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# Kinetic and equilibrium studies of lead(II) adsorption from aqueous media by KIT-6 mesoporous silica functionalized with –COOH☆

## Études cinétiques et d'équilibre d'adsorption du plomb(II) en milieux aqueux sur une silice mésoporeuse KIT-6 fonctionnalisée par COOH

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ABSTRACT

An organic–inorganic hybrid mesoporous silica was synthesized via post-grafting of KIT-6 with 4-(triethoxysilyl)butyronitrile. All samples were characterized using their $N_2$ adsorption–desorption isotherms, XRD, FT–IR, TEM, SEM, and PT. The adsorption potential of this material for removing Pb(II) from aqueous solutions was investigated via the batch technique, and the effects of pH and contact time were studied. Experimental data showed that the maximum Pb(II) adsorption, 76%, occurred in the pH range around 6. The adsorption equilibrium was reached within 40 min for 10 wt.%COOH/KIT-6. The adsorption data were fitted using the Langmuir and Freundlich isotherms, and the obtained modeling equilibrium adsorption data suggested that the 10 wt.%COOH/KIT-6 sample contained homogeneous adsorption sites that fit the Langmuir adsorption model well. The pseudo-second-order model described well the 10 wt.%COOH/KIT-6 adsorption process. The desorption and regeneration experiments indicated that ≈95% of the metal desorbed and the adsorbent could be regenerated via an acid treatment without altering its properties.


RÉSUMÉ

Une silice mésoporeuse hybride organique–inorganique a été synthétisée par greffage du KIT-6 avec le 4-(triéthoxysilyl)butyronitrile. Les échantillons ont été caractérisés par BET, XRD, FT–IR, MET, MEB et TP. Le potentiel d'adsorption de la silice mésoporeuse pour éliminer Pb(II) à partir de solutions aqueuses a été étudié par la technique de traitement par lots. Les effets du pH et du temps de contact ont aussi été analysés. Les données expérimentales montrent que l'adsorption maximale de Pb(II) est de 76 % et a lieu dans une plage de pH entre 5 et 6. L'équilibre d'adsorption a été atteint en 40 minutes pour le 10 wt.%COOH/KIT-6. Les

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données d'adsorption ont été analysées à l'aide des isothermes de Langmuir et de Freundlich. Les données obtenues par la modélisation ont suggéré que l'échantillon 10 wt.%COOH/KIT-6 contenait des sites d'adsorption homogènes qui correspondent mieux au modèle d'adsorption de Langmuir. Le modèle de pseudo-second-ordre décrit mieux le processus d'adsorption du 10 wt.%COOH/KIT-6. Les expériences de désorption et de régénération ont indiqué qu'environ 95 % des métaux sont désorbés et l'adsorbant 10 wt.%COOH/KIT-6 peut être régénéré par un traitement à l'acide, sans modifier ses propriétés.



## 1. Introduction

Environmental pollution is a planetary problem that still threatens human health and ecosystems worldwide [1–4]. Current rigorous regulations have made global environmental pollution (air, soil, water) a major worldwide problem [5–8]. Over the years, scientists have researched a solution to decrease or eliminate the impact of environmental pollution [9–14]. Potable water is essential for human existence and the ecosystem, and has been widely studied [15–24]. Heavy metals are a major pollutant of wastewaters; they primarily originate from anthropogenic activities and have become a major environmental issue due to their toxicity. Heavy metals are not biodegradable and tend to accumulate in living organisms [25–28]. Many heavy metal ions are known to be toxic or carcinogenic. Among the metals that are hazardous to the environment, lead is considered very toxic. High levels of lead can be traced to industrial discharges from a variety of sources, such as batteries, cables, plastics, paints, and the glass industry. Lead contamination also occurs from vehicular traffic effluents. Although inorganic lead is a general metabolic poison and enzyme inhibitor, its organic forms are even more poisonous [29]. Acute lead poisoning has been known to affect the gastrointestinal tract, nervous system or both. Lead can damage the central nervous system. It can also damage the kidney, liver, reproductive system, basic cellular processes and brain function. The toxic symptoms include anemia, insomnia, headache, dizziness, irritability, muscular weakness, hallucinations and renal failure [30]. Therefore, industrial effluents with high lead content must be treated before being released into the environment. Eliminating such metal ions from water and wastewater has become a challenge for researchers. Various techniques have been used to remove metal ions from aqueous solutions, such as ion exchange, reverse osmosis, membrane filtration, evaporative recovery, phytoextraction, precipitation, conventional coagulation, precipitation, sedimentation, electrodialysis, electrochemical treatments and adsorption [31–34]. However, adsorption is considered more appropriate for removing heavy metals. The adsorption process offers a flexible design and operation and generally yields high-quality treated effluents. In addition, because adsorption is sometimes reversible, the adsorbents can be regenerated via suitable desorption processes. Various adsorbents have been used to remove heavy metals from aqueous solutions [35–42]. The demand to develop novel, high-efficiency adsorbents to remove heavy metal ions from aqueous media is growing. The discovery of siliceous mesoporous materials started a new era in the chemistry of porous solids and renewed the interest in designing heavy metal adsorbents. These mesoporous materials exhibit unique properties, such as uniform pore diameter, large specific surface area, large pore volume, highly ordered pore arrangement, good mechanical and thermal stabilities and free surface silanol groups [43], for versatile applications.

Currently, different mesoporous materials are tested for various possible applications: heterogeneous catalysis [44–48], electrochemical battery components/electrode materials [49,50], heavy metal adsorption [51–54], analytical chemistry [55], and the immobilization of enzymes and of other biologically active molecules [56,57].

Furthermore, one of mesoporous silica's most important properties is its potential to modify its chemical surface to incorporate organic functional groups. Adding organic groups by grafting organosiloxane precursors to the pore surface yields functional mesoporous hybrid materials with improved thermal, mechanical, and chemical stabilities.

Mesoporous hybrid materials also show promise as adsorbents for removing heavy metals from aqueous solutions. These hybrid compounds are classified into two categories: (i) those held together via weak forces, such as van der Waals forces, hydrogen bonding, electrostatic (London) and p–p interactions and (ii) those with covalent bonds between the organic and inorganic parts and functional groups inserted onto the porous silica framework. Functional chemical groups on the porous surface are most often amino, mercapto, or carboxylic groups obtained via either co-condensation or post-grafting. Several studies reported the use of mercapto and amino groups; however, only a few articles have studied carboxylic groups [58–61].

According to a bibliographic survey, there has been no study on the Pb(II) adsorption to COOH/KIT-6. Therefore, this work investigated the adsorption of Pb(II) by COOH/KIT-6 from an aqueous solution. During the co-condensation process, the functional groups can destabilize the solid mesoporous framework [62] and, in this case, our work grafted the carboxylic groups by covalently linking free and geminal silanol groups on the surface of the KIT-6 support. Adsorption is a very complex process, and its characteristics were evaluated as a function of the process variables such as pH, contact time, and temperature. Equilibrium data were examined using the Langmuir and Freundlich isotherm models.

## 2. Experimental

### 2.1. Materials

All chemicals used in this study were of analytical grade. Polyethylene oxide–polypropylene oxide–polyethylene