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Dry *Trichoderma* biomass: biosorption behavior for the treatment of toxic heavy metal ions

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ABSTRACT

The dried biomass of *Trichoderma* sp. was investigated to remove toxic heavy metal ions using the batch method in the concentration range of 0.5 to 2.0 mg/L at different pH. The biosorption capacity of *Trichoderma* biomass was found to be pH dependent. Biosorption of nickel at pH 10 was observed 20% higher than at pH 2. The maximum sorption (91%) for Cd(II) was achieved (0.45 mg cadmium/g biomass) at pH 10 within 72 h equilibrium time. The maximum sorption capacity of Cr(VI) was achieved (0.053 mg chromium/g biomass) upon equilibration after 72 h. In comparison with nickel and cadmium, the biosorption of chromium was found to be pH independent, while nickel and cadmium showed a higher absorption capacity at higher pH. In addition, Freundlich and Langmuir adsorption isotherms were used to verify the biosorption performance of *Trichoderma* biomass. Langmuir adsorption isotherm was found to be fit better than Freundlich adsorption isotherm. The dried biomass of *Trichoderma* has been fruitfully applied for the removal and recovery of Ni (II), Cd(II), and Cr(VI) ions. Thus, it can be successfully used for the treatment of toxic heavy metal ions from the industrial effluents as well as natural waters.

Keywords: Biosorption; Freundlich adsorption isotherm; Langmuir adsorption isotherm; FAAS; Removal of metal ions

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1. Introduction

Treatment of industrial effluents for the removal and recovery of toxic heavy metal ions generally includes precipitation [1], coagulation [2], ion-exchange [3–12], membrane processes [12], and solid-phase extraction [13]. These methods have become quite common and found to be more expensive when effluents are treated in high volume and variable concentration of metal ions. So, an alternative cost-effective approach was applied, which circumvents the use of physical–chemical technique (i.e. Biological treatment using a variety of biomass). Because, the

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biomass have been established as one of the alternative processes for the absorption of heavy metal that can be obtained inexpensively or commercially [14–17]. One of the most important feature of biomass is that it can be easily isolated from environment without any unwell effect [18,19]. Treatment of heavy metal ions from aqueous solution using biomaterials such as bacteria, fungi, yeast, and algae is playing an important role owing to their great performance, low cost, and availability [20,21]. The use of *Trichoderma* fungi as biosorbent has added inherent advantage like other fungi due its massive mycelia network that provides a large surface area for the adsorption of metal ions.

These Fungi rapidly grow and its biomass can be easily harnessed as biosorbents. In addition, biosorbents possess multifunctional sites that include carboxyl, imidazole, sulfydryl, amino, phosphate, sulfate, thioether, phenol, carbonyl, amide, and hydroxyl moieties. These functional groups provide metal-sequestering property to the biosorbents which can markedly remove heavy metal ions in the solution. The dissolved metal ions are sequestered out of dilute complex solutions with high propensity and swiftness therefore, making it an ideal method for the treatment of large volumes of industrial effluents. These biomaterials can be converted to biosorbent in its live form as well as dried biomass. Biosorption of metal ions occurs via a conventional adsorption process which involves the reaction mechanism that is predominantly based on chemisorption [22]. This process also demonstrates the interactions between metal ions and functional groups of the cell wall (biopolymers of living and dead organisms) [23–27]. The soil contamination by cadmium was remedied using a combined system of *Trichoderma koningii* and rapeseed (*Brassica napus*) [28]. Biosorption lies in the fundamental ability of biological system to accumulate heavy metal ions from waste streams through the metabolic activity of the live or passive dead cells [29]. Another important aspect of biosorption of heavy metal ions does not only depend on the specific surface properties of the biomass, but also on the incubation temperature, pH, initial metal ion concentration, and biomass concentration as well as cultural conditions [30]. The well-established and simple foundation of biosorption process can be investigated using two widely accepted linear equilibrium (e.g. Langmuir and Freundlich isotherm). Both models are capable of describing the meaningful physical interpretation of the absorption process.

The most interesting theme of this paper is to investigate the biosorption behavior of *Trichoderma* sp. on liquid–solid phase for the removal and recovery of heavy metal ions. Therefore, a comparison was made about the applicability of Freundlich and Langmuir adsorption isotherms.

2. Materials and methods

2.1. Preparation of solutions

All reagents and chemicals were of analytical grade and used without any treatment. The salts of $Ni(NO_3)_2$, $Cd(NO_3)_2$, and $K_2Cr_2O_7$ were procured from Merck, Pvt. Ltd. (Malaysia). The solutions of Ni (II) (1 M), Cd(II) (1 M), and Cr(VI) (0.5 M) were prepared in demineralized water. To perform batch equilibrium adsorption experiments, all the solutions of metal ions were prepared in different pH range (2, 4, 6, 8, and 10).

2.2. Preparation of biomass

A mixture of *Trichoderma harzianum* and *T. viride* was cultured by adding them in a medium of 30% mixed vegetable liquid for 15 d at room temperature (27 ± 2˚C) using white light continuously shaken on an orbital shaker at 160 rpm. The fresh mycelia was harvested and it was dried for 48 h using the freeze dryer (Freeze dryer model: LABCONCO) and finely milled to 250 μm using grinder (IKA model A11 basic). A fixed amount (2.0 g) of dried biomass was used to perform the adsorption experiments. The flasks were kept on an orbital shaker throughout the biosorption process at 160 rpm (27 ± 2˚C). The aliquots of liquid were removed daily, centrifuged at 5,000 rpm for 3 min, and the supernatant was collected for the analysis using atomic absorption spectrophotometer (FAAS, model Perkin Elmer A. Analyst 200).

2.3. Bioadsorption studies

2.3.1. Freundlich and Langmuir isotherm models

Batch sorption studies were performed by shaking 2.0 g biomass of *Trichoderma* with each metal ions (Ni(II), Cd(II), and Cr(VI)) in the concentration range 0.5–2.0 mg/L by varying pH and time at 27 ± 2˚C using a temperature-controlled shaker. The solutions of different metal ions together with the biomass were stirred at 160 rpm. The pH of the solution was maintained within the solubility range of metal species: 2, 4, 6, and 8 for Cd(II); 3, 4, 5, 10, and 11 for Cr (VI); 1.5, 3, 4, 5, and 7 for Ni(II) ions, respectively. The pH was adjusted using 0.1 M NaOH and 0.1 M HCI solutions. At the end of predetermined time interval the reaction mixtures were filtered and analyzed for the determination of metal ion concentrations using FAAS. The adsorption experiments were also conducted to determine the equilibrium time, the optimum pH and initial concentration of metal ions (Ni(II), Cd(II), and Cr(IV)) for maximum sorption. The percentage of metal adsorption by the adsorbents was computed using the equation:

$$\%\ \text{adsorption} = \{(C_i - C_e)/C_i\}100 \tag{1}$$

The biosorption study includes the plot of the corresponding isotherms which were established under different experimental conditions by varying the concentrations of metal ions (Ni(II), Cd(II), and Cr(VI)) between 0.5 and 2.0 mg/L. The biosorption process was quantified using the corresponding equilibrium parameters derived from the two mathematical models:

Freundlich and Langmuir equation were applied to describe the isotherm:

Freundlich equation:

$$q_e = K_f(C_e)^{1/n} \tag{2}$$

where K_f and n are Freundlich constants and the Freundlich isotherms relationship is exponential. However, it can be linearized by plotting the data in log–log format to obtain the Freundlich constants and correlation coefficient (r^2). It is given as:

$$\log\ q_e = \log\ K_f + 1/n \log\ C_e \tag{3}$$

where C_e is the equilibrium for liquid phase ion concentration (mg/L) and q_e is the equilibrium solid phase ion concentration (mg/L). The Freundlich constant K_f (mg/g) and "n" represent the biosorption capacity and biosorption intensity of biosorbent, respectively, at fixed temperature and equilibrium.

Langmuir equation:

$$q = q_{\max}\frac{bC_f}{1 + C_f} \tag{4}$$

where $q_{\max}$ is the maximum sorbate uptake (mg/g) and can be interpreted as the total number of binding sites that are available for biosorption, b and $b = 1/K$ is the coefficient related to the affinity between sorbent and sorbate. While C_f is the final equilibrium sorbate concentration.

The Langmuir relationship can be linearized by plotting: $\frac{1}{q}$ vs. $\frac{1}{C_f}$ or $\frac{C_f}{q}$ vs. C_f

The calculation for sorbate uptake (q) as follow:

$$q = V[\text{L}](C_i - C_f)[\text{mg/L}]/S[\text{g}] \tag{5}$$

where C_i is the initial sorbate concentration and C_f is the final equilibrium sorbate concentration in solution. V (L) is the volume of the metal-bearing solution contacted with the sorbent and all of these had to be analytically determined (mg/L), while S is the amount of the added (dry biosorbent (g)).

3. Results and discussion

In order to explore the potentiality of *Trichoderma* biomass for the separation of toxic heavy metal ions, the effect of pH as a function of time were studied to set the conditions for the optimum biosorption. The concentration of nickel, cadmium, and chromium ions was chosen as 1.0 mg/L and five different pH (2, 4, 6, 8, and 10) were selected for this study. It was observed from Figs. 1–3 that the maximum bioadsorption of metal ions on the biomass was reached in 72 h. It was also found that the adsorption capacity was mainly dependent on the pH of the solution; since, most of the nickel, cadmium, and chromium ions can be easily adsorbed at pH 4, 6, 8, and 10 (because under these pH ranges, the metal ions were found in soluble form). The rate of biosorption for all metal ions (Ni(II), Cd(II), and Cr(VI)) was found

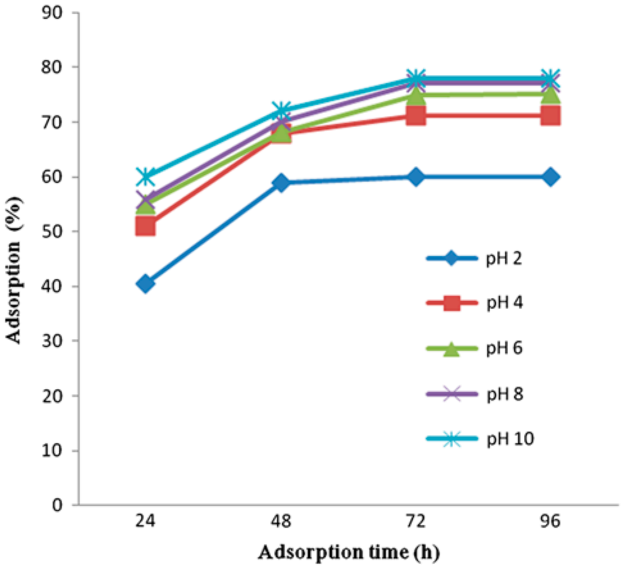

Fig. 1. Adsorption of Ni^{2+} ions using *Trichoderma* biomass at different pH as a function of time (27 ± 2°C).

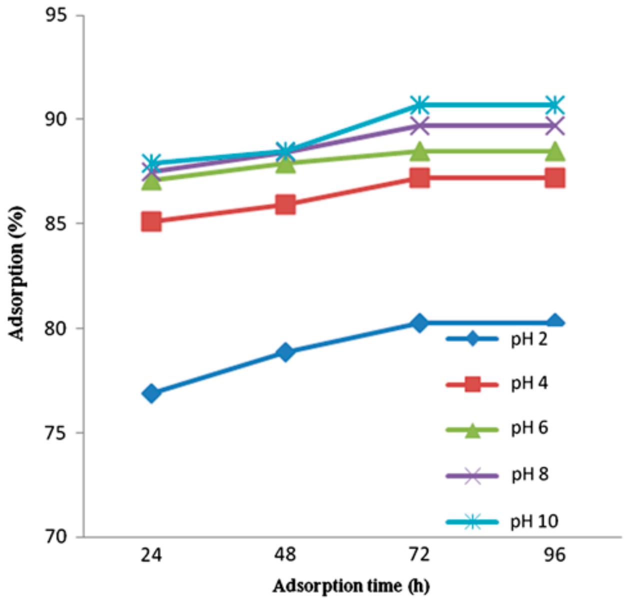

Fig. 2. Adsorption of Cd^{2+} ions using *Trichoderma* biomass at different pH as a function of time (27 ± 2˚C).

greatest during the first 24 h contact time and eventually reached saturation point (up to 72 h). At low concentration (1.0 mg/L), metal ions were completely biosorbed or interact with binding sites. However, at higher concentration, more ions competed for the available binding sites which declined biosorption [31].

Fig. 1 confirms that during 24 h (contact time) pH has influence on the biosorption with 40% uptake at pH 2 followed by higher uptake (50–55%) at pH 4, 6, and 8, and 60% uptake at pH 10, respectively. The amount of sorption at pH 10 was found to be 0.30 mg nickel/g biomass that was 20% higher than at pH 2. After the contact time of 48 h, biosorption of metal ions reduced with hardly any difference in the metal uptake at pH 4, 6, 8, and 10, respectively. Maximum biosorption of Ni(II) (0.37 mg nickel/g biomass) was observed at pH 10 during the contact time of 72 h. However, in acidic medium (pH 2), Ni(II) ions showed maximum adsorption (0.03 mg nickel/g biomass) that was equivalent to 60% to its initial concentration in 48 h. The adsorption of Cd(II) ions at pH 2.0 and 4.0 was about 76 and 85%, respectively, in 24 h. While under the same condition of contact time (24 h), 86–87% adsorption of Cd(II) ions was observed at pH 6, 8, and 10, respectively. At pH 4, 0.43 mg cadmium/g biomass of the metal was adsorbed during the same binding time. At pH 10, the maximum biosorption of Cd(II) observed was equivalent to 0.45 mg cadmium/g biomass after the contact time of 72 h. At pH 2, 55% biosorption of chromium (0.25 mg chromium/g biomass) was found during 24 h (Fig. 3). At higher pH (4, 6, 8, and 10) the adsorption was reached from 65 to 70% in 24 h. Under all pH conditions, the maximum biosorption (65–70%) of Cr(VI) ions reached in 72 h.

To examine the effect of pH, a comparison was made by the biosorption of Ni(II), Cd(II), and Cr(VI) on the biomass of *Trichoderma* at different pH, which clearly revealed that pH 10 was found better for the uptake of all three metal ions. At this pH, 87% biosorption was obtained for Cd(II) followed by 70% for Cr(VI) and 60% for Ni(II) ions. Thus, as compared with higher pH, less effective ion uptake of metal ions carried out at lower pH. The different biosorption behavior of *Trichoderma* was not only seen under pH condition and binding time, but also observed during the biosorption of the metal ions. Cadmium has the greatest affinity towards the biomass of *Trichoderma* that demonstrated more than 75% adsorption in 24 h at pH 2 while 87% at pH 10. The saturation of metal ions onto the biomass was found during 72 h that was about 0.45 mg cadmium/g biomass, similar to that of chromium followed by 0.37 mg nickel/g biomass at pH 10.

The loose structure of dried biomass provides a large surface area for the biosorption of the metal ions. It was generally found that most of the microbial surfaces are negatively charged because of the ionization of functional groups which facilitate metal binding. At lower pH, the functional groups remain in protonated form and create less conducive binding charges condition for the biosorption due the reduction in

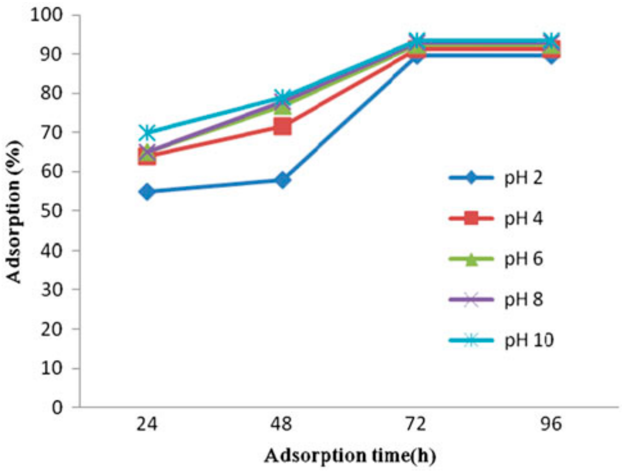

Fig. 3. Adsorption of Cr(VI) ions using *Trichoderma* biomass at different pH as a function of time at room temperature (27 ± 2˚C).

negatively charged surface. In other words, the removal process was highly dependent on the pH of the metal solutions which affects the surface charge of the biosorbents and the degree of ionization. On increasing pH, the functional groups tend to lose the protons and more negatively charged areas are formed on the surface of the biomass, which establishes greater attraction between negatively charged biomass and positive metal ions resulting maximum biosorption.

The binding of these charged groups with metal ions came rapidly in first 24 h and slowed down as lesser active sites are available for binding. The limiting factor for the availability of active sites to bind metal ions indicates that adsorption can achieve equilibrium and saturation. In the study of Fourest and Roux the uptake of metal ions decreased when the biomass concentration increases, which attributed to a shortage of metal ion concentration [30]. It has also been asserted that increasing the metal/biomass ratio will increase metal uptake per gram of biomass. The pH of the solution plays a very important rule for the adsorption of metal ions. It influences the metal adsorption capacity while the presence of other ions in the solution creates competition over the binding sites [29]. The adsorption of metal ions under different conditions of temperature and the presence of organic materials such as complexing agents cell promotes the metal ions precipitation [32]. In live biomass, the absorption of metal ions generally dependents on the metabolic activity of the cells, which generally linked to the defense mechanism of the microbial cells. In this case, the biosorption slowly depends on the swiftness of microbial reaction in the presence of metal ions [33]. Based on the data, the biosorption of *Trichoderma* at five different pH was assumed that adsorption equilibrium reached in 72 h.

By plotting the linearized graph, the values for K_f, *n*, and r^2 for the Freundlich coefficient and q_{max}, b, and r^2 for Langmuir coefficient were obtained and their results are presented in Table 1. Table 1 shows that both models give fairly good linear fit to the adsorption data, according to the value of r^2. However, the Langmuir equation (r^2) yields a slightly better fit than the Freundlich (r^2). It is well known that the Langmuir equation is intended for homogeneous surface. Therefore, a good fit of this equation may reflect monolayer adsorption [34]. Other than homogeneous surfaces, the Freundlich equation was found to be suitable for a highly heterogeneous surface and an adsorption isotherm lacking a plateau which indicates

Table 1
Freundlich and Langmuir coefficients for the biosorption of Ni(II), Cd(II), and Cr(VI) ions using biomass of *Trichoderma* at different pH (27 ± 2 ℃)

pH	K_f (mg/g)	*n*	r^2	pH	q_{max}	*b*	r^2
Freundlich and correlation coefficient (r^2) for the biosorption of Ni(II) ions				Langmuir and correlation coefficient (r^2) for the biosorption Ni(II) ions			
2	0.0467	0.6447	0.9293	2	0.0171	0.9257	0.8952
4	0.0338	1.2732	0.9165	4	0.1353	0.4098	0.9414
6	0.0376	1.4457	0.8780	6	0.0874	0.7885	0.9115
8	0.0377	1.6147	0.8759	8	0.0611	1.4740	0.9286
10	0.0386	1.6324	0.8578	10	0.0616	1.5262	0.9165
Freundlich and correlation coefficient (r^2) for the biosorption of Cd(II) ions				Langmuir coefficient and correlation coefficient (r^2) for the biosorption of Ni(II) ions			
2	0.0327	2.4207	0.8807	2	0.0350	5.4738	0.9586
4	0.0339	2.8703	0.7672	4	0.0364	7.1380	0.8874
6	0.0368	2.8490	0.8245	6	0.0373	8.5730	0.9306
8	0.0383	2.9095	0.8185	8	0.0374	10.0368	0.9326
10	0.0385	3.0479	0.8114	10	0.0370	11.6200	0.9301
Freundlich and correlation coefficient (r^2) for the biosorption of Cr(VI) ions				Langmuir and correlation coefficient (r^2) for the biosorption of Cr(VI) ions			
2	0.0319	1.8864	0.9677	2	0.0335	3.9841	0.9442
4	0.0723	1.8619	0.9906	4	0.0421	3.6661	0.9973
6	0.0516	1.5803	0.9508	6	0.0485	3.5619	0.9642
8	0.0557	1.5581	0.9635	8	0.0497	3.7774	0.9657
10	0.0601	1.5773	0.9588	10	0.0527	3.9478	0.9724

a multilayer adsorption [35]. Besides that, it also frequently provided an adequate description of adsorption data over a restricted range of concentration. Therefore, the metal concentrations range of 0.5–2.0 mg/L was found suitable for this experiment. In addition, the values of Freundlich constants K and n represent the adsorption capacity and the adsorption intensity of the adsorbent, respectively. The constant b in the Langmuir model reflects the adsorption bond energy where the constant $q_{\max}$ shows the maximum adsorption capacity. Therefore, it can also be seen that the maximum biosorption capacity of *Trichoderma* was observed above pH 4 for Ni(II), Cd(II), and Cr(VI) ions. This phenomenon shows that pH-dependent biomass of *Trichoderma* showed best biosorption for nickel at pH 10 and 8 with a capacity of 0.1353–0.0874 mg/g; cadmium biosorption at pH 10 followed by pH 6 and 4 with a maximum cadmium adsorption capacity; 0374, 0.0373, and 0.0364 mg/g and chromium adsorption shows the pH trend of pH 10 > pH 8 > pH 6 > pH 4 with maximum adsorption capacity; 0.0527, 0.0497, 0.0485, and 0.0421 mg/g, respectively.

A number of parameters which favor the adsorption efficiency of *Trichoderma* has been studied. These include: electronegativity (Ni, 1.8 Pauling; Cr, 1.6 Pauling and Cd, 1.69 Pauling [36], molecular weight (Cd, 112.4 u; Ni, 58.7 u; Cr, 51.99 u), and ionic radius (Ni, 69 pm; Cd, 95 pm; Cr, 44 pm) [37–40]. These were preferred for the adsorption of metal ions onto *Trichoderma*. The property difference may lie in the number of charges and particle size. Although, adsorption capacity of nickel was found to be high due to its high electronegativity, low atomic weight and lower ionic radius which allow good qualities for entrapment by cell. However, the removal of nickel was found to be lower than cadmium and chromium. This is may be due to the ions that may compete H^+ ions in solution and the fungi biomass, which may be more sensitive by the toxic effect of nickel than that of cadmium or chromium. Lower removal efficiency of chromium than cadmium was found a possible reason that could be the molecular weight (Cd, 112.4 u; Cr, 51.99 u) which plays an important role in the adsorption process. Chromium has a lower molecular weight than cadmium although their electronegativity (Cd, 1.69 Pauling; Cr, 1.6 Pauling) does not allow faster and higher entrapment of metal ions into the biomass cell.

4. Conclusion

Dried *Trichoderma* biomass has been successfully used as biosorbent to remove heavy metal ions from aqueous solution with maximum adsorption capacity. The most rapid uptake of metal ions took place in first 24 h and the rate of biosorption capacity slowed down tremendously the succeeding hours. This most crucial period shows that higher pH provides a better environment for the biosorption of Cd(II) that was more quickly followed by Cr(VI) and Ni(II). The maximum biosorption of Ni(II) was 75% at pH 8 and 10 in 72 h which was 0.37 mg nickel/g biomass. The 91% sorption of Cd(II) showed the maximum limit, equivalent to 0.45 mg cadmium/g biomass under pH 10 after the contact time of 72 h. The maximum biosorption of Cr(VI) was reached in 72 h with 0.90 mg chromium/g biomass sorbed. The characterization of Cr(VI), Cd(II), and Ni(II) ions uptake by fungi biomass showed that the existence of binding kinetics depends on the experimental conditions, particularly the pH and the concentration of metal ions. Both Freundlich and Langmuir adsorption models were applied. However, Langmuir isotherm was found to be slightly better which covers a concentration range of 0.5–2.5 mg/L for heavy metal ions.

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References

[1] H. Li, Z. Chi, J. Li, Application of ion exchange and chemical precipitation process for the treatment of acid-dissolution water of chromium sludge, Desalin. Water Treat. 53 (2015) 206–213.

[2] Y.L. Cheng, R.J. Wong, J.C.T. Lin, C. Huang, D.J. Lee, A.S. Mujumdar, Water coagulation using electrostatic patch coagulation (EPC) mechanism, Drying Technol. 28 (2010) 850–857.

[3] Md. Shahadat, M. Rafatullah, T.T. Tow, Characterization and sorption behaviour of natural adsorbent for exclusion of chromium ions, Desalin. Water Treat. 53 (2015) 1395–1403.

[4] S.A. Nabi, Md. Shahadat, R. Bushra, A.H. Shalla, F. Ahmed, Development of composite ion-exchange adsorbent for pollutants removal from environmental wastes, Chem. Eng. J. 165 (2010) 405–412.

[5] S.A. Nabi, Md. Shahadat, R. Bushra, A.H. Shalla, Heavy-metals separation from industrial effluent, natural water as well as from synthetic mixture using synthesized novel composite adsorbent, Chem. Eng. J. 175 (2011) 8–16.

[6] S.A. Nabi, Md. Shahadat, R. Bushra, A.H. Shalla, A. Azam, Synthesis and characterization of nano-composite ion-exchanger; Its adsorption behavior, Colloids Surf., B 87 (2011) 122–128.

[7] Md. Shahadat, S.A. Nabi, R. Bushra, A.S. Raeissi, K. Umar, M.O. Ansari, Synthesis, characterization, photolytic degradation, electrical conductivity and applications of a nanocomposite adsorbent for the treatment of pollutants, RSC Adv. 2 (2012) 7207–7220.

[8] R. Bushra, Md. Shahadat, A. Ahmad, S.A. Nabi, K. Umar, M. Oves, A.S. Raeissi, Synthesis, characterization, antimicrobial activity and applications of polyanilineTi(IV)arsenophosphate adsorbent for the analysis of organic and inorganic pollutants, J. Hazard. Mater. 264 (2014) 481–489.

[9] S.A. Nabi, R. Bushra, Md. Shahadat, Removal of toxic metal ions by using composite cation-exchange material, J. Appl. Polym. Sci. 125 (2012) 3438–3446.

[10] Md. Shahadat, A.H. Shalla, A.S. Raeissi, Synthesis, characterization, and sorption behavior of a novel composite cation exchange adsorbent, Ind. Eng. Chem. Res. 51 (2012) 15525–15529.

[11] S.A. Nabi, R. Bushra, Md. Shahadat, Application of Zr (IV) tungstate for removal of metal ions from aqueous solutions, Toxicol. Environ. Chem. 94 (2012) 468–481.

[12] Md. Shahadat, T.T. Teng, M. Rafatullah, M. Arshad, Titanium-based nanocomposite materials: A review of recent advances and perspectives, Colloids Surf., B 126 (2015) 121–137.

[13] Y. Cai, J. Li, X. Zhang, Y. Zhang, *In-situ* monitoring of polysulfone membrane formation via immersion precipitation using an ultrasonic through-transmission technique, Desalin. Water Treat. 32 (2011) 214–225.

[14] V.N. Bulut, A. Gundogdu, C. Duran, H.B. Senturk, M. Soylak, L. Elci, M. Tufekci, A multi-element solid-phase extraction method for trace metals determination in environmental samples on Amberlite XAD-2000, J. Hazard. Mater. 146 (2007) 155–163.

[15] M. Tuzen, A. Sari, D. Mendil, M. Soylak, Biosorptive removal of mercury(II) from aqueous solution using lichen (*Xanthoparmelia conspersa*) biomass: Kinetic and equilibrium studies, J. Hazard. Mater. 169 (2009) 263–270.

[16] M. Tuzen, O.D. Uluozlu, C. Usta, M. Soylak, Biosorption of copper(II), lead(II), iron(III) and cobalt(II) on *Bacillus sphaericus*-loaded Diaion SP-850 resin, Anal. Chim. Acta 581 (2007) 241–246.

[17] D. Harikishore Kumar Reddy, S.-Mok Lee, Application of magnetic chitosan composites for the removal of toxic metal and dyes from aqueous solutions, Adv. Colloid Interface Sci. 201–202 (2013) 68–93.

[18] D. Harikishore Kumar Reddy, S.-M. Lee, Magnetic biochar composite: Facile synthesis, characterization, and application for heavy metal removal, Colloids Surf., B 454 (2014) 96–103.

[19] D. Harikishore Kumar Reddy, K. Seshaiah, A.V.R. Reddy, M. Rao, M.C. Wang, Biosorption of Pb^{2+} from aqueous solutions by *Moringa oleifera* bark: Equilibrium and kinetic studies, J. Hazard. Mater. 174 (2010) 831–838.

[20] J.M. Lezcano, F. González, A. Ballester, M.L. Blázquez, J.A. Muñoz, C. García-Balboa, Biosorption of Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) using different residual biomass, Chem. Ecol. 26 (2010) 1–17.

[21] J. Wang, C. Chen, Biosorbents for heavy metals removal and their future, Biotechnol. Adv. 27 (2009) 195–226.

[22] N. Das, Recovery of precious metals through biosorption—A review, Hydrometallurgy 103 (2010) 180–189.

[23] B. Volesky, Biosorption and metal, Water Res. 41 (2007) 4017–4029.

[24] C.J. Daughney, D.A. Fowle, D. Fortin, The effect of growth phase on proton and metal adsorption by *Bacillus subtilis*, Geochim. Cosmochim. Acta 65 (2001) 1025–1035.

[25] T.G. Beveridge, The immobilization of soluble metals by bacterial walls, Biotechnol. Bioeng. Symp. 16 (1986) 127–140.

[26] G.M. Gadd, Accumulation of metals by microorganisms and algae, Biotechnology (1988) 401–433.

[27] C. Sing, J. Yu, Copper adsorption and removal from water by living mycelium of white-rot fungus *Phanerochaete chrysosporium*, Water Res. 32 (1998) 2746–2752.

[28] B. Volesky, H. May, Z.R. Holan, Cadmium biosorption by *Saccharomyces cerevisiae*, Biotechnol. Bioeng. 41 (1993) 826–829.

[29] J.L. Wang, C. Chen, Biosorption of heavy metals by *Saccharomyces cerevisiae*: A review, Biotechnol. Adv. 24 (2006) 427–451.

[30] E. Fourest, J.C. Roux, Heavy metal biosorption by fungal mycelial by-products: Mechanisms and influence of pH, Appl. Microbiol. Biotechnol. 37 (1992) 399–403.

[31] S. Pradhan, S. Singh, L.C. Rai, Characterization of various functional groups present in the capsule of *Microcystis* and study of their role in biosorption of Fe, Ni and Cr, Bioresour. Technol. 98 (2007) 595–601.

[32] N.R. Bisnoi, R. Kumar, K. Bisnoi, Biosorption of Cr(VI) with *Trichoderma* viride immobilized fungal biomassand cell free cell free Ca-alginate beads, Ind. J. Expt. Biol. 45 (2007) 657–664.

[33] J.M. Tobin, D.G. Cooper, R.J. Neufeld, Uptake of metal ions by *Rhizopus arrhizus*, Appl. Environ. Microbiol. 47 (1984) 821–824.

[34] S.S. Ahluwalia, D. Goyal, Microbial and plant derived biomass for removal of heavy metals from wastewater, Bioresour. Technol. 98 (2007) 2243–2257.

[35] R.S. Juang, S.L. Swei, Effect of dye nature on its adsorption from aqueous solutions onto activated carbon, Sep. Sci. Technol. 31 (1996) 2143.

[36] R.S. Juang, F.C. Wu, R.L. Tseng, Adsorption isotherms of phenolic compounds from aqueous solutions onto activated carbon fibers, J. Chem. Eng. Data 41 (1996) 487.

[37] S.J. Allen, P.A. Brown, Isotherm analyses for single component and multi component metal sorption onto lignite, J. Chem. Technol. Biotechnol. 62 (1995) 17–24.

[38] C. Quintelas, T. Tavares, Lead(II) and iron(II) removal from aqueous solution: Absorption by a bacterial biofilm supported on granular activated carbon, J. Res. Environ. Biotechnol. 3 (2002) 1926–1926.

[39] R. Shawabkeh, A. Al-Harahsheh, M. Hami, A. Khlaifat, Conversion of oil shale ash into zeolite for cadmium and lead removal from wastewater, Fuel 83 (2004) 981–985.

[40] R.D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, Acta Crystallogr., A 32 (1976) 751–767.