MAGNETIC NANO-BIOSORPTION OF HEAVY METAL FROM AQUEOUS SOLUTIONS USING SUGARCANE BAGASSE[*]

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Abstract– Uranium in the environment is hazardous to human health and requires better methods for detection and remediation. Bioadsorbent coated on nanocrystalline iron oxides offers a number of advantages as sorbents for water purification and environmental remediation. In this study, first highly uniform and crystalline iron oxide nanocrystals (nMAG) were prepared using iron salts in presence of NaOH by co- precipitation process and then sugarcane bagasse coated on synthesized iron oxide nanocrystals has been used as a bioadsorbent for uranium solution with low concentration. The effect of different parameters on optimum function of this process has been analyzed. The results showed that maximum uranium absorption occurs at pH levels of about 3. Optimum amounts of biomass, uranium concentration and contact time are 0.1 gr, 50 ppm and 120 min, respectively. Thus, the uranium biosorption by magnetic biosorbent can be considered a potential technology of treatment process for uranium removal in which the adsorbents and the adsorbed pollutant can be quickly recycled by simply applying a magnet.

1. INTRODUCTION

Magnetic nanoparticles have been synthesized in different methods[1, 2]. Iron oxide nanoparticles were produced from $FeCl_3 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$ by adding ammonia solution (3.2M), after that produced nanoparticles were centrifuged and washed [3, 4]. Other methods such as using $FeCl_3 \cdot 6H_2O$ and iron sulphate in presence of ammonia by argon atmosphere, $FeCl_3 \cdot 6H2O$, $FeCl_2 \cdot 4H2O$ and NaCl in presence of NH_4OH, and $FeCl_3 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$ in presence of HCl (0.5M) have been suggested for nanoparticles synthesis[5-7]. The synthesized sample by magnetic nanoparticles has various applications in adsorption of so many different heavy metals. For example, it was used for removing Cr (VI) from wastewaters and the adsorption capacity was found to be very high[8]. Recently the most common method which has been used for heavy metal removal is biosorption. The word 'biosorption' consists of using biomass as polymeric matrix. The biomasses, because of their significant advantages such as: cheapness, availability, recycleability and etc. are the most common materials used in adsorption processes [9, 10]. Biosorption is effective for both organic and inorganic pollutants (heavy metals) as investigated by many researches [11-21]. Sugarcane bagasse is one of the inexpensive biomasses which can be found in Iran with high quality. Preparation of biosorbent and its use as a polymeric matrix for magnetic nanoparticles embedding is a method with high level of efficiency to remove the heavy metals from wastewaters and

aqueous solutions [15-17]. In this study the sorption of uranium (VI) ions on nano magnetite oxide coated by sugarcane bagasse from aqueous solutions has been investigated.

2. EXPERIMENTAL

a) Materials

All commercial reagents were purchased from Merck. The sugarcane bagasse used came from Ahwaz province, Iran, and was provided by the Sugar Cane Development & By- Products Commercial Co. (SUDCCO), Uranyl Nitrates were provided by Iran Atomic Energy Organization.

b) Preparation

The sugarcane had impurities and had to be purified. The sugarcane bagasse was washed with water several times to purify it from impurities, cut and sieved. The sieve used for this process was 125 micron. Then, sugarcane bagasse was placed in a furnace at 300°C, after that it was powdered. Magnetic nanoparticles were synthesized by using $FeCl_3 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$ in presence of NaOH by co-precipitation process. At first, 2.35gr $FeCl_3 \cdot 6H_2O$ and 0.86gr $FeCl_2 \cdot 4H_2O$ were added into the 3- inlet baloon, then by adding 19mL distilled water and 1mL HCl (37%), 30mL NaOH (1M) was added drop by drop to the system thorough the burette on top of the baloon during a period of about 20 minutes. Before opening the burette valve which contained NaOH, the produced sugarcane bagasse carbon in the last stage was added to the balloon (about 2gr) and by pouring sodium hydroxide, the black precipitate was seen. After 20 minutes of stirring, the process was stopped and the solution was placed on a magnet. At this stage, the solution was separated into two phases, 1st is the clear water on top, and 2nd is the precipitate at bottom, under the effects of magnetic field. The precipitate was washed 3 times by distilled water to remove the sodium chloride which formed during NaOH pouring. Finally, the precipitate was inserted into an oven at about 80 °C. After drying, the precipitate was powdered and sent to SEM analysis for characterization. The produced material in this process was called magnetic nano- biosorbent powder.

c) Characterization

The XRD spectra was used for determining the crystallographic identity of the sugarcane carbon coated with magnetic nanoparticles, phase purity, and for calculating the mean particle size based on the broadening of the most prominent peak in the XRD profile. CHN analysis was done to characterize the sugarcane sample and scanning electron microscopy (SEM) was used for the determination of morphology and size distribution of sugarcane carbon coated with magnetic nanoparticles in the scales of 1micron and 500nm. Table 1 shows the amount of carbon, nitrogen and hydrogen from CHN analysis. Furthermore, scanning electron microscopy (SEM) was used to determine the particle size and morphology.

Table 1. CHN analysis of sugarcane bagasse

Content	Amount (W/W%)
N	0.77
H	3.93
C	29.07

3. RESULTS AND DISCUSSION

a) Formation of magnetic nanoparticles

Diffraction peaks reveal the good crystallinity of the Fe_3O_4 specimens, located at 2θ of 21.8, 37.4, 44.3, 54.9, 69.4, 74.2 and 82.5. In the XRD pattern of freshly synthesized sugarcane carbon coated magnetic nanoparticles, no signal for the hematite (Fe_2O_3) and halite (NaCl) was observed.

XRD patterns of the sugarcane carbon coated with magnetic nanoparticles are shown in Fig. 4. The crystallite sizes were calculated the using Scherrer equation:

$$D = \frac{k\lambda}{\beta Cos\theta}$$

(1)

Where k is a constant about 0.9, λ is the wavelength of the X-rays, β is the full width of diffraction peak at half maximum intensity and θ is the Bragg angle. The calculated crystallite sizes were found to be in the range of 35–44 nm.

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┌─────────────────────┐              ┌─────────────────────┐
│    FeCl₃·6H₂O       │              │    FeCl₂·4H₂O       │
└─────────────────────┘              └─────────────────────┘
              │                                │
              └────────────────┬───────────────┘
                               ▼
              ┌──────────────────────────────────┐
              │     19cc H₂O + 1cc HCL(37%)       │
              └──────────────────────────────────┘
                        │            ◄──── ┌──────────────────┐
                        │                  │ Sugarcane carbon │
                        │                  └──────────────────┘
    ┌──────────────┐    │
    │  20cc NaOH   │──► │
    └──────────────┘    ▼
              ┌──────────────────────────────────┐
              │  Precipitation of iron oxide in   │
              │           nano scale              │
              └──────────────────────────────────┘
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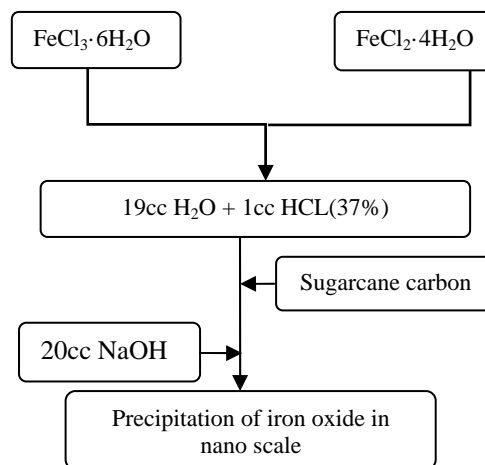
Fig. 1. Stages of magnetic nanoparticle formation

Figures 2 and 3 show the SEM micrograph for iron oxide in nano scale in 1micron and 500nm, respectively, which indicated low agglomeration and semi spherical in shape.
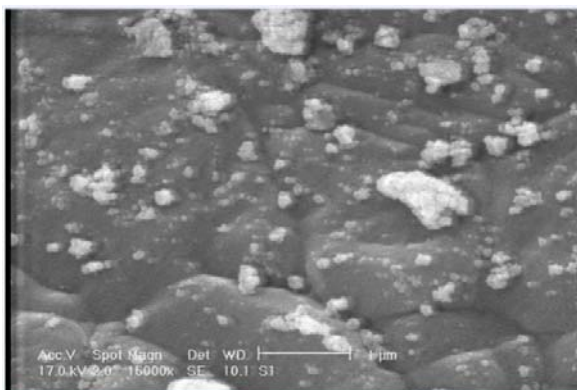

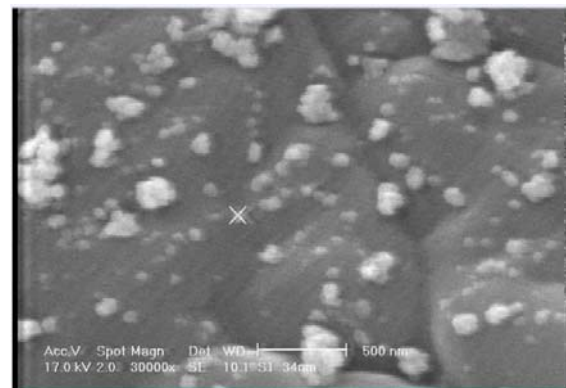Fig. 2. SEM graph of sugarcane carbon coated with magnetic nanoparticles (1 micron)

Fig. 3. SEM graph of sugarcane carbon coated with magnetic nanoparticles (500 nm)
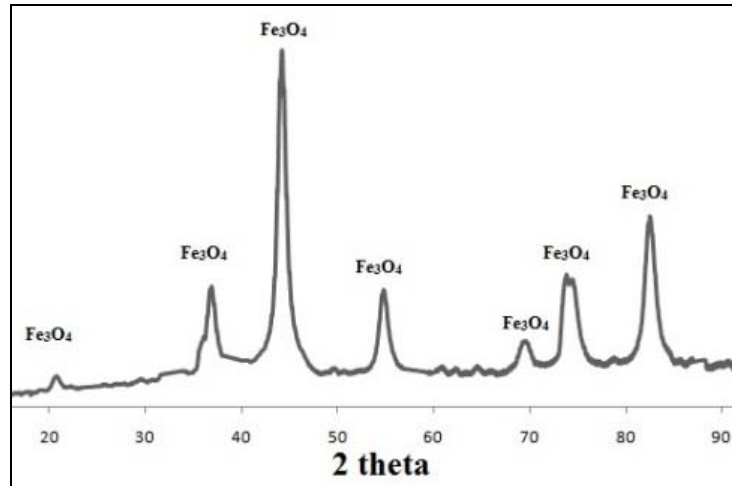
Fig. 4. XRD pattern of sugarcane carbon coated with magnetic nanoparticles

4. ADSORPTION PROCESS

Batch adsorption experiments were conducted at $(27 \pm 2)°C$ by agitation with 2 mL uranyl nitrate solution and an amount of magnetic biosorbent. After stirring at specified speed and time, the supernatant was separated by Liquid Syntillation Counter (L.S.C.) The removal percentage was determined by this equation:

Removal % = (C0 – C) x 100/C0

Where,

C0 = concentration of U ions (mg.L-1), before the contact;

C = concentration of U ions (mg.L-1), after the contact.

The uranium mass adsorbed per gram of magnetic biosorbent was calculated by difference between the U concentration of the solution before equilibrium and in the equilibrium, multiplied by the uranium volume used in batch experiment and divided by magnetic biosorbent mass. The adsorption capacity was determined as:

Capacity of adsorption (mg.g-1) = (Co - C) x V/M

Where,

V = volume of uranyl ions solution (L) in contact with the magnetic biosorbent;

M = mass (g) of the magnetic biosorbent.

5. RESULTS AND DISCUSSIONS

a) Influence of solution pH

The pH is one of the most important parameters on adsorption of metal ions from aqueous solutions. The contact time between solution's uranium and magnetic biosorbent was fixed at 120 min. The results are illustrated in Fig. 5. Uranium removal by magnetic biosorbent increased varying pH from 2 to 8. The H+ competition with uranyl ions at lower pH and the formation of $UO_2 (OH)_3$- uranium species at higher pH explain the lower adsorption on the biosorbent surface which is negatively charged. The similar results were found for the adsorption of uranium from aqueous phase using nano magnesium oxide by Camtakan et al. [22].
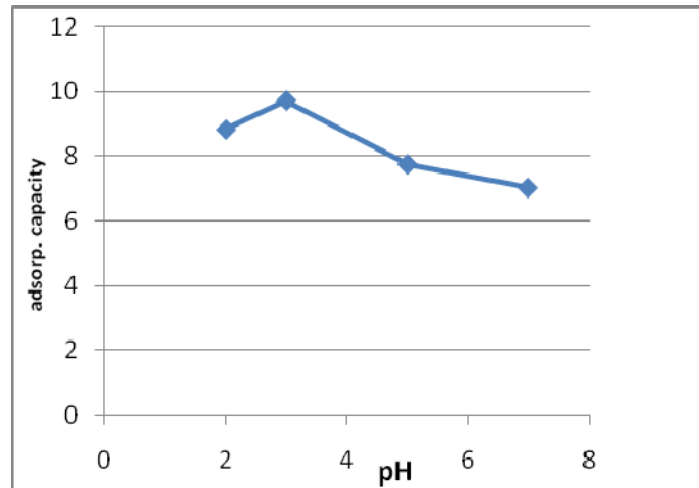
Fig. 5. Influence of pH on uranium (VI) removal (%). Variables fixed: time at 120 min, biosorbent dose 5 g.L-1, and initial concentration 50 mg.L-1.

b) Influence of contact time and kinetics

The adsorption experiments were carried out for different contact times with fixed biosorbent dose at 5 g.L^{-1}, pH 3, and concentration initial 50 mg.L^{-1}. The results were plotted in Fig. 6, which indicates that the equilibrium for uranium adsorption was attained in 120 min of contact with 98% adsorption and can be analysed by both Langmuir and Freundlich isotherms which will be presented later.
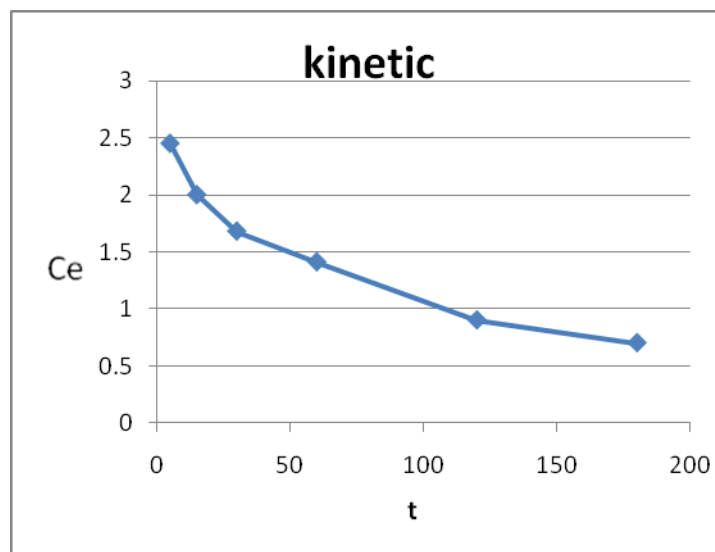

Fig. 6. Influence of contact time on uranium (VI) removal (%).

c) Influence of biosorbent dose

In this paper the magnetic biosorbent dose was defined as the amount of magnetic biosorbent in contact with a determined volume of uranium solution. The biosorbent concentration varied from 1 g.L-1 to 7 g.L-1, pH 3 and the stirring time was fixed at 50 min. The results of 98% removal and the adsorption capacity of 10 mg.g-1 are attained and shown in Fig. 7.
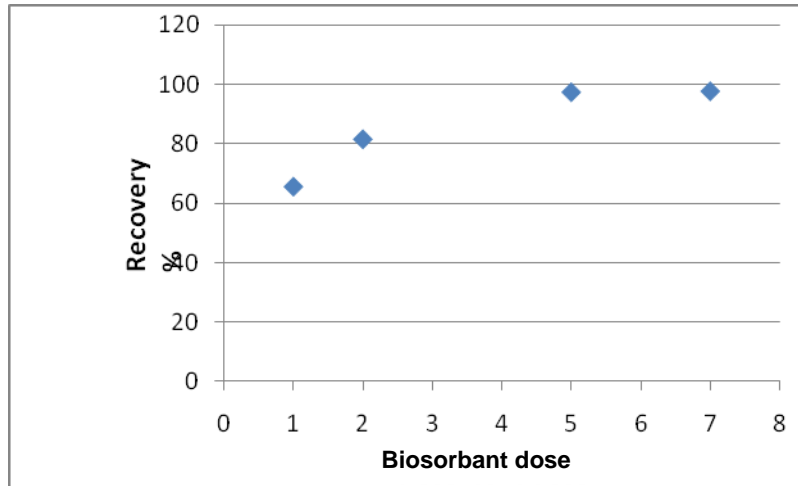
Fig. 7. Influence of biosorbent dose on uranium (VI) removal (%). Variables fixed:
pH 3, 3 3 initial concentration 50 mg.L-1

d) Influence of initial concentration of uranyl ions

The initial concentration of uranyl ions varied from 10 mg/L to 200 mg/L, pH 3 and the stirring time was fixed at 50 min. The results of 98% removal are attained and shown in Fig. 8.
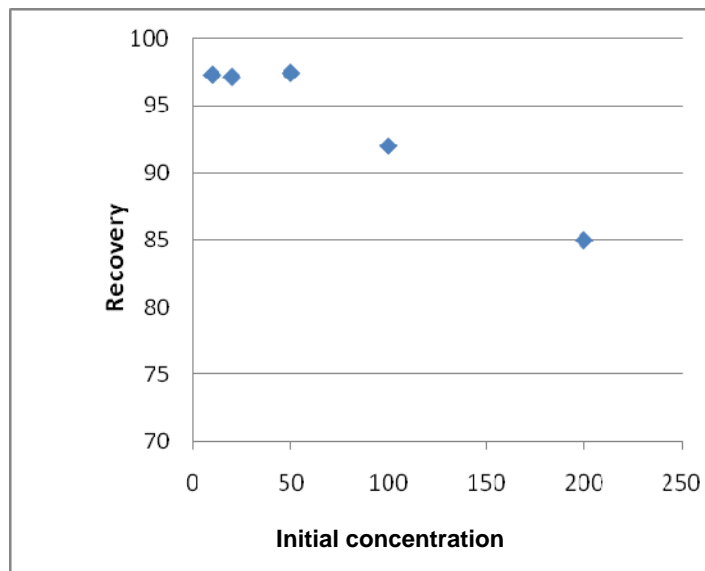

Fig. 8. Influence of initial concentration of uranyl ions on uranium (VI) removal (%).
Variables fixed: pH 3, optimum initial concentration 50 mg.L-1

6. ADSORPTION ISOTHERMS MODELS

The models of Langmuir and Freundlich isotherms were studied for the equilibrium adsorption isotherm for the uranium, varying the concentration from 10 to 200 mg/L.

Plot of specific sorption, Ceq/Qeq versus equilibrium concentration, Ceq for uranium is shown in Fig. 9.

The Langmuir isotherm was found to be linear over the entire concentration range studied with high r^2 value, which suggest being a good model for this sorption system.

The values of Qm and KL were determined from the slope and intercept of the linear plots of Ceq/Qeq versus Ceq and presented in Table 2.
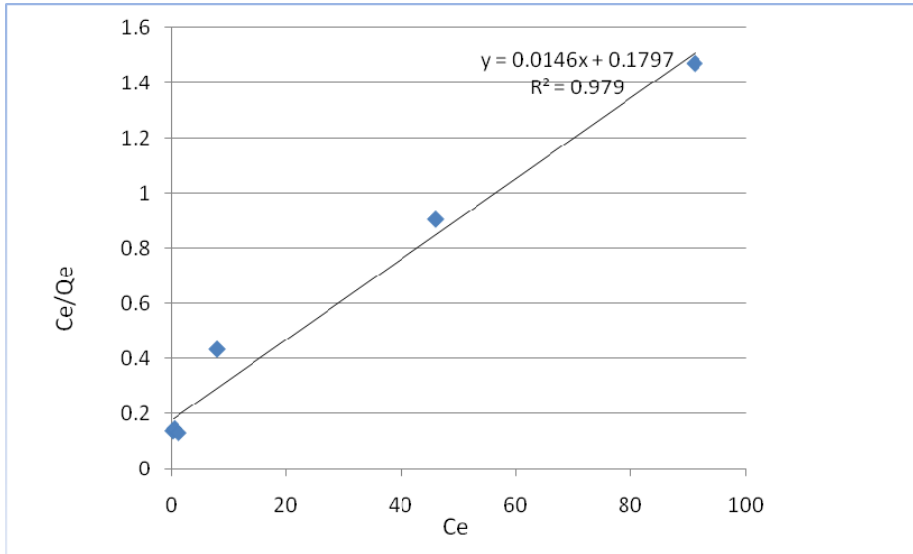
Fig. 9. Linear Langmuir isotherm for uranium adsorption process by magnetic biosorbent

The linear Freundlich isotherm for the sorption of the uranium on magnetic biosorbent is presented in Fig. 10. The values of kf and 1/n were determined from the slope and intercept of the linear plot of ln Qeq versus ln Ceq, and are shown in Table 3.
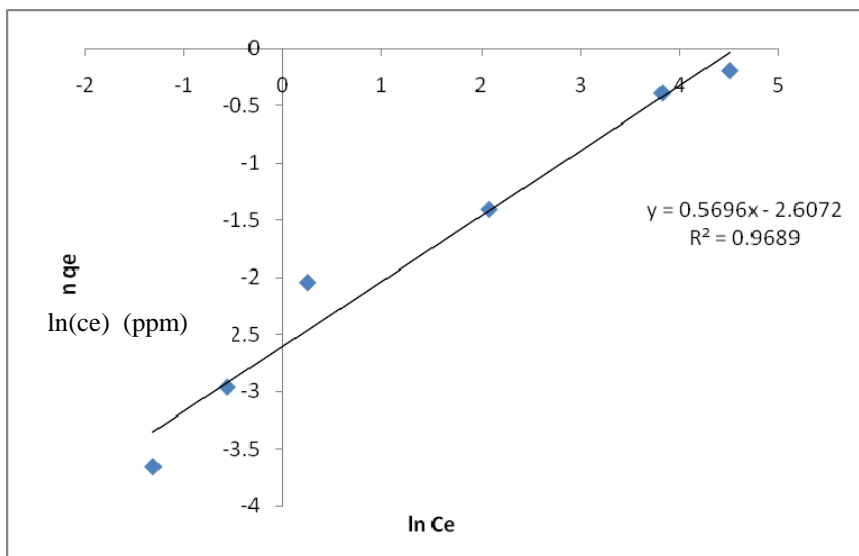

Fig 10. Linear Freundlich isotherm for uranium adsorption process by magnetic biosorbent

The better fit occurred with both Langmuir and Freundlich linear isotherms, with high r^2 value, 0.979 and 0.968 respectively, which can be observed in the table below. The values of r^2 are regarded as a measure of the goodness fit of experimental data on the isotherms models (Table 3).

Table 2. Langmuir parameters

b_L	R^2	q_{max}	R_L
0.0025	0.979	71.42	0.88

Table 3. Freundlich parameters

R^2	n	k_f
0.968	1.757	0.356

7. CHARACTERIZATION SUGARCANE CARBON COATED WITH MAGNETIC NANOPARTICLES AFTER URANIUM BIOSORPTION

Figures 11 and 12 show the SEM micrograph for iron oxide in nano scale after biosorption process in 1micron and 500nm, respectively, which indicated formation of uranyl ions on the synthesized biosorbent.
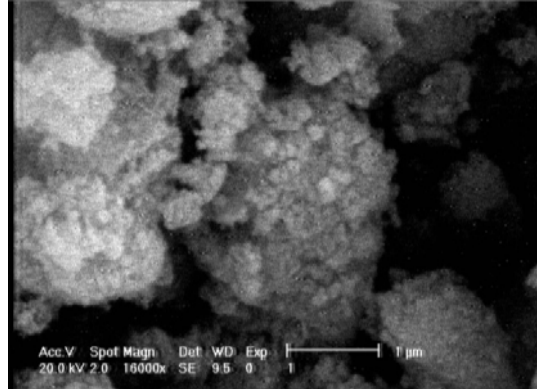

Fig. 11. SEM graph of sugarcane carbon coated with magnetic nanoparticles after
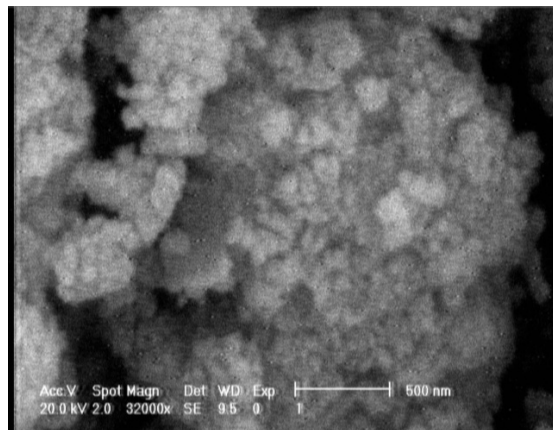uranium biosorption process (1 micron)

Fig. 12. SEM graph of sugarcane carbon coated with magnetic nanoparticles after
uranium biosorption process (500 nm)

8. CONCLUSION

The objective of this work was to study the sorption of uranium (VI) ions on nano magnetite oxide coated by sugarcane bagasse from aqueous solutions. The nano iron oxide has been prepared via hydroxide precipitation. The adsorbent was characterized by X-ray powder diffraction and scanning electron microscope. The relative importance of test parameters such as concentration of adsorbate, pH and contact time on adsorption performance of adsorbent for U(VI) ion were studied and the optimum sorption efficiency was found to be 98.0 %. Adsorption of uranium (VI) by magnetic biosorbent was highly pH dependent. The optimum adsorption occurred at pH level of about 3. Besides, it was verified that the equilibrium for uranium adsorption was attained in 120 min of contact. The uranium adsorption at dose 5 g.L-1 was of 98% under studied conditions. The equilibrium isotherm correlated to both Langmuir and Freundlich isotherms, as adsorption maximum capacity of 10 mg of uranium per g biosorbent was found. Thus, the uranium biosorption by magnetic biosorbent can be considered a potential technology of treatment process for uranium removal.

More research is needed to study the size-dependence of the magnetic separation efficiency of nanocrystals; generally as the diameter of particles increased they could be removed under lower applied

magnetic fields. Magnetic separation could be used as a tool to separate broadly distributed populations of magnetic materials. Such work makes it possible to use these materials in multiplexed separation and sensing schemes.

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