New Filamentary Nano Adsorber GZ-BAKI-TAC-Co-88 for Rapid Removal of Cobalt Ion from Aqueous Solutions Using Beshel Tire Activated Carbon

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Abstract

Cobalt is a natural element found throughout the environment. Acute (short-term) exposure to high levels of cobalt by inhalation in humans and animals results in respiratory effects, such as a significant decrease in ventilatory function, congestion, edema, and hemorrhage of the lung.In agriculture solid waste, was chemically treated and used for the adsorption of Co (II) from aqueous solutions. The efficiency of this new adsorbent was studied using batch technique under different experimental conditions such as sorbent amount, initial metal-ion concentration, and contact time. In this project the separation of ion heavy metal cobalt (II) using new filamentary adsorber for Removal of contaminants in environmental were investigated. The purpose of this research work is to build a new nano-absorber, GZ-BAKI-TAC-Co-88, for the adsorption of water soluble chromium ions in polluted water. The sorbent for separation are made by using sodium alginate, Calcium chloride and Beshel Tire activated carbon with nano-holes. The filamentary length of adsorber was 10 cm and 300 µm in diameter in wet state. The tests were done in discontinuous system. The adsorption capacity and the kinetic of maximum percent by metal concentrations in 50, 80,100and 120 ppm were studied. The amount of cobalt uptake was 40.34%, 54.98%, 37.97% and 42.54 % respectively. For kinetic reaction times, 10, 20, 30,40,50,60 and 120 minutes were selected. The maximum adsorption of cobalt (II) achieved 54.989% in 120 minutes with 80ppm primary concentration of cobalt. The share of adsorption was calculated and the results shown that 80% of Co-Adsorption belongs to Tire activated Carbon and 20% to Alginate. The capacity of adsorption with 30 mL of 80 ppm Co and share of 1% of Activated Carbon and with assumption of 50% effectively of adsorber

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surface was 2880 mg Co/g Activated Carbon. Results indicate that the new adsorber calcium alginate filamentary containing activated carbon with nano-holes has good adsorbing character for removal of cobalt (II) in polluted effluent. With increasing of activated carbon in sodium alginate increased the amount of cobalt (II).Scanning Electron Microscope Images from powder activated carbon from tire shows the macro, meso and micro pore before and after adsorption

Key Words: Activated carbon, tire, alginate, Cobalt (II), heavy metal, SEM.

Introduction

Water pollution is the contamination of water bodies such as lakes, rivers, oceans, and groundwater caused by human activities, which can be harmful to organisms and plants which live in these water bodies. Water pollution by toxic heavy metals through the discharge of industrial waste is a worldwide environmental problem. The presence of heavy metal in streams, lakes, and groundwater reservoirs has been responsible for several health problems with plants, animals, and human being. Studies proved that metals such as copper, lead, zinc, cobalt, nickel, chromium, and mercury which have been considered as hazardous heavy metals are very toxic elements and they are commonly found in water and wastewater. So, the removal of these metals from wastewater is necessary. A number of processes exist for the removal of metal pollutions from wastewater, viz. precipitation, electroplating, ion-exchange, solvent extraction, and membrane separation. These processes have several disadvantages such as incomplete metal removal, high reagent and energy requirement and generation of toxic sludge/waste products that require disposal and further treatment. This led to the need to develop an effective, low-cost, and environment friendly process for wastewater treatment. Adsorption is an efficient and economical process used for the removal of heavy metals from industrial wastewater. A low-cost adsorbent is defined as one which is abundant in nature, or is a by-product or waste material from another industry. The review concluded that these low-cost processes involved the use of activated carbon and ion changers. The cost of these biomaterials and mineral materials are negligible compared with the cost of activated carbon or ion-exchange resins. The removal of heavy metals from industrial wastewater is considered an important application of adsorption processes using suitable adsorbent. Cobalt is also present in the wastewater of nuclear power plants. The permissible limits of cobalt in the irrigation water and livestock wastewater are 0.05 and 1.0 mg/L, respectively (Environmental Bureau of Investigation, Canadian Water Quality Guidelines). The acute cobalt poisoning in humans may cause serious health effects e.g. asthma like allergy, damage to the heart, causing heart failure, damage to the thyroid and liver. Cobalt may cause mutations (genetic changes) in living cells. Exposure to ionizing radiation is associated with an increased risk of developing cancer. Cobalt is relatively rare element found in the earth's crust with a concentration of approximately 25 mg/g, (Hamilton, 1994). Although it occurs naturally in the environment, due to anthropogenic activity excessive amounts of cobalt are released from coal combustion and mining, processing of cobalt-containing ores and the production and use of cobalt chemicals. Cobalt has variety of uses: as a metal in electroplating, because of its hardness and resistance to oxidation, in alloys with iron, nickel and other metals, and also in magnet and stainless steels. Its salts have been used for centuries for the production of blue colors in porcelain, glass, pottery, and enamels, while compounds are used as paint pigments. Radioactive, artificial isotope cobalt-60 is an important gamma-ray source and is used extensively as a tracer and radio therapeutic agent (Schö¨nfeld *et al*., 2002). In small amounts

cobalt is essential for human health, because it is a part of vitamin B12. However, higher concentrations of cobalt may damage human health. Soils near mining and melting facilities may contain very high amounts of cobalt. Once it has entered the environment, it may react with other particles or adsorb on soil and sediments. Under acidic conditions, cobalt becomes mobile causing its accumulation in plants and in animals and humans that eat these plants. The sorption studies of Co2+ are essential for nuclear and hazardous waste management. Different inorganic and organic sorbents have been considered for Co2+ immobilization: vermiculite (da Fonseca *et al*., 2005), zeolite (Erdem *et al*., 2004), kaolinite (Yavuz *et al*., 2003), hydrous manganese oxide (Granados Correa & Jime´nez-Becerril, 2004), activated carbon (Demirba, 2003), marine green alga (Vijayaraghavan *et al*., 2005a). Inorganic exchangers have interesting properties such as resistance to decomposition in the presence of ionizing radiation or at high temperatures, which have made them interesting for the treatment of nuclear waste. ARTICLE IN

Alginates are commercially extracted from brown seaweed (Phaeophyceae) and utilized in the food and pharmaceutical industries because of their gelling, viscosifying and stabilizing properties (Draget, Moe, Skjik-Br,k, ; Smidsrd, 2006). From a structural point of view, alginates are linear polysaccharides composed of (1–4) linked b-D-mannuronic acid (M) and a-Lguluronic acid (G) arranged in a blockwise pattern along the chain as homopolymeric (MM or GG) or heteropolymeric (MG) regions. The M/G ratio and blockwise pattern vary according to season, age of population, species and geographic location (Haug Larsen & Smidsrd, 1974; Indergaard,Skjik-Br,k,& Jensen,1990; Stockton, Evans, Morris, Powell, & Rees, 1980). Therefore, access to reliable methods for compositional analysis of alginates is essential, and for screening of large sample sets and quality control, rapid analytical methods requiring limited sample preparation are of great importance. 1H nuclear magnetic resonance (NMR) spectroscopy has proven to be highly effective in the characterization of alginates in solution (Grasdalen, 1983). However, at the concentrations suitable for an acceptable signal-to-noise ratio, alginate solutions are too viscous to give well-resolved spectra. Thus, the viscosity must be lowered by partial acid hydrolysis of the alginate chain, which is a relatively time-consuming and labor intensive procedure and perhaps more important the hydrolysis will alter the sample significantly compared to the intact sample. Another issue related to the analysis of alginates in solution is the possible selective micro-aggregation when divalent cations (e.g. calcium ions) are present. Calcium ions preferentially bind to the G-blocks (Draget *et al*., 2000), resulting in G-block association and the formation of a gel network. This can give rise to a broadening of the 1H NMR resonances originating from the G-units beyond the level of detection (Grasdalen, Larsen, & Smidsrd,1981), resulting in an overestimation of the M/G ratio.(Fig1&2)
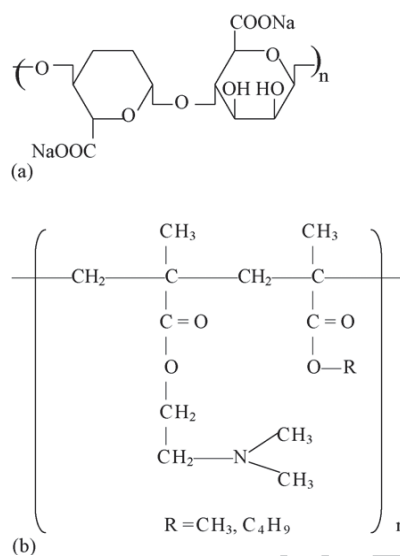
(a)

(b)
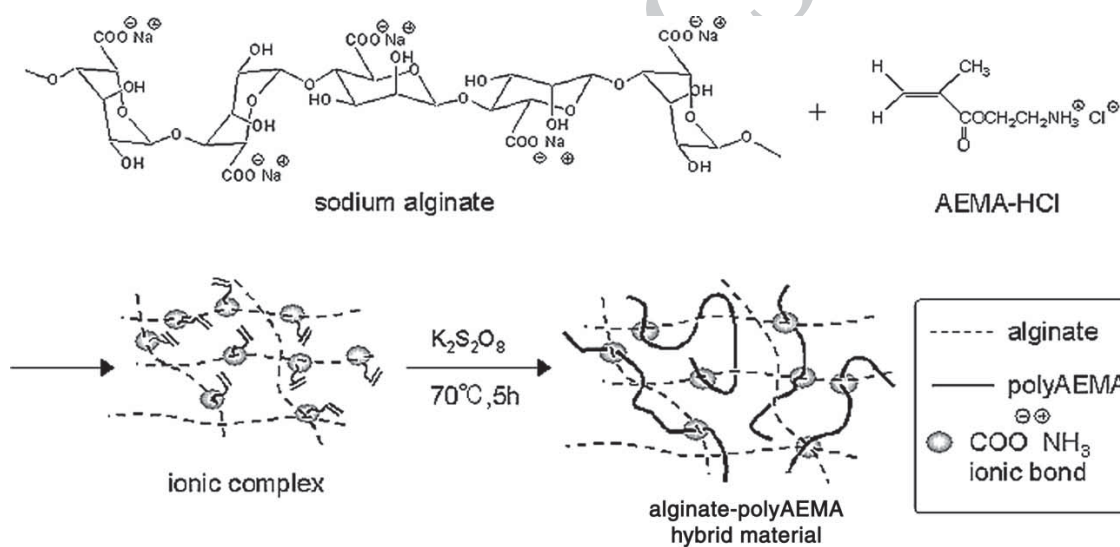Fig 1. Molecular structures of alginic acid (a) and Eudragit E 100

Fig 2. Schematic image for preparation of hybrid material by polymerization of 2-aminoethyl methacrylate hydrochloride in the presence of sodium alginate

Carbon nanotubes (CNTs), a novel kind of carbon, were first reported by Iijima in 1991.CNTs can be thought of as cylindrical hollow micro-crystals of graphite. Because of relatively large specific area, CNTs have attracted researchers' interest as a new type of adsorbent and offer an attractive option for the removal of metals, fluoride, organic pollutants, and radionuclide 243Am(III) **(Yang, 2006; Gauden, 2006; Peng**, 2003; **Lu, 2005)**. CNTs can also be used as supports for adsorption materials. Aluminum and iron oxide-coated CNTs for metal removal have been proved successful for the enhancement of treatment capacity **(Peng, 2005**. **Li, 2001)**. Compared to Fe or Al oxides, Mn oxides have a higher affinity for many heavy metals and it was coated on activated carbon, zeolite, and sand for metal ions removal **(Sahoo**, 2001; **Fan**, 2005; **Han, 2006)**.

Materials and methods
All solution for the metal sorption experiments were prepared using $CoCl_2$purchased from Merck. Sodium Alginate ($NaC_6H_7O_6$) and Calcium Chloride $CaCl_2$ with 99% purity made by

Merck. The activated carbon from tire was prepared by Beshel Active Carbon(BAKI) .   All solutions were made by using distilled water.

.Alginate bead preparation

 Solutions of 4% w/v of Sodium Alginate were prepared with dissolving 4 g of it in 100cc of distilled water. By using magnet, Sodium alginate is dissolved with 0.04 g Activated Carbon nano powder without water, after that slowly in water and make jelly solution .

The solution was left 25min to degas and 50cc of the alginate and activated carbon solution was used to build filament into 250ml 0.5 mol/l $CaCl_2$. The 0.5 molar solution of calcium chloride is prepared by dissolving 13.8 g of it in 250 ml distilled water at room temperature . The diameter and length of this filament are between 3mm to 10 cm.

We call this beads GZ-BAKI-TAC-Co-88.(Fig3)

Fig3. Filament adsorber GZ-BAKI-TAC-88

Empirical method

$CoCl_2$ solution was prepared with using Merck salt were dissolved in ultrapure water , then was poured in four 100 ml erlens.

The absorption method was used in this experiments was the discontinues system(batch).

The initial concentration were tested 50,80,100& 120 ppm in this research.

Results

Effect of pH

The pH of the metal solutions usually plays an important role in the biosorption of metals. preliminary studies of GZ-BAKI-TAC-Co-88 on the base of Cobalt revealed that highest Co uptake was observed at pH= 4. Further increase or decrease in pH resulted in decrease Co uptake. This may be due to nature of binding sites in alginate beads .

Also hydrogen ion competition at low pH and solution of chemistry of metal are other important factors responsible for variation of metal uptake at different pH values.(Davis et al ,2000).(Table1 & Fig 4)

Time	pH	Ci	Ce	Y
120	3	80	60.04	24.950
120	4	80	74.3	7.125
120	5	80	57.288	28.390

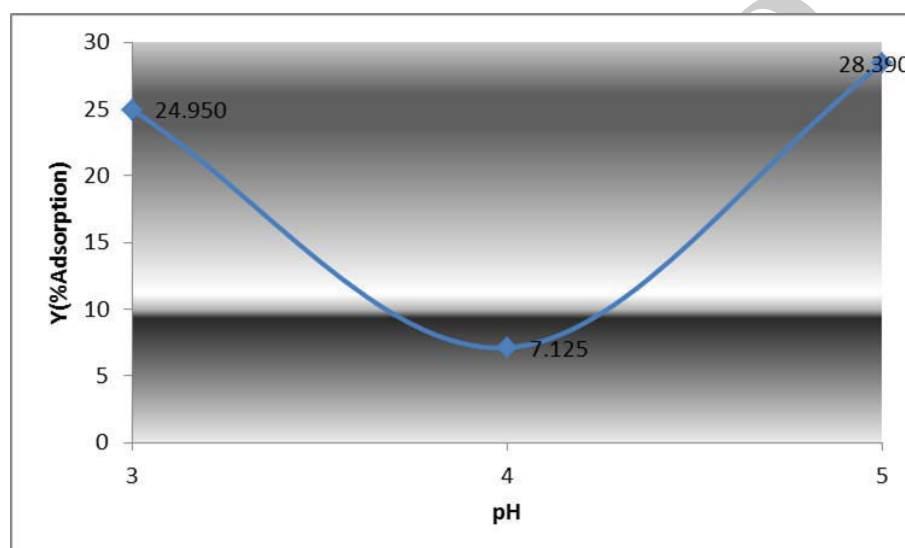Table 1. Effect of pH in 120 ppm Co

Fig. 4 :. Effect of pH in 120 ppm Co

Effect of retention time

The results of the different experiments showed that by increasing retention time , the remained concentration of heavy metals in the solution was reduced. 120 minutes retention time for removing the metal was enough. However increase in retention time from 10 min to 120 min resulted in decrease the remained concentration of heavy metal . kinetic studies (at pH =5) showed that about 54.989% of the total metal ions adsorption occurred within 120 min.

Also by increasing initial concentration, the metal uptake was increased. the maximum uptake for Co with initial concentration 80 ppm and pH=5 with using GZ-BAKI-TAC-Co-88 were obtained 54.989% at 120 min.(Table 2 & Fig 5)

Table 2. Effect of retention time in 80 ppm Co

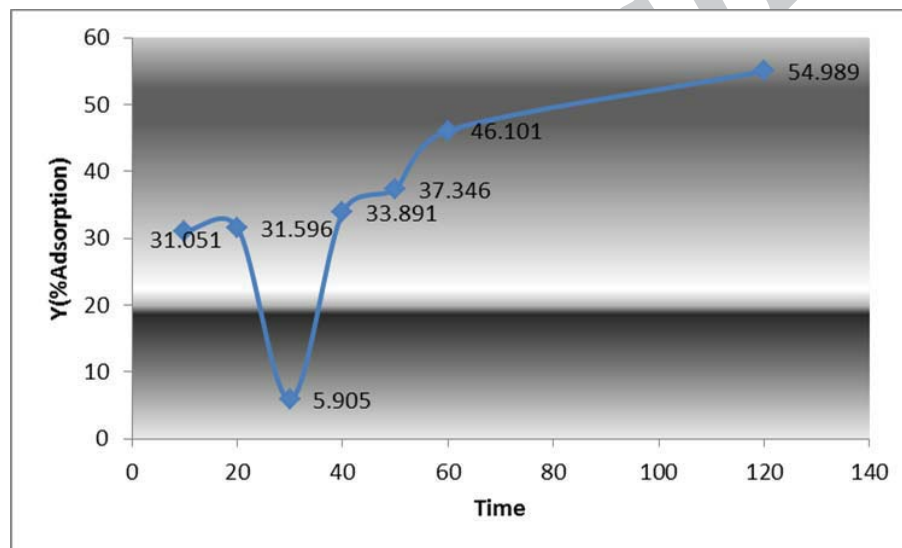| Co	80ppm		
Time	Ci	Ce	Y
10	80	55.159	31.051
20	80	54.723	31.596
30	80	75.276	5.905
40	80	52.887	33.891
50	80	50.123	37.346
60	80	43.119	46.101
120	80	36.009	54.989

Fig.5 : The effect of retention time initial concentration of Co 80 ppm

Calculation of adsorption capacity:

The adsorption capacity are calculated according the following H-equation :

X/M= V*C*P(AC)*P(Co)/m
    m= A*F
    A= [(B+C)/B]*100
X=Amount of adsorbed Co [mg]
M=Amount of Tire Activated Carbon [g]
V=Used volume of Co in experiment [mL]
C=Concentration of Co [mg/mL]
P(Co)= Adsorption percentage of Co
P(AC)= 1/Percentage of activated carbon on the surface (In this experiment calculated for 50% activated carbon response for adsorption, P(AC)=2)

m=weight of tire activated carbon in the surface of filament [g]
A=Percentage of tire activated carbon on filament
B=weight of alginate in filament [g]
C=weight of tire activated carbon in filament
F= Weight of used filament [g] (In this experiment 0.125 g)

Discussion
The adsorptions of Co in Tire Powder Activated Carbon with & without alginate were measured and the share of adsorption was calculated and the results shown that 80% of Co-Adsorption belongs to Tire activated Carbon and 20% to Alginate.
Results of Scanning Electron Microscope Images from tire powder activated carbon shows the macro , meso and micro pore before and after adsorption(Fig. 6 and 7). SEM-images indicate that the new adsorber calcium alginate filamentary containing activated carbon with nano-holes has good adsorbing character for removal of cobalt (II) in polluted effluent. With increasing of activated carbon in sodium alginate increased the amount of cobalt (II).
 The maximum capacity of adsorption of Cobalt with 1% share of Activated Carbon and 50% affectivity of adsorber surface was by H-equation 2880 mg Co/g Activated Carbon.
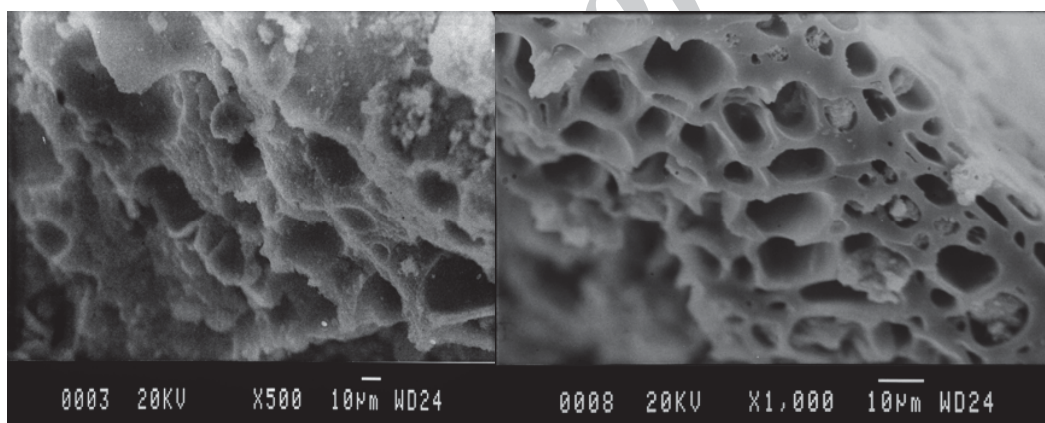

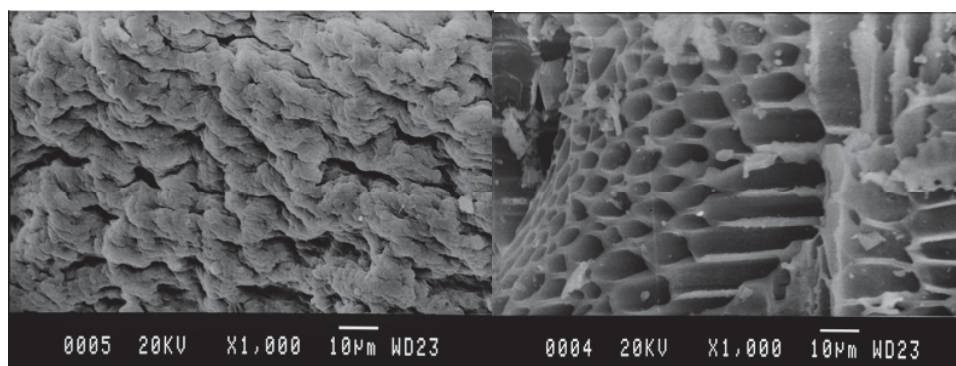Fig 6. Powder Activated Carbon (from Tire) SEM before adsorption

Fig 7. Powder Activated Carbon (from Tire) SEM after adsorption

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