Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.961562

56 (2015) 1898–1907
November

Taylor & Francis
Taylor & Francis Group

Biosorption of chlorophenoxy acid herbicides from aqueous solution by using low-cost agricultural wastes

Veysi Okumuş[a,*], K. Serdar Çelik[b], Sadin Özdemir[a], Abdurrahman Dündar[c], Ersin Kılınç[c,*]

[a]*Faculty of Art and Science, Department of Biology, Siirt University, 56100 Siirt, Turkey, email: veysiok@hotmail.com (V. Okumuş)*
[b]*Faculty of Art and Science, Department of Chemistry, Batman University, Batman, Turkey*
[c]*Medical Laboratory Techniques, Vocational Higher School of Healthcare Studies, Mardin Artuklu University, 47200 Mardin, Turkey, email: kilincersin@gmail.com (E. Kılınç)*

Received 27 April 2014; Accepted 3 August 2014

ABSTRACT

The potential biosorption abilities of apple shell (AS), orange peel (OP), banana peel (BP), and millet waste (MW) as a bio-waste material to remove 2,4-dichlorophenoxy acetic acid (2,4-D), 2,4-dichlorophenoxy propanoic acid (2,4-DP), and 2,4-dichlorophenoxy butyric acid (2,4-DB) from aqueous solution were investigated in batch condition. Optimum biosorption conditions were determined as a function of contact time, pH of the solution, amount of biomass, and initial pesticide concentrations. The concentrations of the pesticides in the remaining solutions were simultaneously determined by high performance thin layer chromatography. Langmuir and Freundlich models were applied to describe the biosorption isotherm of the pesticides by agricultural wastes. The experimental adsorption data were fitted to Langmuir adsorption models ($r^2 > 0.99$). It was found that adsorption of 2,4-DP was higher for all biosorbent. The highest maximum adsorption capacities of 2,4-DP were found as 40.08, 22.71, 33.26, and 45.45 mg/g, respectively, for AS, OP, BP, and MW. Maximum adsorption capacity was obtained for 2,4-D as OP > MW > BP > AS, 2,4-DP as MW > AS > BP > OP, and 2,4-DB as OP > AS > BP > MW. From the results, it can be said that MW was an effective biosorbent for removal of 2,4-DP and OP was an effective biosorbent for removal of 2,4-D and 2,4-DB through the studied pesticides. Optimum biosorption conditions were determined as 60 min of contact time, 100 mg of biomass, AS at pH 6.0, OP at pH 6.0, MW at pH 7.0, and BP at pH 7.0. FT-IR was employed to understand the surface properties of biosorbents. According to the results, agricultural wastes have high adsorption capacity.

Keywords: Biosorption; Chlorophenoxy acid herbicide; Chromatography; Agricultural waste

1. Introduction

The potential damages of organic and inorganic pollutants from antrophogenic activities on environment and human health are well known. Many treatment procedures are employed to reduce the level of pollution [1]. Tolerance of organic and inorganic compounds varies in a wide range from ppb to % [2]. It is reported that phenols and phenolic compounds such as nitrophenols, chlorophenols from coke, petroleum, and unconscious use of pesticides, paints, sol-

---

*Corresponding authors.

vents, pharmaceuticals, food additives, and wood preserving are the most important pollution sources [3–7].

The common use of organochlorine compounds, persistent and highly water-soluble pollutants lead to accumulation in the environment [8]. Chlorophenoxy acid herbicide formulations, alkyl esters and free carboxylic acids are widely applied to prevent the growth of unwanted plants [9]. They are inexpensive and very potent even at low concentrations [10]. They also can be used for rapid growth of plants. Due to their toxicity and high water solubility, the European Community has established legal directives to restrict the use and to control their maximum residue levels in several matrices and monitoring of ground and drinking water [9,10]. Among these, chlorophenoxy acid herbicides are used extensively as plant growth regulator. Chlorophenoxy acid herbicides, include 2,4-D, 2,4-DP, and 2,4-DB, are widely used in agriculture to control the weeds and other vegetation. It is well known that the excessive use of herbicides lead to different disorders on human and animals [11]. Acidic herbicides are toxic for many living organisms even at low concentrations. Hence, the removal of chlorinated phenols from wastewater is a necessary obligation to preserve the quality of drinking water resources [12]. Nowadays, water quality is one of the most important problems especially in undeveloped countries.

Biosorption is accepted as a physico-chemical process that consists of adsorption of a chemical substance on biological materials [13,14]. Currently, an increasing amount of studies has focused on the treatment technologies by applying biosorption methods [6,15]. Biosorbents are materials from biological origin, often composed of secondary industrial or agricultural by-products or organic wastes, such as algae, bacteria, plants, yeast or fungi [14]. From the industrial point of view, the use of biosorbents for treatment provides many advantages such as high adsorption capacity, low cost, environment friendly, easy to find [16–18].

Agricultural waste is one of the rich sources for low-cost biosorbents besides industrial by-product or natural material [19]. Most of the biosorption studies have been focused on untreated agricultural wastes such as eggshell powder [20], hen feather leaf [21], peanut hull pellets [22], grape stalk wastes [23], oil palm ash [24], wheat bran [25], rice husk [26], rice bran and wheat bran [27], oil palm trunk fiber [28], yellow passion fruit peel [29], sugarcane dust [30], and durian peel [31]. Some of the advantages of using agricultural wastes for wastewater treatment include simple technique, requires little processing, good adsorption capacity, low cost, free availability, and easy regeneration [32].

In this research paper, biosorption study of the chlorophenoxy acid derivates, namely, 2,4-D, 2,4-DP, and 2,4-DB on low-cost agricultural wastes, is carried out along with isotherm studies.

2. Materials and methods

2.1. Preparation of the biosorbent materials

Apple shell (AS), orange peel (OP), banana peel (BP), and millet waste (MW) materials were washed thrice with distilled water in order to remove the dust and soil, and then dried in an oven at 80°C until constant weight. The dried biosorbent materials were crushed and sieved to get the biomass particles of 0.1–0.2 mm diameter.

2.2. Chemicals and reagents

2,4-D, 2,4-DP, and 2,4-DB were obtained as individual standards from Sigma-Aldrich (Missouri, USA) and used for preparing the stock standard solutions without purification. Chromatographic grade organic solvents were supplied from Merck (Darmstadt, Germany). All solutions were passed through 0.45 μm membrane filter (Sartorius Goettingen-Germany) before injection to the TLC plate. High performance thin layer chromatography (Camag) was used for the analysis of the pesticides. Chromatographic conditions given in literature were employed for separation of pesticides [14].

2.3. Experimental procedure

pHs of the solutions were about 6.0 during the batch experiments and no pH adjustment was performed. Approximately, 100 mg of agricultural wastes as a biomass was added to each flask and placed on the orbital shaker. The initial pesticide concentrations for the contact time experiments were 7.5 mg/L for each of the pesticides and the incubation times ranged from 5 to 120 min at 150 rpm shaking rate. The data used to derive the Langmuir constants were obtained using 1.0 g/L of biomass and using the pesticides solutions at the concentrations of 7.5, 15.0, 22.5, 30.0, 37.5, and 45.0 mg/L of pesticides. After contacting, the contents of the flask were centrifuged to separate the biomass from the solution. The results of pesticides analysis were used to calculate specific adsorption (mg pesticides adsorbed per g of biomass). All the experiments were repeated three times and average values were used for further calculations. The biosorption capacities of biosorbents were calculated from the equation given in literature [14].

3. Results and discussion

3.1. Effect of pH on biosorption

The effect of pH on the biosorption of 2,4-D, 2,4-DP, and 2,4-DB was investigated in the range of pH 2.0–8.0. It was observed that the maximum biosorption recoveries were obtained in the pH interval of 4.0–7.0. The influence of pH on the biosorption of OP and BP was not effective (Fig. 1(a) and (b)). There were no such variations on maximum adsorption capacities for these. Hence, pH 6.0 and 7.0 are employed for orange and banana peels, respectively. In contrast, AS and MW showed maximum adsorption at pH 6.0 and 7.0, respectively (Fig. 1(c) and (d)). At the lower pH, ionization of the pesticides which have acidic characteristics are suppressed. Therefore, they stayed in molecular state in contrast to acidic form. It can be said that the interaction of the pesticides with surface of biosorbent is mainly due to the result of molecular interaction. Oppositely, at higher pH, where pesticides concentration are much greater than H_3O^+ concentration, the pesticides uptake increases. At pH range of 6.0–7.0, functional groups of the agriculture waste surface, e.g. carboxyl and sulfate, become negatively charged, increasing the electrostatic interactions with the functional groups of studied pesticides.

3.2. Effect of contact time on biosorption

The rapid biosorption is a significant parameter for large-scale application in industrial processes. It is important to fix the optimum contact time in view of economical perspective [17]. So, the cost of operation is increased with time over the optimum value. In other words, extra energy must be used in this state. From this point of view, effect of contact time on biosorption was examined for 15, 30, 45, 60, and 120 min. From Fig. 2, it reached to the maximum adsorption value nearly about contact time of 60 min. After 60 min, no significant increase was observed for AS,

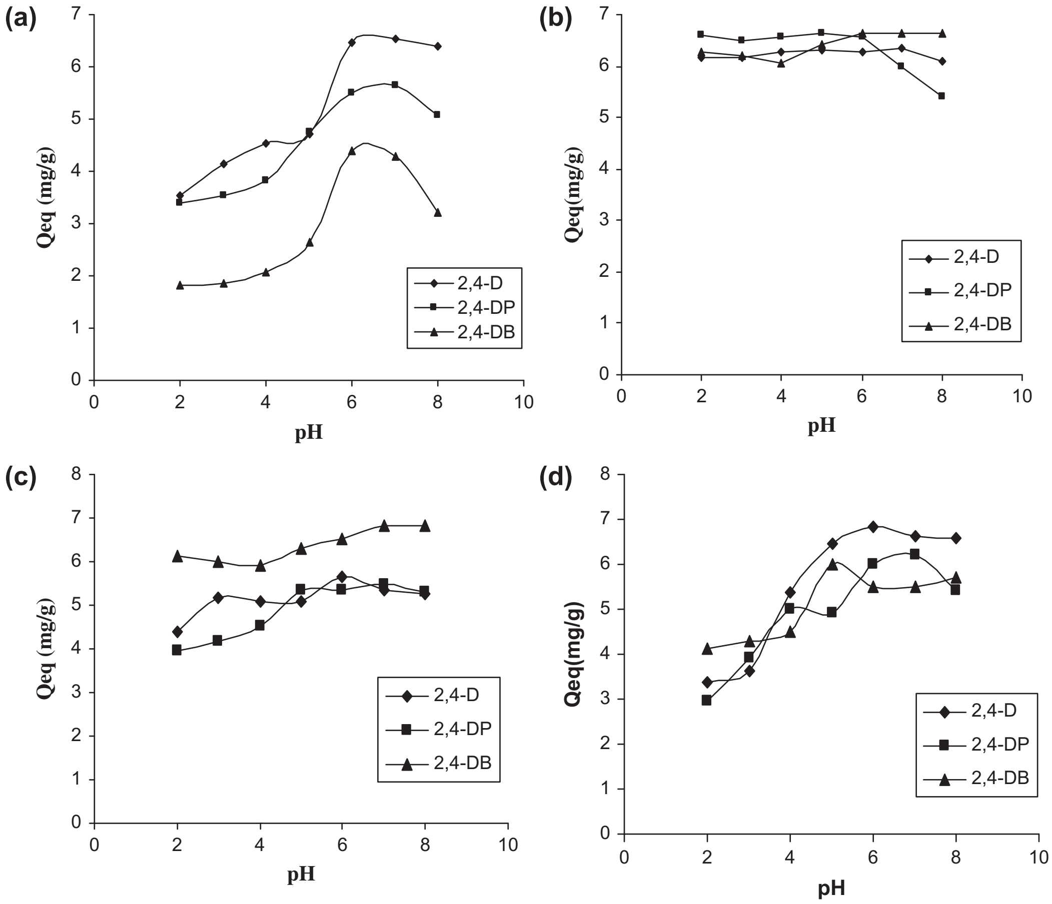

Fig. 1. Effect of initial pH on equilibrium biosorption capacities of 2,4-D, 2,4-DP, and 2,4-DB (conditions: 7.5 mg/L of initial pesticides concentration, 60 min of contact time, 100 mg of biomass) (a) AS, (b) OP, (c) MW, (d) BP.

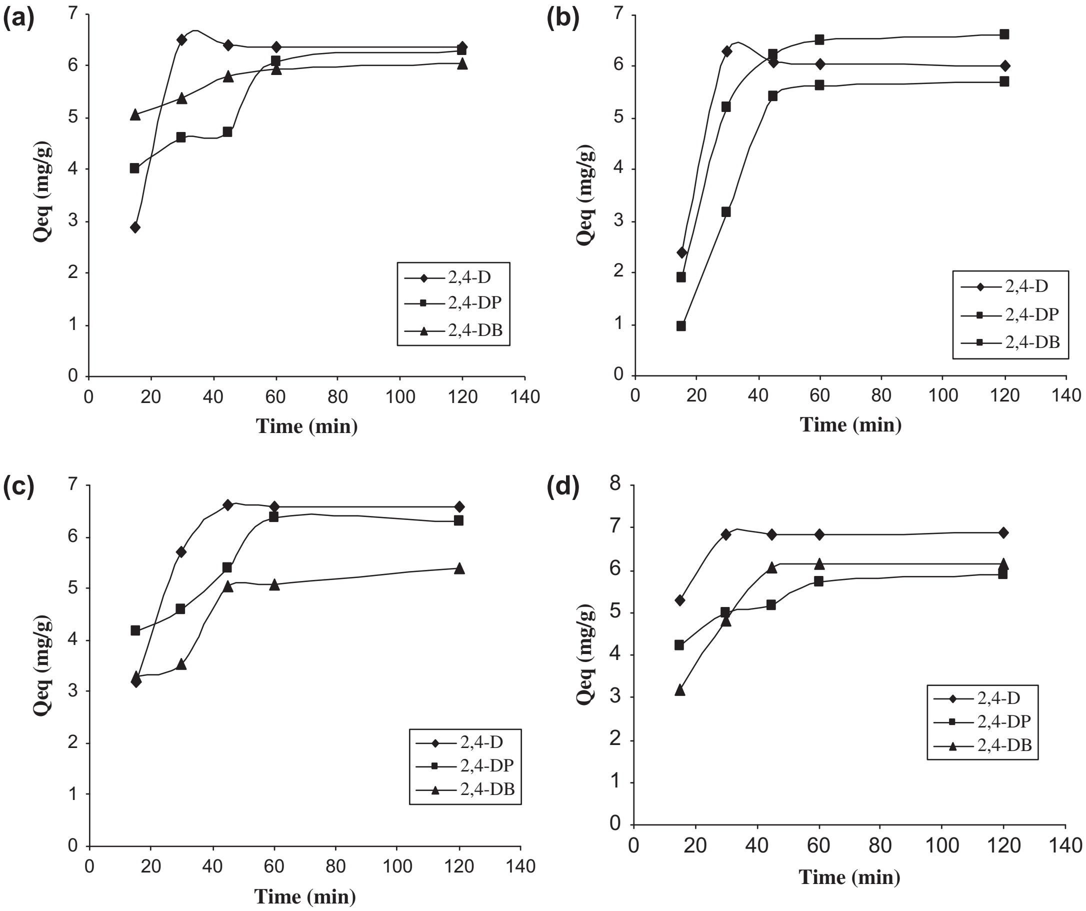

Fig. 2. Effect of contact time on equilibrium biosorption capacities of 2,4-D, 2,4-DP, and 2,4-DB (conditions: 7.5 mg/L of initial pesticides concentration, 100 mg of biomass) (a) AS at pH 6.0, (b) OP at pH 6.0, (c) MW at pH 7.0, (d) BP at pH 7.0.

OP, BP, and MW. At shorter biosorption periods, maximum adsorption values were also found lower. Therefore, further experiments were performed for a time of 60 min.

3.3. *Effect of pesticides concentration on biosorption*

The effect of initial pesticide concentration was investigated for the concentrations of 15.0, 22.5, 30.0, 37.5, and 45.0 mg/L of pesticides. When initial pesticide concentrations were increased, an increase in maximum adsorption capacities was observed. As expected, increasing was slowed down nearly about surface saturation. This was probably due to the increasing driving force in the concentration gradient and increasing in electrostatic interactions between surface sites and pesticides [33]. Among the pesticides, 2,4-DP showed the highest maximum adsorption capacity overall. Q_{eq} was obtained as 28.5, 29.6, 25.0, and 24.9 mg/g, respectively, for AS, OP, BP, and MW (Fig. 3).

3.4. *Effect of biomass concentration on biosorption*

The biosorbent concentration is an important factor that determines the capacity of a biosorbent for a given initial concentration [17]. Effect of biomass amount on equilibrium biosorption capacity of pesticides was shown in Fig. 4. Different amounts of agricultural biomass, 25, 50, 100, 200, and 400 mg, were employed for biosorption. It was observed that there was an important decrease in Q_{eq} with increase on biosorbent amount. From the results, it can be said that low amount of biosorbents were more effective than higher one [17,34]. The decrease in biosorption with the increase in biosorbent dosage can be attributed to saturation of biosorbent surface.

3.5. *Adsorption isotherms*

The equilibrium biosorption isotherms are the most important information to realize the biosorption

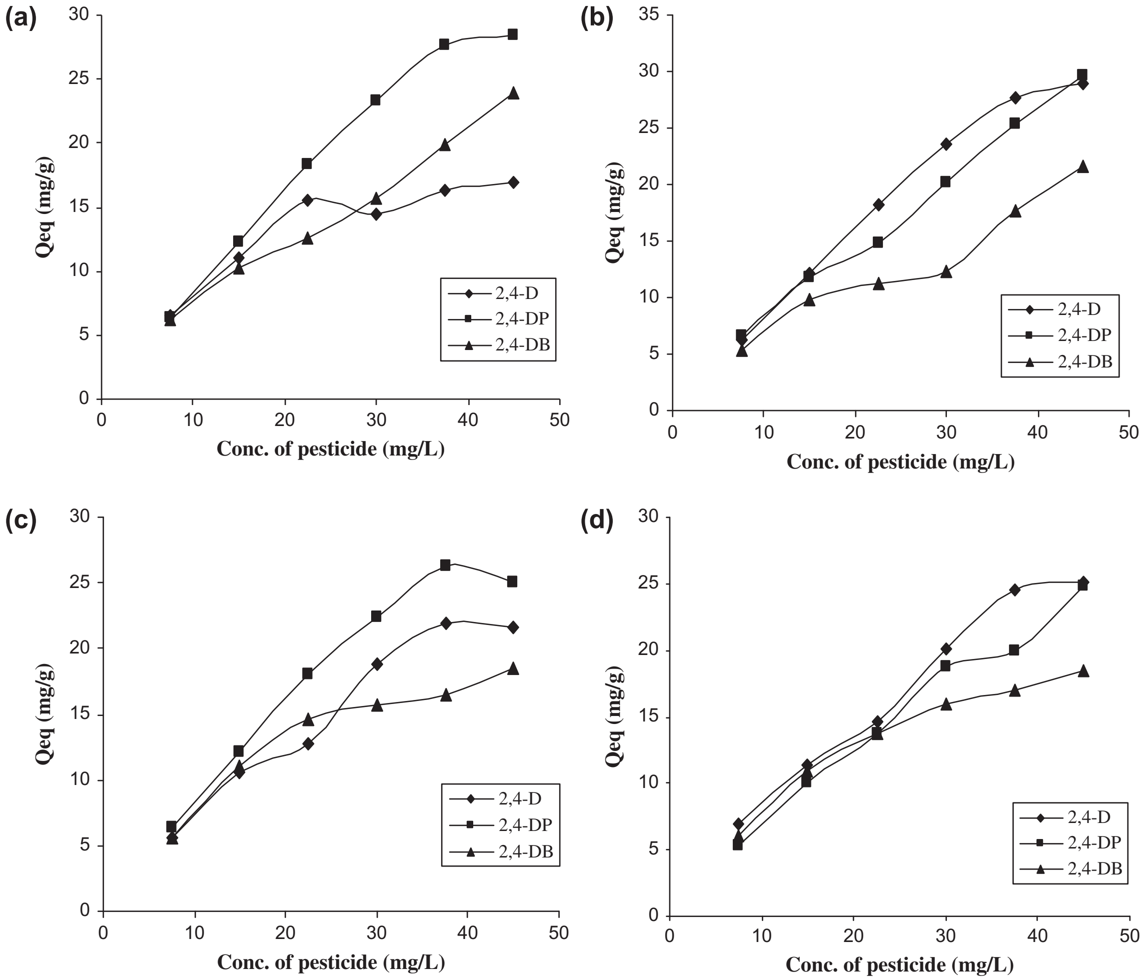

Fig. 3. Effect of initial pesticides concentration on equilibrium biosorption capacities of 2,4-D, 2,4-DP, and 2,4-DB (conditions: 7.5 mg/L of initial pesticides concentration, 60 min of contact time, 100 mg of biomass) (a) AS at pH 6.0, (b) OP at pH 6.0, (c) MW at pH 7.0, (d) BP at pH 7.0.

mechanism. Langmuir and Freundlich isotherms were utilized for the modeling of the experimental biosorption data obtained from the batch system [17]. The Langmuir isotherm theory assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface [14]. The Freundlich isotherm model assumes a heterogeneous sorption surface [14]. The Langmuir (Eq. (1)) and Freundlich (Eq. (2)) isotherms are represented by the equations below:

$$\frac{c_{eq}}{q_{eq}} = \frac{1}{K_b A_s} + \frac{c_{eq}}{A_s} \tag{1}$$

$$\ln q_{eq} = \ln K_F + \frac{1}{n} \ln c_{eq} \tag{2}$$

where q_{eq} and c_{eq} are the equilibrium ligand adsorption capacity of the biosorbent and the equilibrium ligand concentration in the aqueous solution, respectively; A_s, K_b, K_F, and n are the adsorption isotherm parameters. A_s is the maximum amount of the metal ions per unit weight of biosorbents to form a complete monolayer on the surface bound at high c_{eq}, and K_b is the constant related to the affinity of the binding sites. A_s represents a practical limiting adsorption capacity when the surface is fully covered with metal ions and assists in the comparison of adsorption performance, particularly in cases where the biosorbent did not reach its full saturation in experiments [35,36].

Langmuir and Freundlich adsorption isotherms were employed in order to investigate in detail the adsorption characteristics and to compare the adsorption performance of the adsorbents for the biosorption of metal pesticides. The values of Langmuir and Freundlich constants along with their coefficient of determination are listed in Tables 1 and 2. The

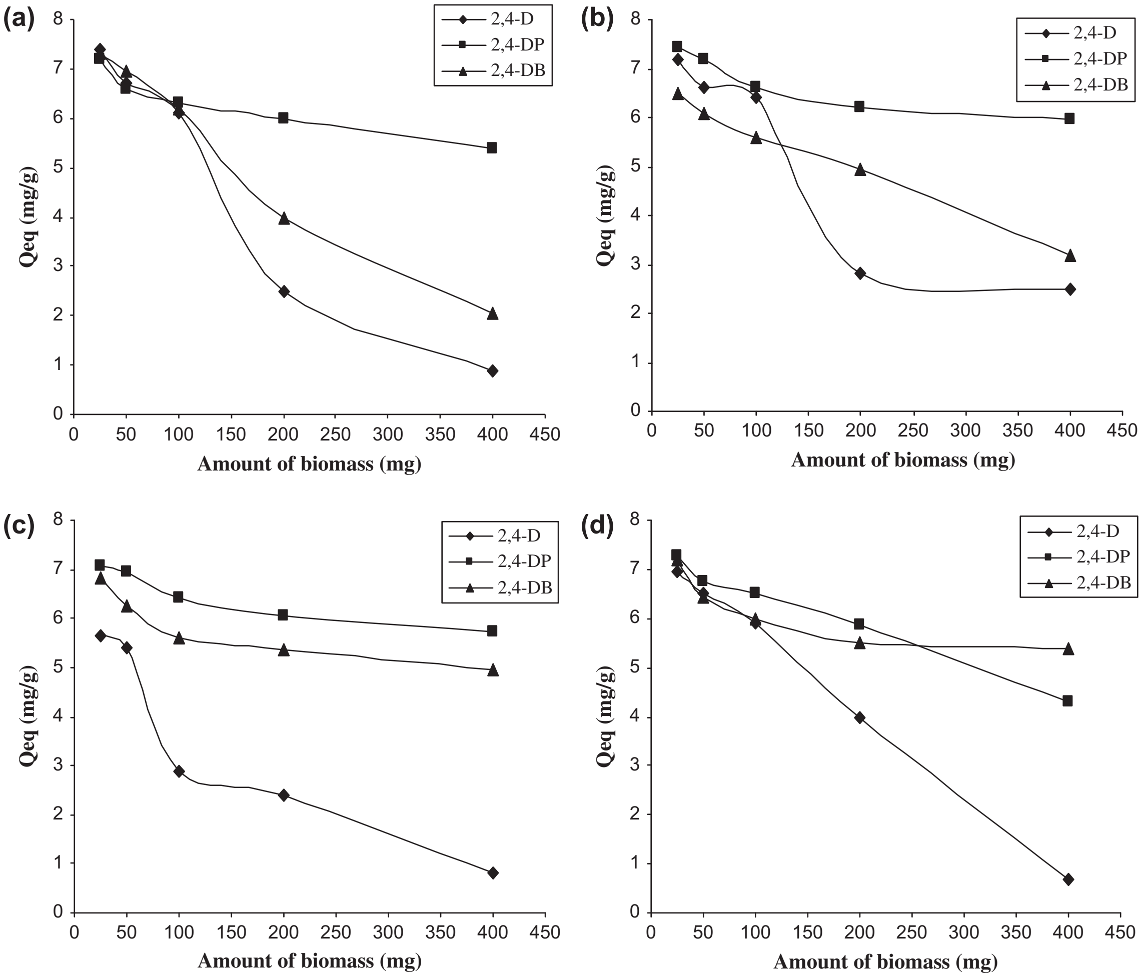

Fig. 4. Effect of biomass amount on equilibrium biosorption capacities of 2,4-D, 2,4-DP, and 2,4-DB (conditions: 7.5 mg/L of initial pesticides concentration, 60 min of contact time, 100 mg of biomass) (a) AS at pH 6.0, (b) OP at pH 6.0, (c) MW at pH 7.0, (d) BP at pH 7.0.

Table 1
Langmuir adsorption isotherm parameters for 2,4-D, 2,4-DP, and 2,4-DB by using agricultural wastes

Biosorbent	2,4-D			2,4-DP			2,4-DB		
	A_s	K_b	r^2	A_s	K_b	r^2	A_s	K_b	r^2
AS	17.86 ± 0.42	2.01 ± 0.21	0.9928	40.08 ± 0.34	5.53 ± 0.32	0.9745	25.64 ± 2.12	5.51 ± 0.32	0.9707
OP	34.48 ± 0.89	6.30 ± 0.23	0.9845	22.71 ± 0.27	2.92 ± 0.21	0.9950	23.25 ± 1.54	7.00 ± 0.45	0.9990
BP	22.73 ± 1.23	5.85 ± 0.34	0.9827	33.26 ± 0.43	4.14 ± 0.69	0.9851	21.27 ± 0.87	4.73 ± 0.40	0.9904
MW	29.4 ± 1.67	6.11 ± 0.19	0.9490	45.45 ± 1.24	16.61 ± 0.68	0.9950	20.83 ± 1.94	4.05 ± 0.34	0.9971

Langmuir isotherms were given in Fig. 5. As can be seen in the Table 1, high regression correlation coefficients (>0.99) were obtained from Langmuir isotherms. Therefore, it can be said that adsorption characteristics of the studied pesticides were monolayer. Freundlich adsorption model was also applied, according to the results it was not fitted to this model. Maximum adsorption capacity was obtained for 2,4-D as OP > MW > BP > AS, 2,4-DP as MW > AS > BP > OP, and 2,4-DB as OP > AS > BP > MW. From the results, it can be said that MW was an effective biosorbent for removal of 2,4-DP and OP was an effective biosorbent for removal of 2,4-D and 2,4-DB through the studied pesticides.

Table 2
Freundlich adsorption isotherm parameters for 2,4-D, 2,4-DP, and 2,4-DB by using agricultural wastes

Biosorbent	2,4-D			2,4-DP			2,4-DB		
	K_f	n	r^2	K_f	n	r^2	K_f	n	r^2
AS	7.29 ± 0.23	3.65 ± 0.09	0.8954	6.56 ± 0.12	1.66 ± 0.01	0.9371	5.79 ± 0.09	2.37 ± 0.03	0.9853
OP	5.94 ± 0.32	1.88 ± 0.01	0.9731	7.36 ± 0.15	2.90 ± 0.01	0.9812	4.14 ± 0.12	2.06 ± 0.08	0.9702
BP	4.72 ± 0.01	2.22 ± 0.01	0.9571	6.99 ± 0.15	1.91 ± 0.03	0.9311	5.01 ± 0.07	2.38 ± 0.01	0.9061
MW	5.93 ± 0.08	2.19 ± 0.01	0.9897	3.21 ± 0.06	1.40 ± 0.01	0.9876	5.69 ± 0.20	2.64 ± 0.07	0.9610

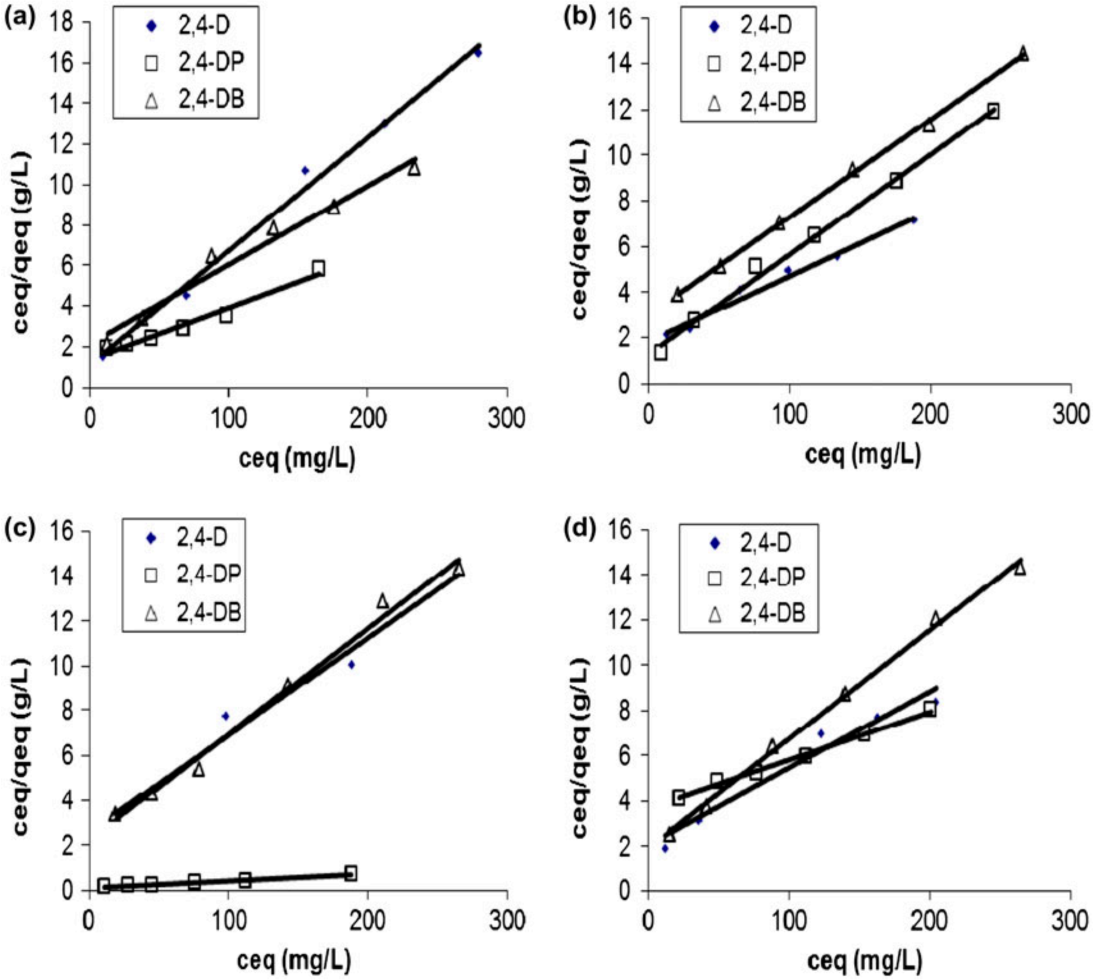

Fig. 5. Langmuir isotherms of 2,4-D, 2,4-DP, and 2,4-DB (a) AS at pH 6.0, (b) OP at pH 6.0, (c) MW at pH 7.0, (d) BP at pH 7.0.

3.6. FT-IR studies

From the Fig. 6, it was clear to see that surfaces of MW, AS, BP, and OP was functionalized after treatment with the mixture of 2,4-D, 2,4-DP, and 2,4-DB. From the FT-IR spectrum peaks at 2,700–2,620 (C=O), 1,715 cm^{-1} (C=O stretching), 1,467 cm^{-1} (C–H aromatic), 1,401 cm^{-1} (C–H stretching), 1,280, 1,211, and 1,060 cm^{-1} (C–C aromatic) for AS + Pest., cm^{-1} () for BP + Pest., 2,700–2,620 (C=O), 1,715 cm^{-1} (C=O stretching), 1,467 cm^{-1}, for OP + Pest., for MW + Pest., were attributed to differences 3,309 cm^{-1} (N–H stretching), 2,919, 1,730, 1,610, 1,240, and 1,050 cm^{-1} were

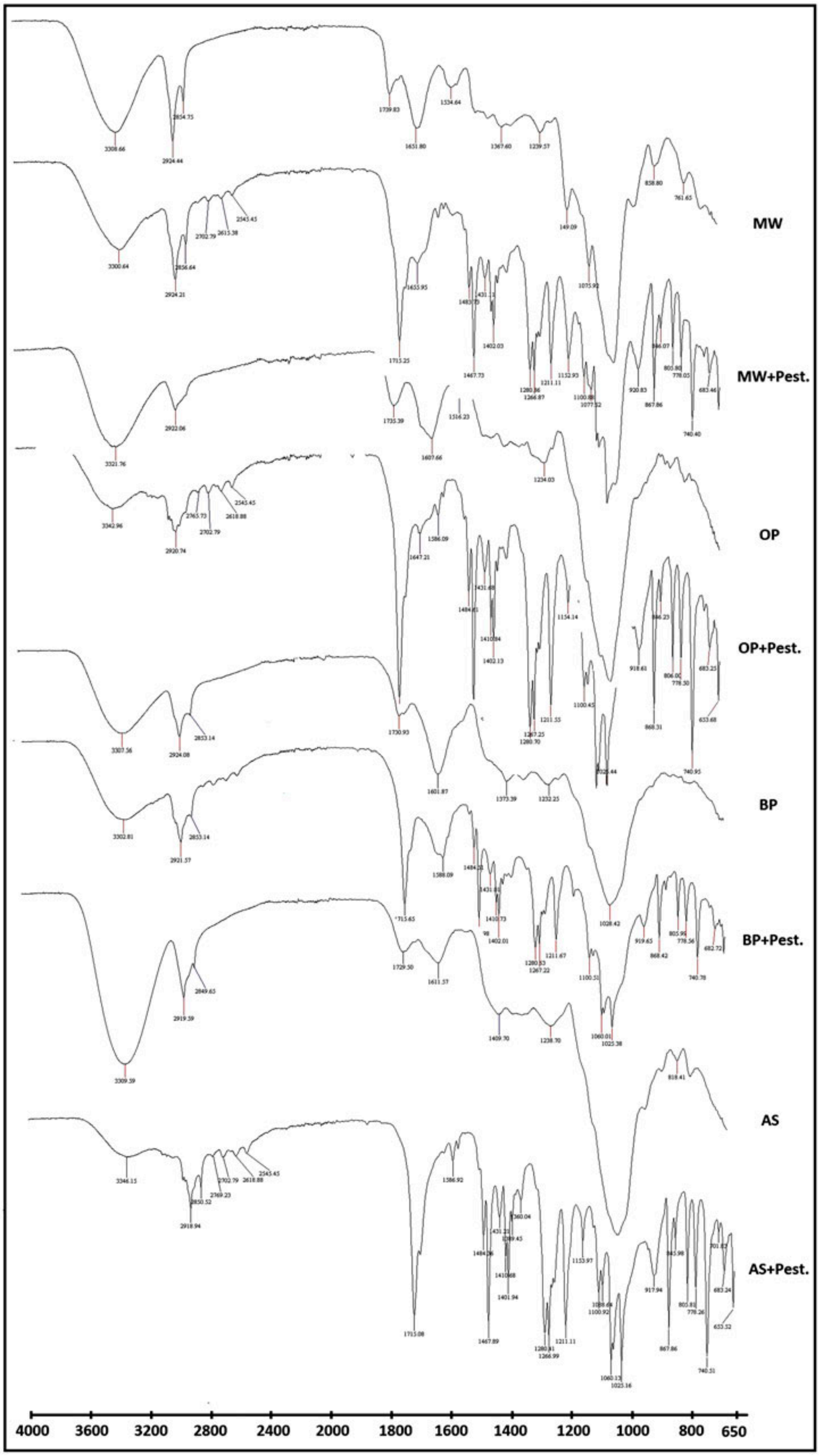

Fig. 6. Comparison of FT-IR spectra of biosorbents and biosorbents loaded with pesticides mixtures.

observed, whereas the mixture of pesticides adsorbed on AS showed different peaks at 1,715 cm^{-1}(C=O stretching), 1,467 cm^{-1} (), 1,280 cm^{-1}, 1,100 cm^{-1}, and 1,060 cm^{-1}. These changes of the spectra clearly show the complexation/coordination of the pesticides during the adsorption process. Difference peaks were attributed to adsorption of pesticides to biosorbent. They were commented and presented on above by considering to chemical structures of pesticides.

4. Conclusion

The results of the present batch studies show that the adsorptions of pesticides on agricultural wastes are quite satisfactory. The equilibrium data were tested using Langmuir and Freundlich adsorption isotherm models. The data fitted well to Langmuir isotherms. From the isotherm models it can be said that adsorption of 2,4-D, 2,4-DP, and 2,4-DB on agricultural wastes is monolayer. FT-IR was employed to understand the surface functionalities of the biosorbents. The results showed that optimum pHs for the biosorbent were in the range of pH 6.0 and 7.0. Thus, it can be said that acidity of the sample solution could be adjusted easily. Contact times of biosorbents with pesticides were short as 60 min. Thus, developed biosorption process can be applied to wastewater with soft conditions. In our developed method, pesticides can be removed from wastewater up to concentration of 45.0 mg L^{-1}. Results showed that 25 mg of biomass was most effective for removal of pesticides.

By considering the applicability of the Langmuir model and FT-IR spectral comparison, it could be concluded that monolayer sorption onto a homogeneous surface with a finite number of identical sites is a possible mechanism for interaction.

The findings in this study revealed that studied agricultural wastes are promising biosorbents for the removal of pesticides from contaminated wastewater. This kind of low-cost biosorbents make the process highly economical and competitive, particularly, for environmental applications in detoxifying effluents. In addition, it is not necessary to employ the use of commercial sorbents and resins when biosorbents are used. Further studies will help to evaluate the economic implications of using this biosorbent.

Acknowledgments

The authors are grateful to Dr Haci BAYKARA (Department of Chemistry, University of Siirt) for the FT-IR studies.

References

[1] G.M. Gadd, Biosorption: Critical review of scientific rationale, environmental importance and significance for pollution treatment, J. Chem. Technol. Biotechnol. 84 (2009) 13–28.

[2] Z. Aksu, Application of biosorption for the removal of organic pollutants: A review, Process Biochem. 40 (2005) 997–1026.

[3] Z. Aksu, J. Yener, A comparative adsorption/biosorption study of mono-chlorinated phenols onto various sorbents, Waste Manage. 21 (2001) 695–702.

[4] H. Daraei, A. Mittal, M. Noorisepehr, F. Daraei, Kinetic and equilibrium studies of adsorptive removal of phenol onto eggshell waste, Environ. Sci. Pollut. R. 20 (2013) 4603–4611.

[5] J.R. Rao, T. Viraraghavan, Biosorption of phenol from an aqueous solution by *Aspergillus niger* biomass, Bioresour. Technol. 85 (2002) 165–171.

[6] V. Okumus, E. Oral, D. Basaran, A. Onay, Simultaneous removal of indomethacine, papaverine and allopurinol from aqueous solution by using submerged aquatic plant *Nasturtium officinale*, Asian J. Chem. 22 (2010) 2081–2089.

[7] B.H. Hameed, I.A.W. Tan, A.L. Ahmad, Adsorption isotherm, kinetic modeling and mechanism of 2,4,6-trichlorophenol on coconut husk-based activated carbon, Chem. Eng. J. 144 (2008) 235–244.

[8] B.N. Estevinho, I. Martins, N. Ratola, A. Alves, L. Santos, Removal of 2,4-dichlorophenol and pentachlorophenol from waters by sorption using coal fly ash from a Portuguese thermal power plant, J. Hazard. Mater. 143 (2007) 535–540.

[9] N. Rosales-Conrado, M.E. León-Gonzalez, L.V. Pérez-Arribas, L.M. Polo-Díez, Capillary liquid chromatography of chlorophenoxy acid herbicides and their esters in apple juice samples after preconcentration on a cation exchanger based on polydivinylbenzene-N-vinylpyrrolidone, J. Chromatogr. A. 1076 (2005) 202–206.

[10] M.I. Catalina, J. Dallüge, R.J. Vreuls, U.A. Brinkman, Determination of chlorophenoxy acid herbicides in water by *in situ* esterification followed by in-vial liquid–liquid extraction combined with large-volume on-column injection and gas chromatography–mass spectrometry, J. Chromatogr. A. 877 (2000) 153–166.

[11] M.C.R. Alavanja, M.R. Bonner, Pesticides and human cancers, Cancer Invest. 23 (2005) 700–711.

[12] M.A. Hernández-Mateos, L.V. Pérez-Arribas, F. Navarro-Villoslada, M.E. León-González, L.M. Polo-Díez, Preconcentration of phenoxy acid herbicide residues by using an ion exchanger based on MFE-polymer,
J. Liq. Chrom. Rel. Technol. 22 (1999) 695–704.

[13] J. Wu, H.Q. Yu, Biosorption of 2,4-dichlorophenol from aqueous solutions by immobilized *Phanerochaete chrysosporium* biomass in a fixed-bed column, Chem. Eng. J. 138 (2008) 128–135.

[14] S. Ozdemir, F.M. Bekler, V. Okumus, A. Dundar, E. Kilinc, Biosorption of 2,4-d, 2,4-DP, and 2,4-DB from aqueous solution by using thermophilic anoxybacillus flavithermus and analysis by high-performance thin layer chromatography: Equilibrium and kinetic studies, Environ. Prog. Sustain. 31 (2012) 544–552.

[15] E. Kilinc, A. Dundar, S. Ozdemir, V. Okumus, Solid phase extraction based on the use of *Agaricus arvensis* as a fungal biomass for the preconcentrations of Pb and Al Prior to their determination in vegetables by ICP-OES, Atomic Spectosc. 34 (2013) 78–88.

[16] V.K. Gupta, A. Mittal, D. Jhare, J. Mittal, Batch and bulk removal of hazardous colouring agent Rose Bengal by adsorption techniques using bottom ash as adsorbent, RSC Adv. 2(22) (2012) 8381–8389.

[17] S. Özdemir, V. Okumuş, A. Dündar, E. Kılınç, Preconcentration of metal ions using microbacteria, Microchim. Acta 180 (2013) 719–739.

[18] E. Kilinc, A. Dundar, S. Ozdemir, V. Okumus, Preconcentration of Sn in real water samples by solid phase extraction based on the use of *Helvella leucopus* as a fungal biomass prior to its determination by ICP-OES, Atomic Spectosc. 34 (2013) 133–139.

[19] A. Mittal, V. Thakur, J. Mittal, H. Vardhan, Process development for the removal of hazardous anionic azo dye Congo red from wastewater by using hen feather as potential adsorbent, Desalin. Water Treat. 52 (2014) 227–237.

[20] H. Daraei, A. Mittal, M. Noorisepehr, J. Mittal, Separation of chromium from water samples using eggshell powder as a low-cost sorbent: kinetic and thermodynamic studies, Desalin. Water Treat. doi: 10.1080/19443994.2013.837011.

[21] A. Mittal, V. Thakur, V. Gajbe, Adsorptive removal of toxic azo dye Amido Black 10B by hen feather, Environ. Sci. Pollut. Res. 20 (2013) 260–269.

[22] P.D. Johnson, M.A. Watson, J. Brown, I.A. Jefcoat, Peanut hull pellets as a single use sorbent for the capture of Cu(II) from wastewater, Waste Manage. 22 (2002) 471–480.

[23] I. Villaescusa, N. Fiol, M. Martínez, N. Miralles, J. Poch, J. Serarols, Removal of copper and nickel ions from aqueous solutions by grape stalks wastes, Water Res. 38 (2004) 992–1002.

[24] A.A. Ahmad, B.H. Hameed, N. Aziz, Adsorption of direct dye on palm ash: Kinetic and equilibrium modeling, J. Hazard. Mater. 141 (2007) 70–76.

[25] M.T. Sulak, H.C. Yatmaz, Removal of textile dyes from aqueous solutions with eco-friendly biosorbent, Desalin. Water Treat. 37 (2012) 169–177.

[26] R. Han, D. Ding, Y. Xu, W. Zou, Y. Wang, Y. Li, L. Zou, Use of rice husk for the adsorption of Congo red from aqueous solution in column mode, Bioresour. Technol. 99 (2008) 2938–2946.

[27] X.S. Wang, Y. Zhou, Y. Jiang, C. Sun, The removal of basic dyes from aqueous solutions using agricultural by-products, J. Hazard. Mater. 157 (2008) 374–385.

[28] B.H. Hameed, M.I. El-Khaiary, Batch removal of malachite green from aqueous solutions by adsorption on oil palm trunk fibre: Equilibrium isotherms and kinetic studies, J. Hazard. Mater. 154 (2008) 237–244.

[29] F.A. Pavan, A.C. Mazzocato, Y. Gushikem, Removal of methylene blue dye from aqueous solutions by adsorption using yellow passion fruit peel as adsorbent, Bioresour. Technol. 99 (2008) 3162–3165.

[30] Y.S. Ho, W.T. Chiu, C.C. Wang, Regression analysis for the sorption isotherms of basic dyes on sugarcane dust, Bioresour. Technol. 96 (2005) 1285–1291.

[31] B.H. Hameed, H. Hakimi, Utilization of durian (Durio zibethinus Murray) peel as low cost sorbent for the removal of acid dye from aqueous solutions, Biochem. Eng. J. 39 (2008) 338–343.

[32] W.S. Wan Ngah, M.A.K.M. Hanafiah, Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review, Bioresour. Technol. 99 (2008) 3935–3948

[33] K. Vijayaraghavan, Y. Yun, Bacterial biosorbents and biosorption, Biotechnol. Adv. 26 (2008) 266–291.

[34] S. Özdemir, V. Okumuş, E. Kılınç, H. Bilgetekin, A. Dündar, B. Ziyadanogˇulları, *Pleurotus eryngii* immobilized Amberlite XAD-16 as a solid-phase biosorbent for preconcentrations of Cd^2 and Co^2 and their determination by ICP-OES, Talanta. 99 (2012) 502–506.

[35] Z. Aksu, E. Kabasakal, Batch adsorption of 2,4-dichlorophenoxy-acetic acid (2,4-D) from aqueous solution by granular activated carbon, Sep. Purif. Technol. 35 (2004) 223–240.

[36] S. Özdemir, E. Kilinc, A. Poli, B. Nicolaus, K. Güven, Biosorption of Cd, Cu, Ni, Mn and Zn from aqueous solutions by thermophilic bacteria, Geobacillus toebii sub. sp. decanicus and Geobacillus thermoleovorans sub. sp. stromboliensis: Equilibrium, kinetic and thermodynamic studies, Chem. Eng. J. 152 (2009) 195–206.