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# Mussel inspired preparation of amine-functionalized Kaolin for effective removal of heavy metal ions

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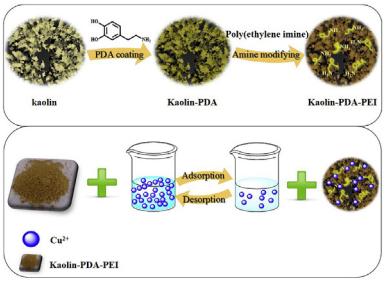
## HIGHLIGHTS

- Functionalization of Kaolin with amine groups through Michael addition reaction.
- Removal of copper ions via aminated Kaolin.
- Surface modification of Kaolin via bioinspired chemistry.
- Amine functionalized Kaolin for environmental application.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Adsorption has been well regarded as a promising and efficient method for the removal of low concentration heavy metal ions in aqueous solutions. And kaolin has been considered as a kind of low cost and environment-friendly adsorbent for its abundant in nature. But the low adsorption capacity to heavy metal ions and severe aggregation in solution restrains its application. In this work, an environment-friendly adsorbent (denoted as Kaolin-PDA-PEI) was prepared based on mussel inspired chemistry and Michael addition reaction between high reaction activity of polydopamine (PDA) and polyethyleneimine (PEI), which was possesses a number of amine groups. The amine groups have displayed strong adsorption affinity towards copper ions. The successful modification of Kaolin by PDA and PEI was confirmed by a series of analyses, such as Fourier transform infrared spectroscopy, transmission electron microscopy, thermal gravimetry analysis and X-ray photoelectron spectroscopy. The effects of various parameters such as contact time, pH, initial concentrations of copper ions and temperature on copper ion adsorption by Kaolin-PDA-PEI were investigated. Kaolin-PDA-PEI shows higher adsorption capacity as compared with the raw Kaolin. The kinetic adsorption data were analyzed using pseudo-first-order, pseudo-second-order and intraparticle diffusion model. The Langmuir isotherm and Freundlich isotherm equilibrium model were applied to adsorption isotherm data to find the better fit isotherm. The results showed that adsorption process was well fitted by Langmuir isotherm model. The values of thermodynamics constants such as entropy change ($\Delta S^0$), enthalpy change ($\Delta H^0$) and Gibbs free energy

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($\Delta G^0$) were also calculated. The results indicated that the adsorption process of Kaolin-PDA-PEI were endothermic and spontaneous.



## 1. Introduction

Water, the base of life, has long been the requirement of human survival and economic development [1]. As the increasing development of economy, the demand of water increasing and the problem of water pollution has become more serious. Heavy metal pollution, defined as a kind of environment pollution resulting from heavy metals or their compounds, is one of the most serious water pollution [2]. Due to its bioaccumulation and toxicity, heavy metal pollution has made seriously effect on ecosystems and human beings [3,4]. Among them, copper ions are one of the most commonly contained heavy metal ions in waste water. On the other hand, copper ions are one of the essential elements for human and play critical roles of human life process. However, the copper ions in high concentrations have toxic and adverse effects to living organism. Recent research shows that long-term drinking with high concentration copper (>1 mg/L) is associated with hemolytic anemia, hepatic failure, shock and death [5]. However, the concentration of copper ions in water generally increased with increasing industrial activities, which has become a potential threat to public health. Therefore, it is extremely urgent to explore corresponding solutions to reduce the copper ions in solution to keep the hygienic safety of drinking water [6,7].

To date, several technologies, including coagulation, flocculation, membrane filtration, biological treatment, organic material and adsorption, have been developed and implemented for the purpose of removing heavy metal ions in solution. Adsorption has been considered as an efficient method to remove heavy metal ions from waste water because of its low cost and easy operation [8]. Currently, many adsorbents such as activated carbon [9,10], sawdust [11], fly ash [12,13], zeolite [14], chitosan in prawn shell [15], lignin [16], rubber leaf [17], manganese oxide coated sand [18], green algae [19], carbon nanotubes [20–24], graphene related materials [25,26] and Kaolin [27] have been reported for removal of copper ions. Among them, Kaolin is considered as low cost natural clay that has been widely used in heavy metal ion removal. The physicochemical properties of Kaolin included small size, large specific surface area, and weak interlayer binding force are beneficial to the adsorption of heavy metal in solution. However, its severe agglomeration and low adsorption capacity in solution limits its applications severely. For example, its adsorption capacity to copper ions is only 0.67 mg/g [28]. Tavani EL et al. [29] have investigated the amount of adsorbed chromium ions from tannery wastewater by natural Kaolin clay is only 0.108 mg/g. Thus, numerous modification strategies, including high-temperature, coupling modification, surface grafting [30], radiation modification [31] and so on, have been developed to the modification of Kaolin to improve its dispersibility and adsorption capacity towards heavy metal ions. But many methods mentioned above suffer from defects such as high energy consumption, high cost, and high risk operation etc. Consequently, it is necessary to develop a facile, simple and effective strategy for Kaolin modification.

Mussel inspired chemistry is an emerging surface modification tool that has drawn greater attention in recent years [32]. It started originally by Herbert Waite's [33] research of marine mussel adhesion in 1980s. Subsequently, Lee at al [34,35] carried out the further experimental research about dopamine self polymerization in an alkaline environment. They also demonstrated that mussel-inspired chemistry can be used as a universal and promising strategy for surface modification of various inorganic and organic materials [34]. Fei et al. [36] have successfully synthesized varied thickness PDA coated carbon nanotubes based on dopamine self-polymerization and polymerization time-controlled. Yang et al. [37] have developed a method to prepare a layer of protective shell on the surface of yeast cell combined with covalent conjugate and dopamine self-polymerization. Zhao et al. [38] have prepared two-dimensional PDA/graphene oxide by self-assembly of dopamine monomers on graphene oxide surface for removal of radioactive element uranium. Zhang et al. [39–51] have fabricated well-dispersed carbon nanotubes by surface modification with 3-mercapto-1-propanesulfonic acid sodium salt, normal dodecanethiol, polyethylene glycol and polymers through combination of mussel inspired chemistry and Michael addition reaction. On the other hand, the formation of PDA coating has also investigated by some groups [52,53]. A lot of parameters such as pH, temperature and oxygen might influence the self polymerization of PDA. However, the detailed mechanism is still not clear for the complexity of self polymerization procedure.

In this study, we prepared an environment-friendly adsorbent combined with mussel inspiration and Michael addition reaction (Scheme 1). Kaolin was first coated with a thin layer of PDA coating via the self-polymerization of dopamine, and then PEI was conjugated with PDA coating through Michael addition reaction. The successful preparation of amine functionalized Kaolin was confirmed by a series of analyses. This prepared adsorbent was used to the removal of copper ions from waste water and the effect of contact time, pH, contact temperature, and initial concentration of copper ions were studied. The adsorption kinetics and thermodynamics of the adsorption process were also investigated.

## 2. Experimental procedure

### 2.1. Materials and methods

#### 2.1.1. Materials

Kaolin ($Al_2Si_2O_9H_4$) was purchased from Aladdin Industrial Co., Ltd. Polyethyleneimine (PEI) (molecular weight of 800 Da), copper nitrate trihydrate (>99.99%) and bis-(cyclohexanone)-oxalyldihydrazone (98.0%) used in this study were purchased from Aladdin Industrial Co., Shanghai, China. The dopamine hydrochloride (>98%) was purchased from Sangon Co. and tris-(hydroxymethyl)-aminoethane (Tris) (>99%) was purchased from Tianjin Heowns Biochem. LLC.Co.

#### 2.1.2. Preparation of Kaolin-PDA-PEI

The surface functionalization of Kaolin with amine groups was performed according to previous study [54]. Briefly, 500 mg Kaolin and 500 mg dopamine were dispersed into 100 mL alkaline buffer solution (10 mM Tris) in a flask. The mixture was constantly stirred at room temperature for 8 h. After that, the mixture was centrifuged under 8000 r/s for 5 min and washed 3 times with deionized water. The product (named as Kaolin-PDA) was obtained via dried under vacuum at 353 K. Then 500 mg Kaolin-PDA and 500 mg PEI were added into a flask with 100 mL 10 mM Tris buffer solution and