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Bioremediation of Waste Water from Cadmium Pollution using Silicon Dioxide Nanoparticles and Fungal Biomasses

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Abstract

The aim of this paper was cadmium removal from waste water using SiO_2 nanoparticles and fungal biomasses. Five treatments were used for cadmium removal. They were inactivated mycelia of *Cladosporium sphaerospermum* (CLA) and *Fusarium oxysporum* (FUS), SiO_2 nanoparticles (N-Si) and their combinations (N-Si-CLA and N-Si-FUS). The biosorbents natures and combinations were examined by Fourier Transform Infrared (FT-IR) and Scanning Electron Microscope (SEM) where close attachments between combined biosorbents were detected. Different factors affecting cadmium biosorption capacity were tested. It was found that (N-Si-CLA) and (N-Si-FUS) were the most potent biosorbents at pH 7. Thirty minutes contact time exerted maximum sorption capacity. Initial cadmium concentration was optimum at 0.5 mol^{-1} for highest biosorption capacity. Ca^{2+} displayed synergistic interfering more than Na^+ and K^+, respectively. Two real waste water samples collected from two factories were tested to depollute cadmium using the five sorbents. (N-Si-CLA) and (N-Si-FUS) were the most potent adsorbents, where 65.73 % and 54.30% removed in the first sample and 61.33 % and 56.50 % in the second one, respectively. From the results, it was concluded that bioremediation of cadmium from waste water was possible by using SiO_2 nanoparticles and fungal biomasses with high efficiency of their combinations.

Keywords: Silicon dioxide nanoparticles, Waste water, Cadmium pollution, Bioremediation, Heat inactivated fungal biomasses, Immobilization.

INTRODUCTION

In aquatic environment, heavy metals are reported as the main inorganic pollutant even if they present at small concentrations because they can lead to a significant risk to public health and environment due to their non-biodegradability, poisonousness, carcinogenicity and subsequent bio-magnifications[1,2]. Heavy metal such as Pb, Hg, Cd, Cu, Cr, As and Zn are serious pollutants to human health.

Cadmium has many toxic effects on microorganisms and can denature protein, destruct nucleic acid, prevent cell division and transcription and inhibit nitrogen and carbon mineralization. However arsenic metal can cause cancer; mercury metal can cause genetic damage and mutations, while lead, mercury and copper metals can cause bone and brain damage[3].

Because of high mobility of cadmium in the environment, it can be considered as one of the highest toxic element[4]. It can also lead to bone degeneration, renal dysfunction, hypertension, liver damage and lung insufficiency in humans[5]. The United Kingdom Red List Substances[6] has been recorded cadmium as dangerous metal in the environment. Furthermore, the US Environmental Protection Agency[7] has categorized cadmium ions as group B1 carcinogen. Waste water produced from industry, mining plants, alloys, fertilizers, batteries and plastic manufacturing were considered as the main sources of cadmium pollution. Incineration of municipal wastes and fossil fuels are the major sources of cadmium in the air. Another serious origin of cadmium exposure is smoking[5]. Agency for Toxic Substances and Disease Registry ATSDR[8] claimed that smokers have in their bodies about twice cadmium amount than do nonsmokers. They also reported that Cadmium has acute (short-term) effects on human lungs through inhalation exposure, such as pulmonary irritation. Chronic oral exposure to cadmium or inhalation causes kidney disease due to accumulation of cadmium in the kidneys. Animal studies provide evidence that oral exposure and inhalation of cadmium has adverse progressive effects, such as small fetal weight, skeletal abnormalities, interference with fetal metabolism, poor neurological development and some reproductive effects, such as testicular damage and decreased reproduction[8,9,10].

Heavy metals exist in waste waters have severe effects on biological systems. These elements do not decompose and tend to bio-magnify in human by food chain. Hence, there is a necessity to eliminate heavy metals from the aquatic ecosystem[11]. Removal of heavy metals from waste water mainly done by the osmosis of solution, the precipitated ability of metals and chromatographic exchange of ions. All these techniques are expensive especially at low metal concentrations and generally non selective and inefficient[12,13]. So, bioremediation of heavy metals from polluted environments through microbial biosorption uptake is considered as a save efficient technique.

Biosorption process is defined as an interaction between metal ion and binding sites of biomass through numerous mechanisms comprising ion exchange, complexation, and electrostatic attraction[14,15]. Biosorption by employing non-living microbial biomass was more effective and favorable for elimination and remediation of heavy metals from aqueous media[15,16,17,18,19]. Various adsorbents such as silica gel, graphite oxide and activated carbon can be used in the purification of water from pollutants[20,21].

Nanomaterial has several applications, such as technological and environmental solar energy conversion, medicine, catalysis and water treatments[22,23]. Numerous studies have considered nano-particles, especially metal oxides, as effective adsorbents in the cleanup of environmental contaminants, because nanoparticles can penetrate into the contamination zone where micro-particles cannot.

Moreover, Immobilized cells are commonly easier to handle because they need less complex separation systems, permit a great biomass density to be kept and offer more chance for reuse and recovery. The entrapment of non-living microbial cells on synthetic or natural polymers improved the performance and biosorptive capacity and increasing the life time of these biosorbents for regeneration and re-cycling numerous times[24,25,26,27].

Through the present decade, immobilized fungal cells pay an attention in bioremediation of heavy metals such as cadmium from waste

water[15]. The applications of immobile fungi for cadmium removal from aqueous solution were studied under the effects of contact time, initial concentration, pH, agitation rate and temperature[28]. Microbial immobilization was achieved by differed techniques and polymers, for example, usage of calcium alginate and entrapment by different matrices. These immobile cells proved to have high biosorption capacity toward waste water pollutants with toxic metals such as Mn^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, Fe^{3+}, Cd^{2+} and $Zn(II)$[29].

The aim of this study was the depollution of cadmium from waste water using silicon dioxide nanoparticles, heat inactivated fungal biomass and their combinations.

MATERIALS AND METHODS
Collection of waste water samples
Two waste water samples were collected in sterile bottles from General Motors Factory (S1) (6 October City, Egypt) and Egyptian Plastic and Electricity Factory (S2) (Cairo, Egypt).

Isolation of fungi from waste water samples
Fungi were isolated from waste water using pour plate method. Glucose peptone medium was used as an isolation medium. It composed of (g l^{-1}) 10.0 glucose; 0.5 $MgSO_4.7H_2O$; 1.0 KH_2PO_4; 5.0 peptone and 20.0 agar and pH of 6.7[30]. The inoculated Plates with one ml waste water were incubated at 30°C for 7 days. The growing fungi were counted and identified according to Moubasher[31].

Production of thermal inactivated fungal biomasses
Glucose peptone broth was used to grow the waste water fungal isolates; the inoculated cultures were incubated for 7 d at 30°C then centrifuged. The biomass washed using distilled water then dried in an oven at 80°C till constant weight to inactivate cells. The dried cells were grinded into powder and stored at 25°C in vacuum desiccators.

Preparation of thermal inactivated fungal biomass combined with silicon dioxide nanoparticles
Mixtures of silicon dioxide with either *Cladosporium sphaerospermum* or *Fusarium oxysporum* were prepared as follows: 2.5 g of heat inactivated fungal biomass was mixed with dried nanopowdered of SiO_2 (10-20 nm BET) of the same weight and 5ml distilled water and left for 15 min. The mixture put in an oven at 80°C till constant weight. The process of mixing and drying was repeated successively for 5 times[32].

SEM and FT-IR examination of the combined mixtures
Scanning Electron Microscope (SEM) (JEOL-JSM-5600LV-Japan) was used for studying the morphology and nature of the surface and for description of heat inactivated fungal biomass before and after combination with silicon dioxide nanoparticles. This combination was also emphasized by Fourier Transform Infrared (FT-IR) spectra by using SHIMADZU FT-IR Spectrophotometer (FT-IR 4100- JASCO-japan).

Factors affecting biosorption capacity of cadmium from aqueous solution
Effect of pH on Cd(II) sorption capacity were investigated using 15 mg of the dry solid sorbent either SiO_2 nanoparticles (N-Si), *Cladosporium sphaerospermum* (CLA), *Fusarium oxysporum* (FUS), or their combinations (N-Si-CLA) and (N-Si-FUS) with one ml of 0.1 M Cd^{2+} solution and add nine ml of buffer solutions to adjust different pHs at 3.0, 5.0 and 7.0. These sorption mixtures were kept under shaking for 30 min, filtered and washed with 30 ml distilled water[32]. Complexmetric titration process against 0.01 M EDTA was done to determine the residual Cd^{2+} in the filtrate. Triplicate titrations were done for each experiment. The sorption capacity (q) was calculated as follow:

$$q = (C_o - C) V \times 10^3 / m$$

Where, q (μmol g^{-1}) is the amount of cadmium adsorbed per gram of sorbent, C_o (mol l^{-1}) initial Cd^{2+} concentration, C (mol l^{-1}) final residual Cd^{2+} concentration, V (ml) volume of the sorption mixture and m (g) biomass of sorbent.

Another factors that affect Cd(II) sorption capacity were also studied. The effect of contact time between sorbents was investigated at different periods (10, 20, 30 min) under shaking, the effect of initial Cd(II) concentration was studied (0.025, 0.1, 0.5 mol^{-1}) and the effect of metal interference on Cd(II) sorption capacity was investigated using different metals such as Na^+, Ca^{2+} and K^+, in equimolar concentration. In all experiments, the residual Cd^{2+} concentrations in filtrate was determined using EDTA titration and

Cd(II) sorption capacities were calculated from the previous equation. Each experiment was done in triplicates and results given are the mean values.

Cadmium bioremediation from real waste water samples

Two samples of waste water (item 2.1) were analyzed for determination of cadmium concentration by the atomic absorption spectrophotometer (JASCO V-630- Japan). The previously mentioned sorption experiment procedure was carried out at 0.0006 mol l⁻¹ and

0.00152 mol l⁻¹ as initial cadmium concentration and at the optimum condition of pH, contact time and sorbent dosage. The cadmium sorption capacity after sorption process was determined by EDTA titration.

RESULTS
Isolation of fungi from waste water samples

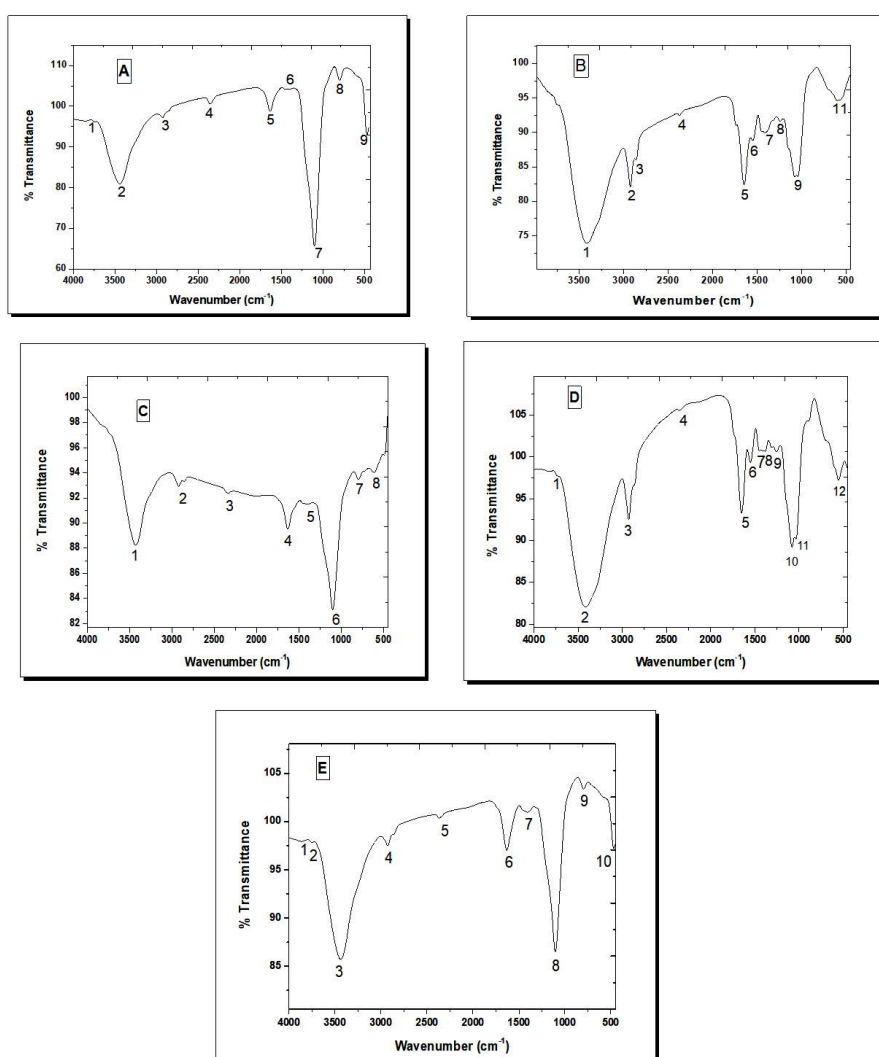Only two fungal species were detected in the two waste water samples. These tolerant

Fig. 1. FT-IR spectra. (A) Silicon dioxide nanoparticles (N-Si), (B) Heat inactivated *Cladosporium sphaerospermum* (CLA), (C) Silicon dioxide nanoparticles combined with heat inactivated *C. sphaerospermum* (N⁻Si⁻CLA), (D) Heat inactivated *Fusarium oxysporum* (FUS) and (E) Silicon dioxide nanoparticles combined with heat inactivated *F. oxysporum* (N⁻Si⁻FUS)

species were *Cladosporium sphaerospermum* and *Fusarium oxysporum*.

FTIR and SEM examination of the biosorbents

The ability of heat inactivated fungal mycelium to be adsorbed on the surface of SiO_2 nanoparticles were confirmed by FT-IR and SEM.

Many bands were appeared when SiO_2 particles were studied by FT-IR (Fig 1A). The examinations of fungi by FT-IR were characterized by several peaks as shown in Fig 1 (B and D). The several peaks of silicon dioxide nano particles combined with heat inactivated fungi were displayed in Fig 1 (C and E).
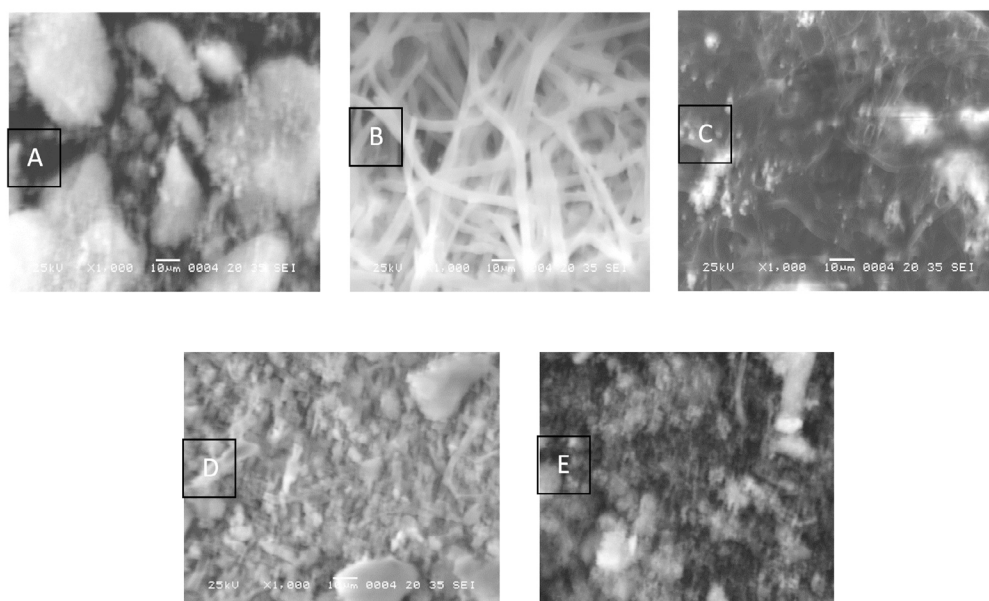

Fig. 2. SEM images of various sorbents at magnification of 1000 x. (A) Silicon dioxide nanoparticles (N-Si)*,* (B) Heat inactivated *Cladosporium sphaerospermum* (CLA), (C) Heat inactivated *Fusarium oxysporum* (FUS)*,* (D) Silicon dioxide nanoparticles combined with heat inactivated *Cladosporium sphaerospermum (*N-Si-CLA) and (E) Silicon dioxide nanoparticles combined with heat inactivated *Fusarium oxysporum* (N-Si-FUS)
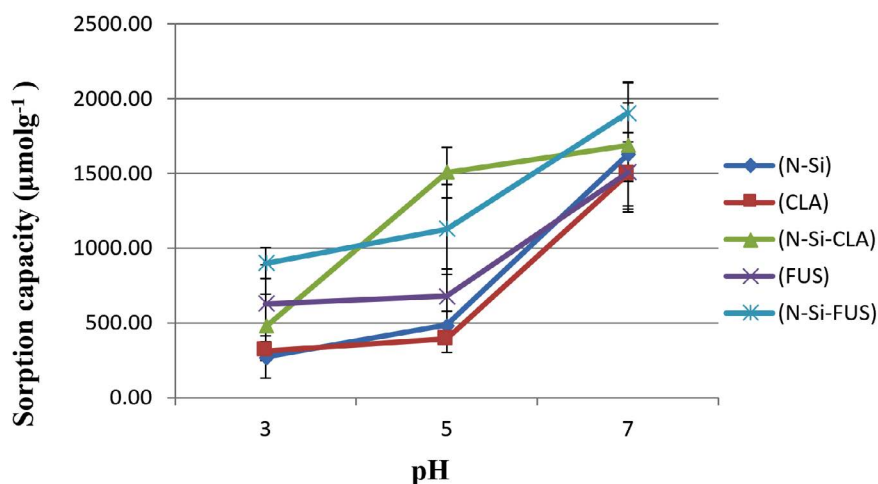

Fig. 3. Effect of pH on cadmium (II) sorption capacity. (♦) Silicon dioxide nanoparticles (N-Si), (■) Heat inactivated *Cladosporium sphaerospermum* (CLA), (▲) Silicon dioxide nanoparticles combined with heat inactivated *Cladosporium sphaerospermum (*N-Si-CLA), (X) Heat inactivated *Fusarium oxysporum* (FUS) and (Ж) Silicon dioxide nanoparticles combined with heat inactivated *Fusarium oxysporum* (N-Si-FUS)

Surfaces of silicon dioxide nanoparticles and heat inactivated fungi were examined using SEM (Fig 2). Silicon dioxide nanoparticles were clearly showed as regular and homogenous particles distributed in uniform shapes (Fig 2A). Combinations of sorbents were showed in Fig 2D and E.
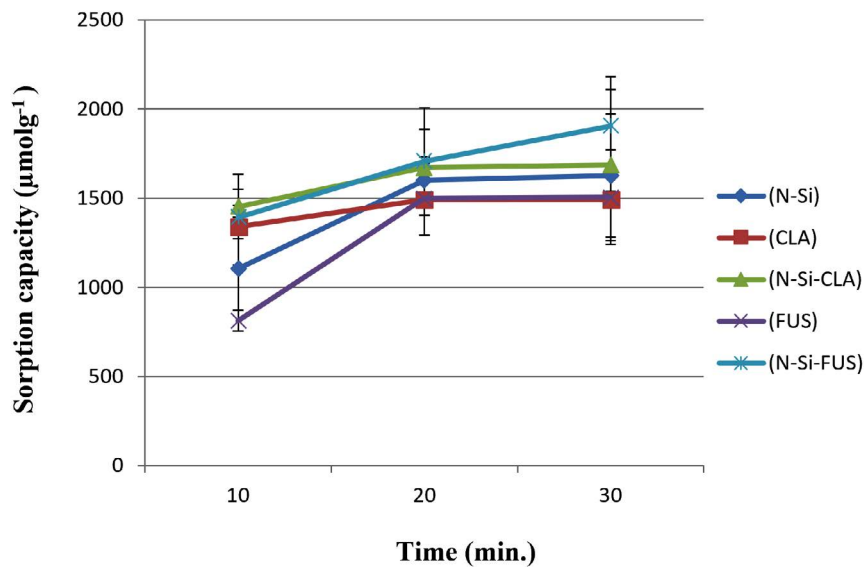

Fig. 4. Effect of contact time on cadmium (II) sorption capacity by different sorbents. (♦) Silicon dioxide nanoparticles (N-Si), (■) Heat inactivated *Cladosporium sphaerospermum* (CLA), (▲) Silicon dioxide nanoparticles combined with heat inactivated *Cladosporium sphaerospermum (*N-Si-CLA), (X) Heat inactivated *Fusarium oxysporum* (FUS) and (Ж) Silicon dioxide nanoparticles combined with heat inactivated *Fusarium oxysporum* (N-Si-FUS)
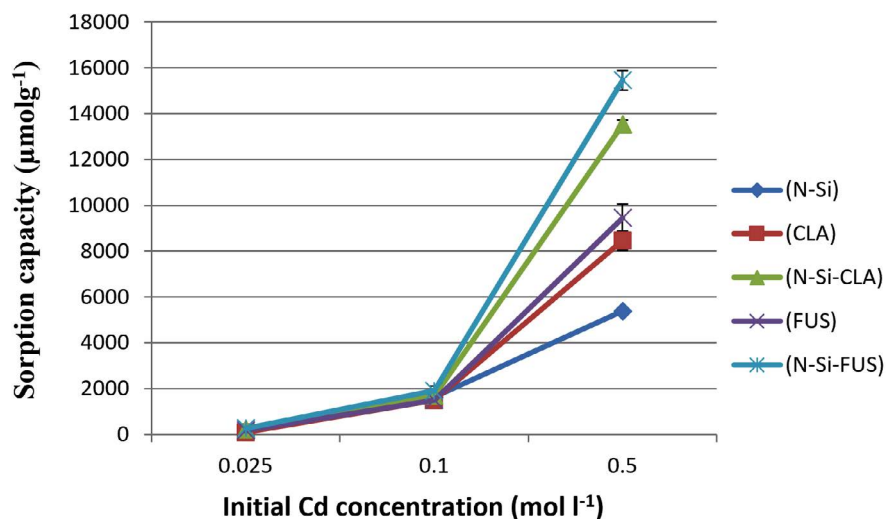

Fig. 5. Effect of initial cadmium concentration on cadmium (II) sorption capacity. (♦) Silicon dioxide nanoparticles (N-Si), (■) Heat inactivated *Cladosporium sphaerospermum* (CLA), (▲) Silicon dioxide nanoparticles combined with heat inactivated *Cladosporium sphaerospermum (*N-Si-CLA), (X) Heat inactivated *Fusarium oxysporum* (FUS) and (Ж) Silicon dioxide nanoparticles combined with heat inactivated *Fusarium oxysporum* (N-Si-FUS)

Factors affecting Cd(II) sorption capacity from aqueous solution

Effect of PH on biosorption of Cd(II)

The effect of pHs of contact solution on cadmium sorption capacity was studied in several solutions with pHs 3.0, 5.0 and 7.0 (Fig 3). The sorption capacity of Cd(II) recorded the lowest value at pH 3. Sorption was found to be gradually increased as the pHs were increased from 3-7.

Effect of contact period on biosorption of Cd(II)

It was found that as the contact time of shaking increased from 10 to 30 min, the contact between Cd(II) and all tested sorbents (N-Si), (CLA),(FUS),(N-Si-CLA) and (N-Si- FUS) was enhanced (Fig 4).

Effect of initial Cd concentration on cadmium sorption capacity

The sorption capacity of Cd(II) increased as the initial concentration of it has been increased in all sorbents used (Fig 5).

Effect of interference between ions on cadmium sorption capacity

Addition of different salts (NaCl, KCl and $CaCl_2$) to Cd(II) aqueous solution indicated that Ca^{2+} displayed synergistic interfering capability in cadmium ion sorption process comparing to Na^+ and K^+ (Fig 6).
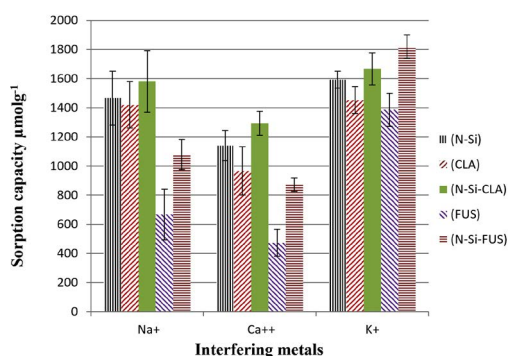

Fig. 6. Effect of metals interference on cadmium (II) sorption capacity. (▥) Silicon dioxide nanoparticles (N-Si), (▨) Heat inactivated *Cladosporium sphaerospermum* (CLA), (■) Silicon dioxide nanoparticles combined with heat inactivated *Cladosporium sphaerospermum (*N-Si-CLA), (▢) Heat inactivated *Fusarium oxysporum* (FUS) and (▤) Silicon dioxide nanoparticles combined with heat inactivated *Fusarium oxysporum* (N-Si-FUS)

Bioremediation of cadmium from real waste water samples

Two waste water samples collected from different factories were amended with different sorbents to study their efficiency in biosorption of Cd(II) (Fig 7). Generally, the sorption capacity of the combined mixtures (N-Si-CLA and N-Si-FUS) achieved higher value than single treatments (N-Si, CLA and FUS). In the first sample, (N-Si-CLA) and (N-Si-FUS) removed 65.73 % and 54.30% of cadmium, respectively, while 61.33 % and 56.50 % were removed in the second one. The combination mixture of N-Si-CLA proved to be the most potent sorbent for cadmium removal from the two real waste water samples.
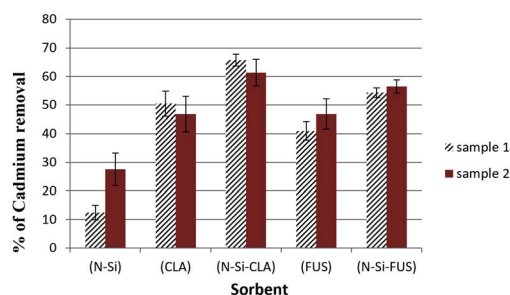

Fig. 7. Application of silicon dioxide nanoparticles (N-Si), heat inactivated *Cladosporium sphaerospermum* (CLA), silicon dioxide nanoparticles combined with heat inactivated *Cladosporium sphaerospermum (*N-Si-CLA), heat inactivated *Fusarium oxysporum* (FUS) and silicon dioxide nanoparticles combined with heat inactivated *Fusarium oxysporum* (N-Si-FUS) for cadmium removal from real waste water. (▨) Sample 1 and (■) Sample 2

DISCUSSION

Few fungal species were isolated from waste water samples. Fungal and bacterial growths were inhibited as a result of the toxic effect of the higher concentration of heavy metals in the tested water samples[33, 34]. Although some heavy metals play remarkable roles in physiological, biochemical and metabolic process of living organisms, functioning as co-factors for some enzymes, stability of molecules and regulators of osmotic pressure, most of them has no known biological function in living organisms and are toxic when present in excess[35].

In examination of SiO_2 particles by FT-IR (Fig 1), bands at 950 cm^{-1} (peak 8) and 1090 cm^{-1} (peak 7) were due to Si-OH and Si-O-Si, respectively (these bands very intense for formation of SiO_2 network)[36]. Absorption band at 3600 cm^{-1}(peak 1) was corresponding to fundamental vibration stretching of different (OH) groups and combination of silicon dioxide located at 1640 cm^{-1}.

By FT-IR observation of fungi, NH_2 was found at 3418 cm^{-1}(peaks 1 and 2 in Fig 1B and D, respectively); CH was found at 2940 cm^{-1} (peaks 2 and 3 in Fig 1B and D, respectively), Phosphate group was found at 1040 cm^{-1}, (peaks 9 and 10 in Fig 1B and D, respectively) and CO bind NH to form amide linkage (peak 6) found at 1640cm^{-1} .[37]

Fig 1 (C and E) revealed that the peaks specific for individual sorbents were mostly similar to combined (N-Si-CLA) and (N-Si-FUS).

At pH 7, (N-Si) practically achieved higher biosorption capacity than heat inactivated fungal cells of (CLA) and (FUS). This may be due to the presence of silanol group, the large surface area and great porosity expanded to larger number of nanoparticles. The improvement of biosorption capacity of the fungal biosorbents upon combination and immobilization on the surface of silicon dioxide nanoparticles may be due to increasing the surface area of biosorbent subjected to binding with metal ions. Also, the reduction of biosorption at low pH may be due to the increasing of H$^+$ ions which bind to the active binding sites causing Cd(II) sorption inhibition[13,38,39]. Moreover, Saglam *et al.*[40] reported that glycoprotein contain phosphate which display negative charges at pH 3 so it affected biosorption significantly. Gadd and White[41] found that chitin and other proteins on fungal cell wall containing many carboxyl groups.

Rates of adsorption of heavy metal ions via several biosorbents have displayed a broad range of adsorption time. For example, polyvinyl alcohol-yeast and alginate-yeast biosorbent systems used for copper biosorption kinetic studies of 12-h and 24-h equilibrium time have been displayed, respectively[42]. The equilibrium time of biosorption of chromium(IV) on the inactivated and immobilized biomass of *Rhizopus arrhizus* was 2 h[43].

The cadmium biosorption high rates were noticed during the first 48 h by green micro algae[44]. The biosorption rate of lead on *Phanerochaete chrysosporium* is rapid and attained saturation during 1 h[45]. The equilibrium time of lead biosorption on *Aspergillus niger* biomass was 5 h[38]. Cadmium biosorption onto pre-treated biomass of marine alga *Durvillaea potatorum* was so rapid, 90% uptake occurred during 30 min[46].

Many parameters detect the biosorption rate such as, amount of sorbent, aqueous phase stirring rate, structural properties of biosorbent and support, properties of ion under test, initial ion concentration and presence of other interfering metal ions for the active biosorption sites. So, it is very hard to compare the rates of biosorption reported[47,48].

There is wide range of sorption capacity of Cd(II) proportional to initial concentration; for example biosorption capacity by dead *Fusarium flocciferum* increased with initial concentration[49].

Different factors controlling the degree affinities of mixed interfering ions on the competitive capacity of sorption such as type of functional groups of microbial cell walls, the kind of charge on ions and the ionic radii[19,50].

CONCLUSION

The present study displayed that all tested sorbents were able to remove Cd(II) from waste water. Combined sorbents treatments (N-Si-CLA and N-Si-FUS) were proved to be more efficient in Cd(II) removal from waste water than used singly.

ACKNOWLEDGMENTS

CONFLICT OF INTEREST

The authors declares that there is no conflict of interest

AUTHORS' CONTRIBUTIONS

All authors have made substantial contribution to the work and approved it for publication.

FUNDING

None.

DATA AVAILABILITY

All datasets generated or analyzed during this study are included in the manuscript and/or the Supplementary Files.

ETHICS STATEMENT

Not aplicable.

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