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Layer-by-layer strategy for adsorption capacity fattening of endophytic bacterial biomass for highly effective removal of heavy metals

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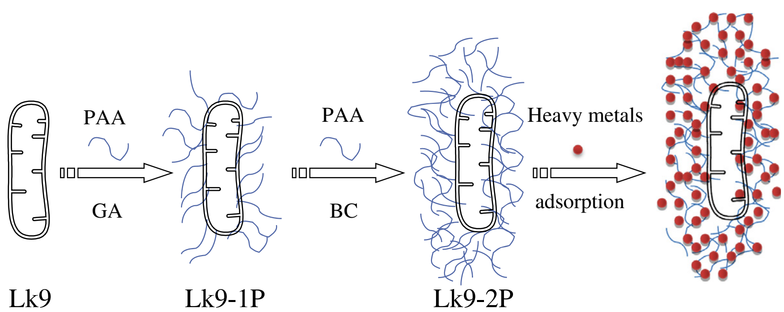
HIGHLIGHTS

- Sharp fattening of function groups on bacterial biomass by layer-by-layer method.
- The biosorbent exhibited high adsorption capacities toward heavy metals.
- The sorption can be conducted in pH 3–6 and equilibrium fast reached in 45 min.
- The biosorbent showed a good recyclability.
- The biosorbent can effectively treat practical industrial effluent.

GRAPHICAL ABSTRACT

A new biosorbent with high adsorption capacity towards heavy metals was constructed by modifying endophytic bacterial biomass through layer by layer fattening strategy.



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ABSTRACT

In this study, the layer-by-layer fattening of functional groups on the surface of endophytic bacterial biomass of *Pseudomonas* sp. Lk9 was achieved by stepwise grafting polyallylamine (PAA). The presence of the PAA layer on the biomass surface was confirmed by FTIR, X-ray photoelectron spectroscopy (XPS), and elemental analysis. The PAA modification drastically enhanced the adsorption capacity of biomass LK9 toward heavy metals. In contrast, the PAA bilayer-modified Lk9 (Lk9-2P) showed the highest uptake capacity and presented high uptake capacities for Cd^{2+} and Cu^{2+}. The adsorption could be conducted in a wide pH range of 3–6 and the equilibrium fast reached in 45 min. The results of XPS and FTIR analysis reflected that the binding of heavy metals on the biosorbents occurred mainly through coordination. Recyclability test revealed that Lk9-2P remained stable and high sorption capacity after five successive cycles. More importantly, the application of Lk9-2P to practical industrial effluent demonstrated that the new biosorbent could effectively treat practical wastewater with all the heavy metals brought down to lower than 0.001 mg/L. This study shows that the layer-by-layer fattening strategy is very effective for the development of high performance adsorbents for the removal of heavy metal ions from wastewater.

1. Introduction

Water pollution by heavy metals due to the indiscriminate disposal of wastewater from industries such as metallurgical and chemical manufacturing, mining, and battery, has risen a worldwide environment concern [1–3], and due to its high toxicity to living organisms [3,4], insusceptibility [5] and non-biodegradable [4], it is very urgent to seek effective methods to remove heavy metals from wastewater.

There are various traditional techniques for the treatment of heavy metal pollution, including reduction, chemical precipitation, membrane filtration, ion exchange, electrochemical treatment,

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evaporation, etc [1,6]. However, these methods are deemed extremely expensive, not environment-friendly and ineffective in the case of metal concentrations less than 100 mg/L [6,7]. Adsorption, however, is highly recommended for removing low concentrations of heavy metals, appropriate for batch and continuous processes, ease of operation, and the adsorbent can be easily regenerated and reused [8,9]. But traditional adsorption on activated carbon is ineffective either at a low concentration of 1–100 mg/L or higher concentration. Moreover, it also produces toxic sludge which is quite difficult to treat [7]. Biosorbents, because of their abundant in nature or widely derived from agricultural or industrial wastes and the high efficiency in treating waste water, have been considered to have enormous commercial potential and application feasibility [10]. Most of the biosorbents have a certain sorption capacity for heavy metals, because there are many functional groups such as carboxyl, phosphonate, amine and hydroxyl groups on the cell wall of the biosorbents. However, the concentration of effective functional groups for binding heavy metals is usually low, which extremely limit the sorption capacities of natural biosorbents [11].

Recently, interest has been focused on increasing the sorption capacity of biosorbents via grafting polymers with a large amount of functional groups onto the surface of biomasses. However, because of the limited amount of functional groups on the surfaces of raw adsorbents, this simple cross-linking modification did not endow biosorbents high sorption performance. How to enhance the sorption capacity of biomasses is still a challenge. Layer-by-layer grafting is a very effective strategy to greatly increase the function groups on the surface of many materials, which has been widely used in many fields [12–15], but the technology has not been employed in the modification of adsorbents for wastewater treatment yet.

Bacterial endophytes from heavy metal hyperaccumulators, which can endure high concentrations of a certain heavy metal, might have a special cell wall containing special functional groups because of their special growing environment, and are expected to be promising biosorbents [16,17]. It has been found that the groups containing nitrogen-based ligands (such as amino, amidoxime, imidazole, and hydrazine groups) were effective in forming complexes with metal ions [4]. Polyallylamine (PAA) possesses a handsome amount of primary amine groups in its molecules, which endows it strong sorption ability for heavy metals. When it is linked onto the surfaces of adsorbents, the modified adsorbents are expected to have enhanced sorption capacities. In this study, a bacterial endophyte, *Pseudomonas* sp. Lk9, which had been isolated from Cd-hyperaccumulator *Solanum nigrum* L., was modified through the multilevel grafting of PAA to achieve layer-by-layer fattening of functional groups (Scheme 1). To the best of our knowledge, for the first time the method of layer-by-layer fattening of functional groups was applied to modify biomass for enhancing the adsorption capacity of biosorbents. Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and elemental analysis, scanning electron microscopy (SEM), and zeta potential measurement were used to characterize the new adsorbents, the sorption performance (especially the sorption capacity) of the adsorbents were investigated in detail, and the mechanisms involved in adsorption were also elucidated.

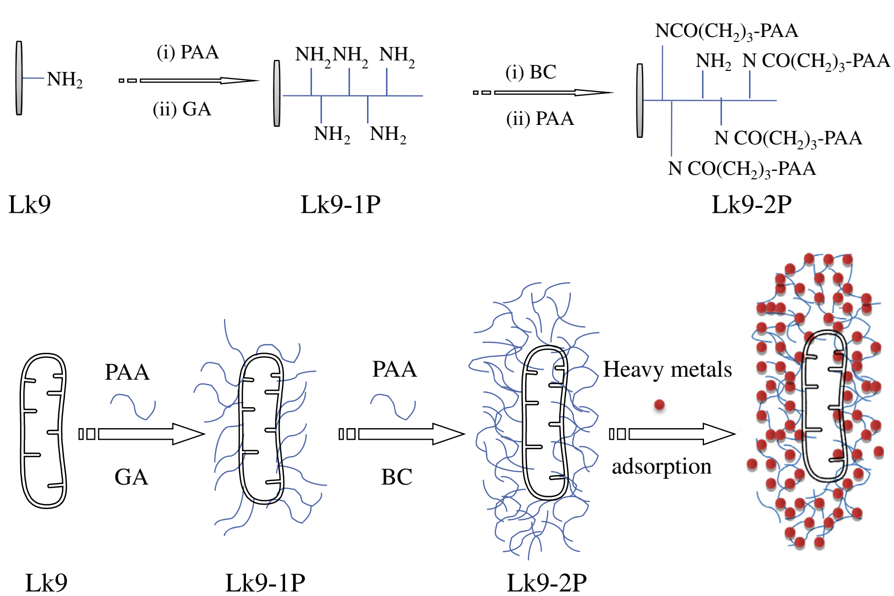
2. Materials and methods

2.1. Materials

The heavy metal-tolerant endophytic bacterial strain, *Pseudomonas* sp. Lk9 (GenBank accession no.: KC802085; CCTCC M2012302), was isolated from a Cd-hyperaccumulator, *Solanum nigrum* L., which was collected in Shuikoushan mine tailings, Hengyang, Hunan province, China. The isolation process of the endophytic bacterium was conducted according to our previous work [18]. The *Pseudomonas* sp. Lk9 was cultivated at 30 °C in LB broth medium, harvested and at last lyophilized. The obtained biomass was hereafter in this study called as raw Lk9. The poly(allylamine hydrochloride) (PAA, molecular weight 58,000) was purchased from Sigma-Aldrich, USA. Glutaraldehyde (GA, 25%). 4-Bromobutyryl chloride (BC), $PbSO_4$, $CuSO_4$, $CdSO_4$ and other chemicals were used as received.

2.2. Surface modification

The modification of raw Lk9 was conducted by the following processes: the first PAA layer was grafted to the surface of raw Lk9 using GA as cross linking agent to get PAA monolayer-modified Lk9 (Lk9-1P). Then, Lk9-1P was activated by BC to further graft PAA



Scheme 1. Schematic diagram of Lk9 modification.