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Experimental Design for Removal of Fe(II) and Zn(II) Ions by Different Lactic Acid Bacteria Biomasses

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ABSTRACT: This paper investigates the removal of iron and zinc from aqueous solution with dairy wastewater in three different biomasses such as *Lactobacillus delbrueckii ssp bulgaricus* (Lb-12), *Streptococcus thermophillus* (STM-7) and a combination of both this bacteria culture (YC-380) and the optimization of removal efficiency using MINITAB program. A full 2^3 factorial design of experiments was applied to determine the optimum conditions of removal of Fe(II) and Zn(II) from aqueous solution. The three tested factors were biomass concentration (5-15 g/L), pH (3-9), and temperature (20-40 °C). The optimum biomass concentration, pH and temperature were found to be 15 g/L, 9 and 20 °C, respectively. Under optimal value of process parameters, 90-100% Fe(II) and 70-90% Zn(II) removal were obtained with all tested biomasses. Removal results indicated that a combination of both this bacteria might be a promising biomass alternative to ST-M7 and Lb.12 in removing Zn(II) and Fe(II) ions from waters.

Key words: Lactobacillus delbrueckii ssp bulgaricus, Streptococcus thermophillus, *Removal*

INTRODUCTION

Removal of metals/heavy metals from wastewater has become a serious problem in all over the world. The main sources of heavy metals pollution are waste streams of different industries such as metal cleaning and plating, paper board mills, pulp and wood sectors and municipal wastewater (Basso *et al.*, 2002; Özer *et al.*, 2004; Lodeiro *et al.*, 2006). Also, municipal wastewater generally contains significant amounts of zinc. The use of municipal and industrial waste in agriculture results in the accumulation of zinc in the surface layers of soil. Pulp production and fertilizer industries contain high concentrations of copper ions (Özer *et al.*, 2004); besides this, coatings, car, and steel industries generate various concentrations of iron (Selatnia *et al.*, 2004). Heavy metals such as Zn and Fe are present in industrial wastewater, these heavy metals in wastewater are not biodegradable and their existence in receiving lakes and streams causes bioaccumulation in living organisms, which iron and zinc to several health problems in animals, plants and human beings such as cancer, kidney failure, metabolic acidosis, oral ulcer, renal failure and damage in for stomach of the rodent. As a result of the degree of the problems caused by heavy metals pollution, removal of heavy metals from wastewater is important. Investigation into new and cheap methods of metal ions removal has been on the increase lately. Generally, the conventional treatment methods such as precipitation, coagulation/ flotation, sedimentation, flotation, filtration, membrane process, electrochemical techniques, ion exchange are less application due to high treatment cost and the production of toxic sludge (Akar & Tunali 2006; Tunali & Akar 2006; Abu Al-Rub *et al.*, 2006). Adsorption has become one of the alternative sources the search for low-cost adsorbents that have metal-binding capacities has increased in recent years (Leung *et al.*, 2000). The adsorbents may be of mineral, organic or biological origin (removal of metals with using live, dead microbial organisms), zeolites, industrial by-products, agricultural wastes, and polymeric materials (Kurniawan *et al.*, 2005). Investigation into new and cheap methods of metal ions removal from industrial and municipal effluents are gaining continuous research attention, with adsorption process suggested has most economically viable method (Kannanand & Rengasamy 2005). Among the microbial organisms, lactic acid bacteria (LAB) have been reported to efficiently remove metals from water (Davis *et al.*, 2003; Mehta & Gaur 2005; Romera *et al.*, 2006). Halttunen and coworkers have extensively

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investigated cadmium, lead and arsenic binding by different LAB and microcystin-LR and AFB1 from aqueous solution by single strains of LAB and their combination (Halttunen *et al.,* 2003, 2007a, b, 2008a, b; Ibrahim *et al.,* 2006; Mrvcic *et al.,* 2012). Abdel-Ghani *et al.*, (2009) were investigated the biosorption capacity of *Typha domingensis* phytomass for iron and zinc ions present in a mixed metal ions solution. Aksu and Acikel (2000) were studied the biosorption of iron(III) and chromium(VI) binary mixture on *Chlorella vulgaris*. There have been many reports about the removal of Fe(II) and Zn(II) with biomasses. However, the use biomasses of *Lactobacillus delbrueckii ssp bulgaricus* (Lb.12*), Streptococcus thermophillus* (ST-M7) and a combination of both this bacteria (*Lactobacillus delbrueckii ssp bulgaricus* and *Streptococcus thermophillus)* (YC-380) for such purpose has not been investigated in the available literature. The main objective of this study is to optimize removal of Fe(II) and Zn(II) ions in aqueous solution with these biomasses. The bacteria used in this study groups by selecting groups of dairy effluents isolated bacteria was carried out. The aim here is to see it as a lab-scale effect of dairy effluents. The desirable uniqueness of these microorganisms for industrial use is their ability to rapidly and completely ferment cheap raw materials, requiring minimal amount of nitrogenous substances. Therefore dairy isolates of lactic acid bacteria capable of degrading dairy effluent and converting them to Lactic acid are considered to be key to the development of a workable microbial fermentation based value addition process for dairy wastes containing Lactic acid bacteria. The study includes an evaluation of the effects of three process parameters such as biomass concentration, pH and temperature. A 2^3 full factorial design with three replicated central point tests was performed to determine the mathematical models about removal of Fe(II) and Zn(II) with each parameter and their interactions. Thus, this study intends to use adsorption process for Fe and Zn removal from industrial and municipal effluents because it has been reported to be inexpensive, widely applicable, efficiently.

MATERIALS & METHODS

Stock metal ion solutions were prepared from iron sulphate ($FeSO_4.7H_2O$, Merck) and zinc sulphate ($ZnSO_4.7H_2O$, Merck). The 100 mg/L concentrations of both metal ions were prepared from stock solutions.

The pH of the experimental solution was adjusted (Hanna HI 221, Kehl am Rhein, Germany) with NaOH (5 %) and 98 % sulfuric acid (Merck, Darmstadt, Germany). All chemicals used were reagent grade. Distilled and deionized water was used for stock solution preparations and dilutions. Lyophilized cultures of *Lactobacillus delbrueckii ssp bulgaricus* (Lb. 12, Chr Hansen, Denmark), *Streptococcus thermophillus* (ST-M7, Chr Hansen, Denmark) and a combination of both this bacteria of *Lactobacillus delbrueckii ssp bulgaricus* - *Streptococcus thermophillus* (YC-380, Chr Hansen, Denmark) were used in all experiments. The cultures were inoculated in 2,000 mL MRS broth (Merck, Darmstadt, Germany) at 37 °C for 2 days under anaerobic conditions. The cells were harvested by centrifugation at 10,000 rpm for 10 min (Eppendorf, Centrifuge 5804R, Hamburg, Germany). Pellets and supernatants were collected separately. Pellets were freeze-dried, and the freeze-dried biomasses were used as biomasses.

Metal removal experiments were conducted in 50 mL mixed batch reactor bottle-point method. A 11-run full factorial design was applied to evaluate 3 variables for three different biomasses. Table 1 shows the factors and levels investigated in removal tests. Tested variables (biomass concentration, pH, temperature) were denoted as X_1, X_2, and X_3, respectively. Minitab 14 program was used to determine significance of models and regression coefficients. The contour plots of the model-predicted responses were utilized to assess the interactive relationships between the significant variables. It was considered that results with less than 95% confidence interval (p>0.05) were not statistically significant for the model (Sayilgan & Cakmakci 2013). For each experimental matrix, required dose of biomass (Lb.12, ST-M7, YC-380) was put in plastic bottles and pH was adjusted. Then the samples were mixed (150 rpm) in a temperature-controlled orbital shaker (Gallenkamp) at 3 h reaction time. After experiments, the samples were centrifuged at 10,000 rpm for 5 min (Shimadzu centrifuge, Japan) to precipitate the biomasses. Prior to Fe(II) and Zn(II) analyses, each sample was diluted by 1:10 using nitric acid solution (pH~1.5-2) to avoid the precipitation of

Table 1. Factors and levels investigated in Zn(II) and Fe(II) removal tests (biomass: Lb.12, ST-M7 or YC-380).

Code	Factor (variable)	Level		
		-1	0	1
X_1	Biomass concentration (g/L)	5	10	15
X_2	pH	3	6	9
X_3	Temperature (^oC)	20	30	40

metals and then samples were kept in refrigerator at 4 °C until analysis. The Fe(II) and Zn(II) concentration of aqueous solution were measured using (ICP-OES) (Perkin Elmer, DV2100) spectrophotometer. The center point samples (Tests no., 9-11) were used for FT-IR and SEM analysis. The IR spectra of biomasses produced by the Lb.12, ST-M7 and YC-380 biomasses were obtained by IR spectroscopy (Perkin Elmer, BX). The infrared spectrum of the biomasses was recorded at room temperature in the wave number range of 4000–400 cm^{-1} with a FTIR spectrophotometer. The surface morphology of the biomasses after removal experiment was determined using a scanning electron microscope (SEM, Phillips, XL-30S FEG).

RESULTS & DISCUSSION

In this study, 2^3 factorial designs were performed to evaluate the removal of Fe(II) and Zn(II) with three different biomasses. The tested variables shown in Table 1 were chosen considering the preliminary experimental test results. The experimental conditions and removal results were shown in Table 2. Removal results were also shown in Fig. 1 (a, b). It is seen from Fig. 1 that Lb.12 biomass showed better Zn removal performance, while ST-M7 biomass showed better Fe removal performance in most cases. It probably be due to different physiological state of biomasses. Schut *et al.*, (2011) also indicated that the same inference for biosorption of Cu by wine-relevant lactobacilli.

Similar Fe(II) and Zn(II) removals were observed with Lb.12. This may be due to the similar electronegativity of Zn (1.66) and Fe (1.64) (Allred & Rochow, 1958, Schut *et al.*, 2011). However, better Fe removal was obtained with YC-380 and ST-M7 compared to Zn(II) removal, probably because of the characteristics of biomasses. The removal of Zn(II) with YC-380 and ST-M7 biomasses were generally varied between 5-90%, while it varied between 50-90% with Lb.12 biomass. Similarly, it was found that, 40-100% Fe(II) removal was obtained with Lb.12 and 30-100% Fe(II) removal was obtained with YC-380 and ST-M7 biomasses (Table 2).

The experimental design used for the modeling of Fe(II) and Zn(II) ions removal from synthetic solution with three different biomasses (Lb.12, ST-M7, YC-380) was carried out choosing three factors, namely: biomass concentration (X_1, g/L), pH (X_2) and temperature (X_3, °C). A 2^3 full factorial design was used to develop correlation between the selected factors and removal efficiency. The center point tests (Test no: 9, 10, 11) were repeated three times to determine the experimental error and requirement of the model. In this study, the A, B, and C variables in the regression equations are coded (non-dimensional) factors representing the three tested factors. The correlation between the coded and real values was chosen as follows.

$$A = (X_1 - 10) / 5 \quad (1)$$

$$B = (X_2 - 6) / 3 \quad (2)$$

$$C = (X_3 - 30) / 10 \quad (3)$$

Here,

X_1: biomass concentration (g/L), X_2: pH, and X_3: temperature (°C).

Main effects and interaction effects of the variables were estimated using the following equation.

$$Y = a_0 + a_1x_1 + a_2x_2 + a_3x_3 + a_{12}x_1x_2 + a_{13}x_1x_3 + a_{23}x_2x_3 + a_{123}x_1x_2x_3 \quad (5)$$

Here,

Y: removal percentage of Fe(II) or Zn(II) (%), x_1, x_2, x_3: coded non-dimensional factors of biomass concentration, pH and temperature, respectively. a_0:

Table 2. Removal results with different biomasses. Test duration: 3 h.

Test No.	X_1 (biomass concentration, g/L)	X_2 (pH)	X_3 (temperature, °C)	YC-380 Fe(II) removal (%)	YC-380 Zn(II) removal (%)	ST-M7 Fe(II) removal (%)	ST-M7 Zn(II) removal (%)	Lb.12 Fe(II) removal (%)	Lb.12 Zn(II) removal (%)
1	-1 (5g/L)	-1 (3)	-1 (20)	37.00	13.57	28.00	10.55	42.70	49.35
2	1 (15g/L)	-1 (3)	-1 (20)	50.00	9.28	53.00	1.86	51.34	57.48
3	-1 (5g/L)	1 (9)	-1 (20)	96.73	87.38	100.00	92.79	95.67	64.17
4	1 (15g/L)	1 (9)	-1 (20)	94.10	77.14	100.00	92.09	91.34	72.64
5	-1 (5g/L)	-1 (3)	1 (40)	32.00	4.04	97.35	0.93	47.34	51.26
6	1 (15g/L)	-1 (3)	1 (40)	45.00	1.90	97.00	1.62	41.67	51.14
7	-1 (5g/L)	1 (9)	1 (40)	96.52	84.52	98.75	20.93	98.67	91.10
8	1 (15g/L)	1 (9)	1 (40)	99.04	60.23	95.50	88.13	99.34	90.18
9	0 (10g/L)	0 (6)	0 (30)	94.46	7.71	98.10	6.09	62.50	52.70
10	0 (10g/L)	0 (6)	0 (30)	94.20	8.33	97.85	7.44	63.00	53.13
11	0 (10g/L)	0 (6)	0 (30)	93.92	5.12	98.10	5.88	61.00	48.92

the constant term, a_1, a_2, a_3: the main effect terms. a_{12}, a_{13}, a_{23}, a_{123}: the interaction effect terms.

The regression equations were submitted to the F-test to determine the coefficient R^2 (Anupam *et al.*, 2011). The predictive model was insured a representatively of the experimental data of about 95%, it means that the regression was <0.05. The regression coefficients for Fe(II) and Zn(II) removal with Lb.12, ST-M7, YC-380 were not given in tables. The ANOVA results have been used to derive simple empirical equations using Minitab 14 program in order to predict zinc and iron removal yields. Eliminating the insignificant interaction terms from the regression tables and refining the above empirical model equations could be simplified in terms of actual factors to:

$Zn_{YC380} = 42.26 - 10.24X_1 + 70.12X_2 - 9.17X_3 - 7.02X_1X_2$ (R^2: 0.99, R^2adj: 0.99)

$Zn_{STM7} = 38.61 + 14.62X_1 + 69.74X_2 - 21.42X_3 + 18.63X_1X_2 + 19.32X_1X_3 - 16.49X_2X_3 + 14.63X_1X_2X_3$ (R^2: 0.99, R^2adj: 0.99)

$Zn_{Lb12} = 65.92 + 27.21X_2 + 10.01X_3 + 12.23X_2X_3$ (R^2: 0.99, R^2adj: 0.97)

$Fe_{YC380} = 68.79 + 6.47X_1 + 55.59X_2 - 1.31X_3 - 6.52X_1X_2 + 1.28X_1X_3 + 3.68X_2X_3 + 1.28X_1X_2X_3$ (R^2: 1, R^2adj: 0.99)

$Fe_{STM7} = 83.70 + 5.35X_1 + 29.73X_2 + 26.90X_3 - 6.97X_1X_2 - 7.15X_1X_3 - 29.78X_2X_3 + 5.52X_1X_2X_3$ (R^2: 1, R^2adj: 1)

$Fe_{Lb12} = 71.00 + 50.49X_2 + 4.00X_2X_3 + 4.82X_1X_2X_3$ (R^2: 0.99, R^2adj: 0.99)

The graphical interpretation of main effects and interactions such three-dimensional surfaces can provide convenient information about the removal of Fe(II) and Zn(II) within the experimental design, facilitate to show the effects of the experimental factors

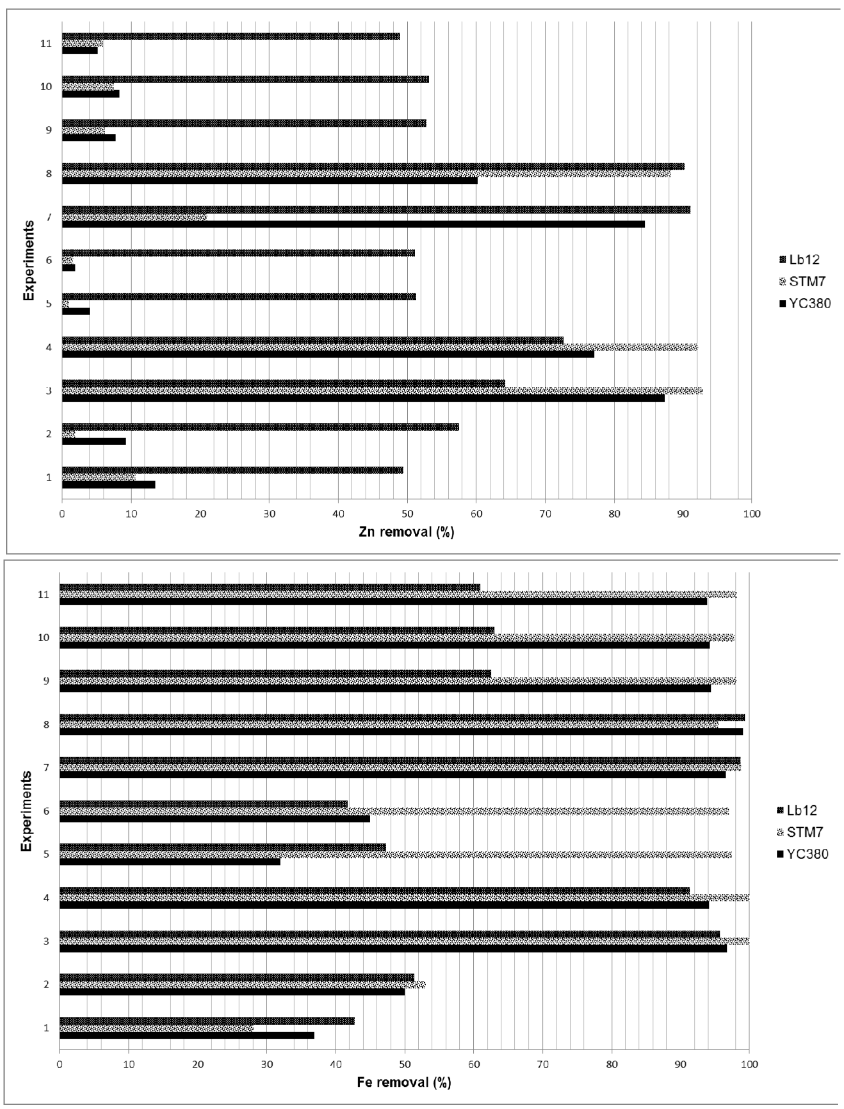

Fig.1. Zn(II) (a) and Fe(II) (b) removal yields after 3 h with tested biomasses

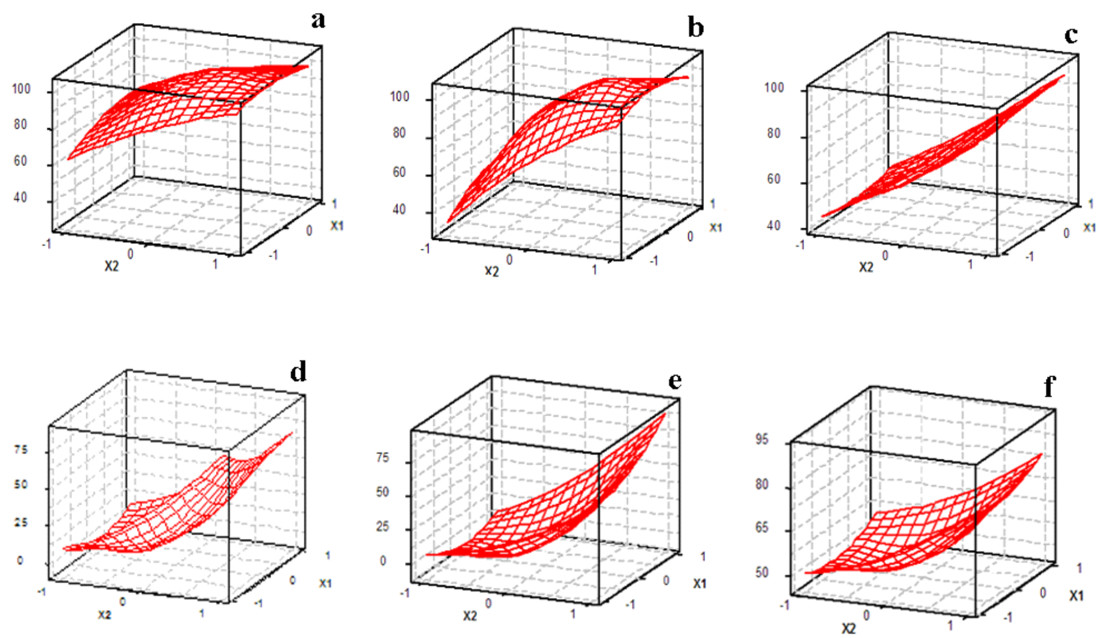

Fig.2. 3D-surface plot showing the interactive of biomass concentration (X_1) and pH (X_2) on removal of Fe(II) by (a) YC-380, (b) ST-M7, (c) Lb.12, and on removal of Zn(II) by (d) YC-380, (e) ST-M7, (f) Lb.12.

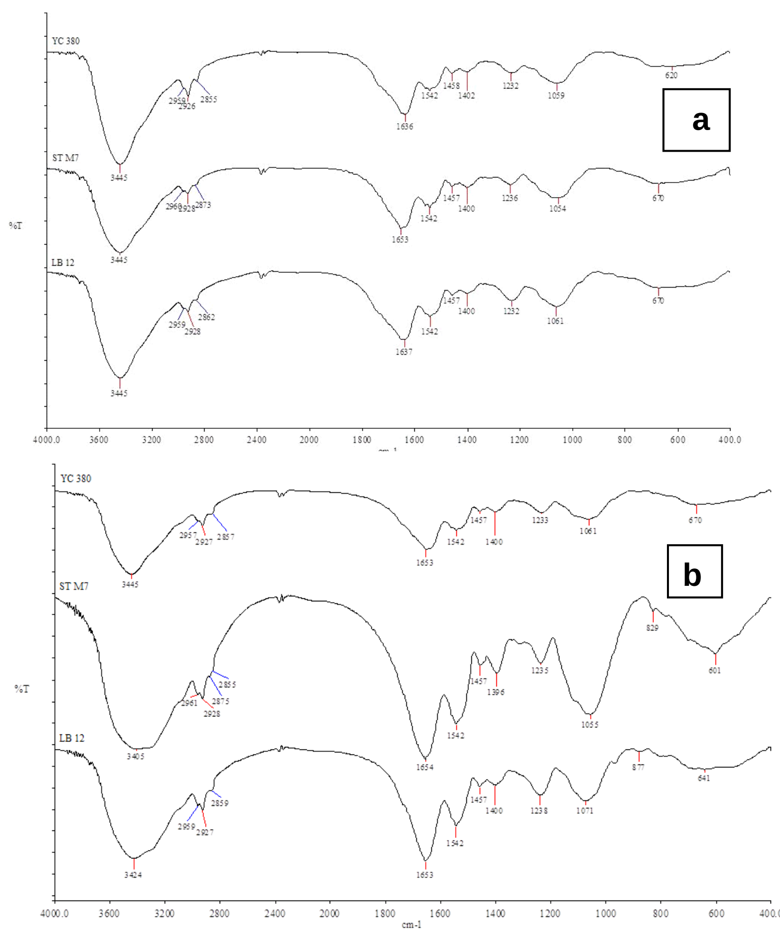

Fig. 3. FTIR spectra of the biomasses after the removal of Fe(II) (a) and Zn(II) (b) ions.

on the responses and contour plots between the factors (Ahmad & Hameed 2010; Anupam *et al.*, 2011). The response surface contour plots of Fe(II) and Zn(II) removal efficiency over independent variables such as biomass concentration (X_1) and pH (X_2) with biomasses were shown in Fig. 2. Fig. 2 shows the relative effects of two variables (X_1 and X_2) while the temperature of solution (X_3) was kept constant at its center point level (30 °C). In Fig. 2 (a-c) the response plots showed that by increasing the biomass (X_1) concentration, Fe(II) removal efficiencies did not change much. The main effect of pH (X_2) significantly enhanced the Fe(II) removal with all tested biomasses (Fig. 2a-c). Among the tested biomasses, Lb.12 appeared to be effective on the pH changes for Fe(II) removal. In other words, the main effect of pH was found to be the most significant with Lb.12 biomass. From Fig. 2(a-c) it can be concluded that, YC-380 biomass can be considered as the most efficient biomass among the tested biomasses in this study. Even if with the lowest biomass concentration and the lowest pH value, about 70% Fe(II) removal was achieved with the YC-380 biomass. This result may be due to the fact that YC-380 biomass contains dairy mix culture as both *Lactobacillus delbrueckii ssp bulgaricus* and *Streptococcus thermophillus*. On the other hand, Fig. 2(b, c) showed that only around 20% and 40% Fe(II) removal was achieved with ST-M7 and Lb.12 biomasses, respectively. Fig. 2(d-f) shows that the Zn(II) removal did not change significantly with biomass concentration (X_1). Besides, pH (X_2) showed almost the same effect for all three tested biomasses. The maximum percent Zn(II) removal was obtained about 75-80% at pH 9. The removal percentage of Zn(II) was increased from nearly 25% to 75% when the pH was increased from 3 to 9. Due to the fact that almost the same removals were obtained with all three biomasses for Zn(II) removal, it can be inferred that YC-380 is good enough biomass for removal of Zn(II) given the conditions set in this study.

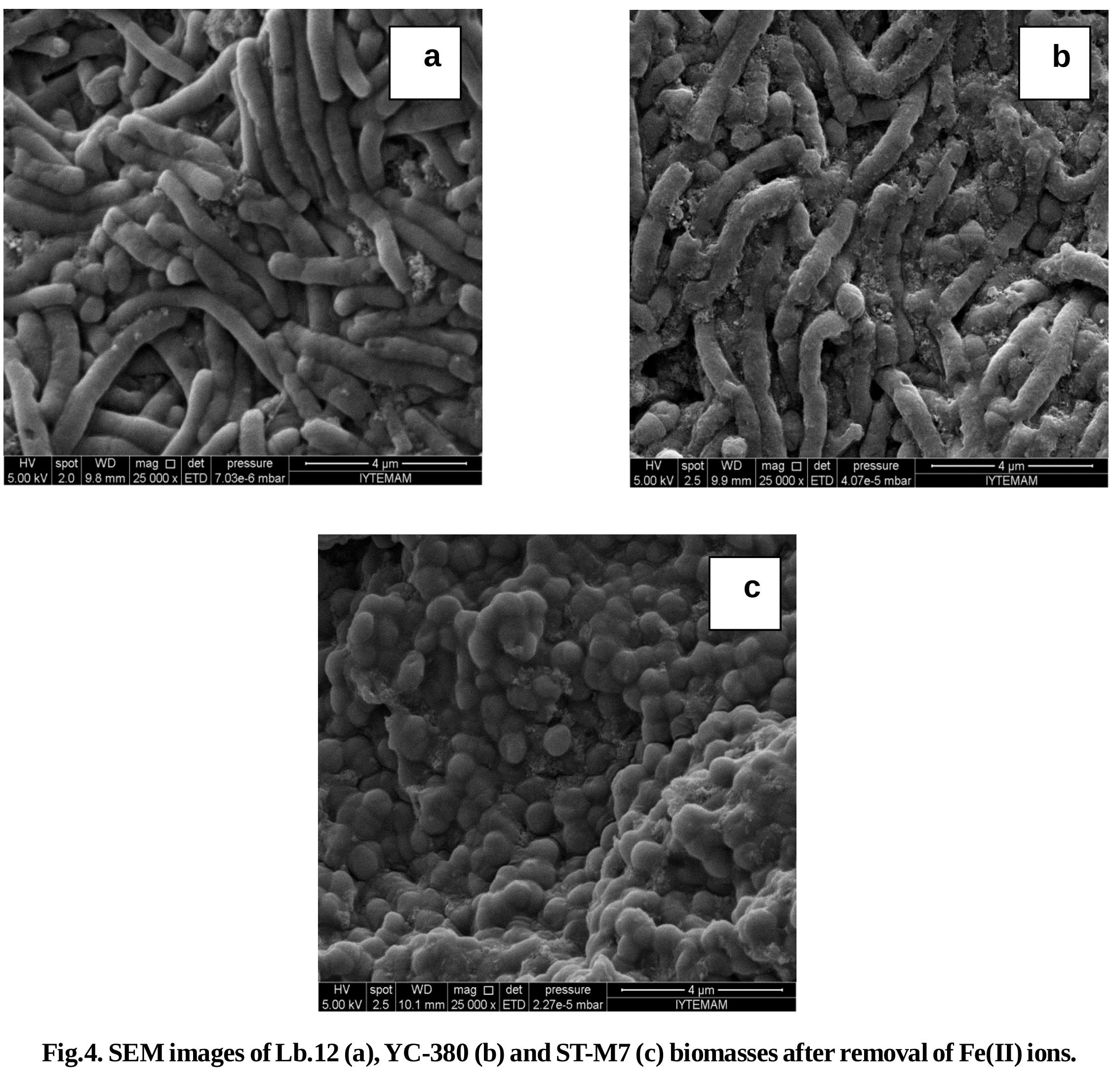

Fig.4. SEM images of Lb.12 (a), YC-380 (b) and ST-M7 (c) biomasses after removal of Fe(II) ions.

The FT-IR spectra after Fe(II) and Zn(II) removal with biomasses is shown in Fig. 3 a and b, respectively. All three biomasses after removal of Fe(II) and Zn(II) had a broad strong band at 3405-3445 cm^{-1}, corresponding to stretching of the O-H and N-H bond (Fig 3a,b). Similar peaks were observed also in other studies (Tan *et al.*, 2010; Jiménez-Cedillo *et al.*, 2013). Strong bands at 1636-1654 cm^{-1} indicates the presence of OH bending vibrations and also amide I and amide II vibrational modes, from the protein fraction (Pistorius *et al.*, 2009; Ferreria *et al.*, 2011; Veneu *et al.*, 2013). The absorption peak around 1050-1060 cm^{-1} are indicative of P-OH bands, Veneu *et al.*, (2013) observed these peaks as well. Furthermore, the FT-IR spectrums were indicated a number of absorption peaks at 600-670 cm^{-1} (indicative of C-H groups). (Selatnia *et al.*, 2004). These FT-IR results showed that investigated biomasses contain carboxyl and hydroxyl groups and these groups may be involved in coordination with Fe(II) and Zn(II) metal ions (Ashkenazy *et al.*, 1997; Veneu *et al.*, 2013). Fig. 4 shows the SEM images of the Lb.12 (a), YC-380 (b) and ST-M7 (c) biomasses after removal of Fe(II) ions. Similar SEM images were also obtained with these biomasses after Zn(II) ions (data not shown). As it seen from Fig.4, the Lb.12 biomass (Fig. 4a) showed a bacillus structure, YC-380 biomass (Fig. 4b) showed both bacillus and coccus structure, and ST-M7 showed coccus structure. As it was expected, YC-380 biomass contains dairy mix culture as both *Lactobacillus delbrueckii ssp bulgaricus* and *Streptococcus thermophillus*. The coverage of the surfaces with Fe(II) ions were observed with all biomasses.

CONCLUSIONS

The present study is based on the removal of Fe(II) and Zn(II) ions by the three different biomasses such as Lb.12, YC-380, and ST-M7. A 2^3 full factorial design was applied for determine the experimental conditions and analysis of results. Removal results showed that YC-380 might be a promising biomass alternative to ST-M7 and Lb.12 in removing Fe(II) and Zn(II) ions from waters. This result may be due to the fact that YC-380 biomass contains mix culture as both *Lactobacillus delbrueckii ssp bulgaricus* and *Streptococcus thermophillus*. The ANOVA results indicated that the main effect of pH (X_2) significantly important for both Fe and Zn removal with all tested biomasses. The FT-IR spectroscopy and SEM images also supported the removal of Fe(II) and Zn(II) with biomasses. In conclusion, the removal process for Fe(II) and Zn(II) by YC-380 biomass was found to be simple and efficient.

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