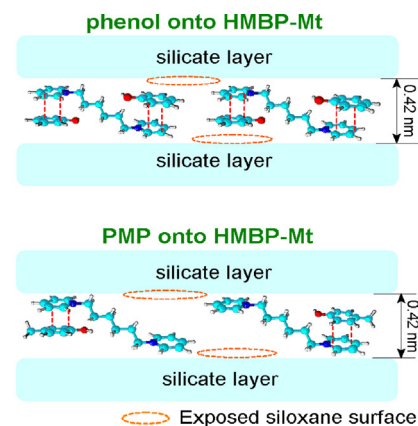
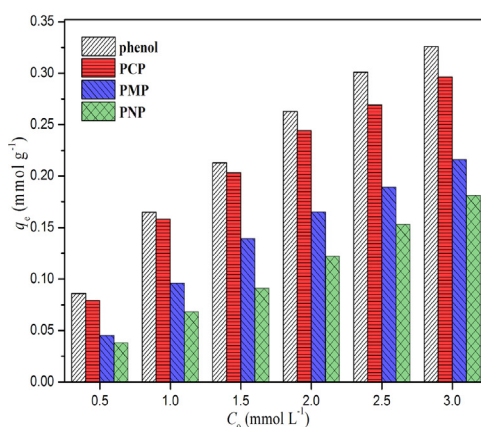
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HIGHLIGHTS

- Organo-RCMs were prepared using HMBP to modify RCMs through ion exchange.
- The uptake of phenol onto HMBP-RCMs was positively related to clay layer charge.
- The uptake of phenols onto HMBP-Mt decreased in the order: phenol > PCP > PMP > PNP.
- The π - π polar interaction played a dominated role in the adsorption of phenols.

GRAPHICAL ABSTRACT



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ABSTRACT

A series of reduced-charge montmorillonites (RCMs) were modified by hexamethylene bispyridinium dibromides (HMBP), then used to remove phenols from aqueous solution. The effects of concentration of HMBP (C), clay layer charge, contact time (t), temperature (T) and pH were investigated using a batch technique. The results implied that the clay layer charge had significant influence on phenol adsorption and the optimum conditions were as follows: C of 1.0CEC, 120 min, 25 °C and pH of 6.0. The adsorption mechanism of phenol on the HMBP-Mt was studied by comparing the adsorption characters of substituted phenols, the results indicated that the uptake of phenols onto HMBP-Mt decreased in the order: phenol > *p*-chlorophenol > *p*-methylphenol > *p*-nitrophenol. This indicated that the π - π polar interaction existing between the pyridine ring and benzene ring in phenols played a dominated role in the adsorption of phenols. The adsorption kinetics demonstrated that the adsorption of phenol onto HMBP-Mt followed the pseudo-second-order model. The adsorption isotherms at the temperatures of 25, 40 and 55 °C were determined and modeled using four different models. The best-fitted adsorption isotherm models were found to be in the order: Langmuir \approx Redlich-Peterson > Temkin > Freundlich. The thermodynamic study of adsorption process showed that the adsorption of phenol with HMBP-Mt was carried out spontaneously, and the process was randomly increasing and exothermic in nature.

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1. Introduction

Phenol and its derivatives are multipurpose raw materials which are used extensively in the areas of paint, coal conversion, pharmaceutical, paper, wood, rubber, polymeric resin, petroleum and petrochemical industries [1]. The depollution of phenol-containing wastewater is considered as one of the top priority since phenols are not only harmful to organisms but also causes bad taste and odor even at low concentrations [2]. Various processes such as biological treatment [3,4], chemical treatment [5], catalytic oxidation [6], ion exchange [7], solvent extraction [8], membrane separation [9] and adsorption [10–12], have been developed to treat the phenol-containing effluents. Among these technologies, adsorption is proved to be one of the most versatile and widely used methods for purification and separation in wastewater treatment, since it is convenient and effective [13]. Activated carbons are the most widely used adsorbents due to their high adsorption abilities for organic pollutants [14–17]. However, the poor mechanical strength, the difficult regeneration and the high disposal cost make it less economically viable as an adsorbent [18–20]. Undoubtedly, low-cost and easily available adsorbents offer a lot of promising benefits for the removal of organic pollutants from wastewater [21].

In recent years, clay minerals have attracted significant attention as adsorbents for the removal of toxic metals and organic pollutants from aqueous solutions due to their low cost and high efficiency [22]. Montmorillonite (Mt), a low-cost and abundant clay, is highly valued for its adsorptive properties because of its favorable physical and chemical characteristics [23]. The adsorption properties of Mt can be extremely improved by the modification with organic modifier. Previous researches [24–27] have shown that when the exchanged quaternary ammonium cation has one or more long-chain alkyl functional groups, the mechanism of sorption has been attributed to solute partitioning between water and the organic phase created by the conglomeration of the flexible alkyl chains, which is characterized by linear, noncompetitive isotherms and aqueous solubility dependence of the sorption process. Conversely, when the exchanged quaternary ammonium cation has benzyl, phenyl, and/or short-chain alkyl groups, the mechanism of sorption has been attributed to a physical adsorption process, which is characterized by competitive, nonlinear isotherms with no clear solubility dependence. The properties of the resultant organo-montmorillonite are highly dependent on the molecular structure of the organic modifier and the layer charge of the parent clay [28]. Huang and Zhu [29] found that the sorption capacity of 2,4-dichlorophenol onto cetyltrimethylammonium bromide (CTMA)-bentonite increased with increasing bentonite layer

charge, while the reverse was observed with tetramethylammonium bromide (TMA)-bentonite. This result can be explained by the fact that CTMA aggregates and siloxane surfaces provided the major sorption sites on CTMA-bentonite and TMA-bentonite, respectively.

The adsorption capacity of organoclays is not only related to the type and size of organic modifier but also associated with the structure of pollutant molecules [28]. Previous investigation showed that Benzyltrimethylammonium bromide (BTMA) modified bentonite displays a high affinity for phenol, possibly because phenol molecules interact favorably with the benzene ring in BTMA ion through increased π - π type interactions [30]. Gu et al. [31] found that the π - π polar interaction existing between the aromatic rings of aniline and pyridine ring plays a key role in the adsorption. Accordingly, it is possible to improve its adsorption capacity towards specific organic compounds present in the wastewater by introducing some special functional groups into the chemical structure of the organic modifier.

In this paper, a series of reduced-charge montmorillonites (RCMs) modified by Hexamethylene bis-pyridinium dibromides (HMBP) were applied in the removal of phenol from aqueous solution. The effects of the concentration of HMBP, clay layer charge, contact time, temperature and pH on phenol adsorption were investigated. The comparison of adsorption characters of phenols with various substituted group on HMBP-Mt was carried out to investigate the adsorption mechanism of phenol. The equilibrium data fitted with four isotherm equations (Langmuir, Freundlich, Temkin, and Redlich–Peterson) and the adsorption kinetics was examined using the pseudo-first-order and pseudo-second-order equations. The thermodynamics parameters (ΔG° , ΔH° , and ΔS°) were also calculated. The results obtained from this work would not only enrich the species of adsorbents for the treatment of phenol-containing wastewater, but also provide the theoretical basis for its further research.

2. Materials and methods

2.1. Materials

The original montmorillonite (Mt), obtained from Zhejiang Institute of Geology and Mineral Resources, China, had a cation-exchange capacity (CEC) of 0.99 mmol g^{-1} . The reduced-charge montmorillonites (RCMs) were prepared by heating a sample of the Li^+ -saturated Mt at 100, 120, 150, 170, and 200 °C, respectively, in a muffle furnace for 24 h [32]. The RCMs thus obtained were denoted as Mt-Tm, where m was the heating tempera-

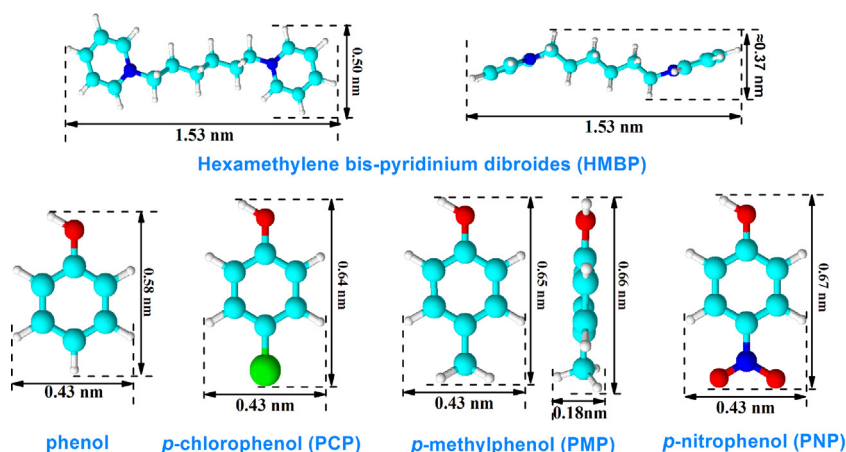


Fig. 1. The chemical structures and molecule dimensions of HMBP and phenols.

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