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### Comparative Analysis of Biosorption of Arsenic on to Acid and Alkali Treated Sugarcane Waste Bagasse

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#### KEYWORDS

Biosorption,  
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#### A B S T R A C T

To standardize the Biosorption of Arsenic from aqueous solution using sugarcane waste bagasse and to optimize various parameters for its effective adsorption with comparison to check the efficiency of the adsorption onto alkali treated and acid treated bagasse. Preparation of adsorptions using bagasse with acid and alkali treatment followed by optimization of the adsorbent with parameters such as pH, temperature, contact time, adsorbent dosage and particle size of the adsorbent. The amount of arsenic adsorbed was further quantified using iodometric titration methods. Acid treated bagasse on conversion into carbonized ash showed considerable adsorption of arsenic than alkali treated bagasse owing to large surface area of the finely powdered ash material. The Physiological parameters checked showed that the adsorption increases with increase in contact time with constant pH throughout the incubation period for efficient adsorption. The study showed certain drawbacks besides capability of acid/alkali treated bagasse of adsorbing Arsenic from aqueous solution. For efficient adsorption and accurate estimation, further studies using highly sophisticated and sensitive methodologies have to be employed for studying the adsorption and equilibrium kinetics.

### Introduction

“Conservation is a state of harmony between land and man”  
-Aldo Leopold

The discharge of heavy metals into aquatic ecosystems has become a matter of concern in India over the last few decades. Increased urbanization and industrialization has led to

generation of enormous amounts of effluents containing heavy metals due to their recalcitrant and toxic nature, that end to accumulate and magnify in various forms of life and enter the food chain posing serious threat to the environment, humans and life (Gupta *et al.*, 2001). Heavy metals have a

tendency to bio-accumulate and end up as permanent destructive elements in the environment (Wasim Ahmad Khan *et al.*, 2004). Arsenic pollution from natural sources was recently reported in China, Taiwan, India, Bangladesh, USA, Canada, Mexico, Chile, Argentina, New Zealand, Poland, Hungary, Croatia, Serbia and Romania (Branislava *et al.*, 2011). Arsenic is widely found in the Earth's crust in oxidation states of  $-3$ ,  $0$ ,  $+3$  and  $+5$ , often as sulfides or metal arsenide's or arsenates (Murugesan *et al.*, 2006). In water, it is mostly present as arsenate ( $+5$ ) but under anaerobic conditions, it is likely to be present as arsenite ( $+3$ ). It usually occurs in natural waters at concentrations of less than  $1$  or  $2 \mu\text{g L}^{-1}$ . The most important routes of arsenic exposure are through food and drinking water. Arsenic in the aquatic environment is predominant in places with high geothermal activity. Soil erosion and agricultural run-offs are also large contributors to the arsenic concentration in sediments. Toxicity of arsenic depends on its chemical form. Arsine is considered the most toxic form, followed by arsenites, then arsenates and organic arsenic compounds (Wang *et al.*, 2004). For the protection of aquatic life, the average concentration of  $\text{AS}^{3+}$  in water should not exceed  $72 \mu\text{g/L}$  and the maximum should not exceed  $140 \mu\text{g/L}$ . Environmental exposure to arsenic through drinking-water has been associated with skin cancer (Jovanovic *et al.*, 2010, Bertocchi *et al.*, 2006). Moreover, long-term exposure to arsenic in drinking water is causally related to increased risks of cancer in the skin, lungs, bladder and kidney, as well as other skin changes, such as hyperkeratosis and pigmentation changes (Mohan *et al.*, 2007). Dermal lesions were the most commonly observed symptom occurring after minimum exposure periods of approximately 5 years (Kanel *et al.*, 2006). The removal technology of arsenic

and disposal of arsenic bearing waste presents a challenging task to the environmental engineers. The chemistry of Arsenic is quite complex and interesting, as it changes its oxidation states and its removal is dependent on the pH of the medium, oxidation state and redox potential. Conventional methods for the removal of heavy metal ions from aqueous solutions are oxidation/chemical precipitation, ion exchange, reverse osmosis, electrochemical treatment (Darnall, 1991; vukasinovic-Pesic *et al.*, 2009) coagulation/coprecipitation, (Crnkovic *et al.*, 2008) sorption (Bailey *et al.*, 1999; Ayub *et al.*, 2002) and membrane technologies (Muthusamy *et al.*, 2012). Among them, adsorption is considered to be a relatively simple, efficient and low-cost arsenic removal technique, especially convenient for application in rural areas (Krishna *et al.*, 2011; Chan-jun *et al.*, 2005). Since other methods have limitations because they often involve high capital and operational cost and may also be associated with the generation of secondary wastes. A wide range of sorbent materials for aqueous arsenic removal is available nowadays: biological materials, mineral oxides, different soils, activated carbons and polymer resins (Amalraj, S., 2005; Sharma *et al.*, 1992). Biosorption is one such attractive option where microbes and agricultural products, food and wood has been proved to be metal biosorbents (Elovear *et al.*, 2008, Volesky *et al.*, 1995). Nevertheless, finding inexpensive and effective sorbents for arsenic removal from water is still highly desired (Kadhirvelu *et al.*, 2001). In recent years, much attention has been focused on the removal of heavy metals using agricultural wastes (Reena singh *et al.*, 2011). In an effort to evolve a useful user-friendly, eco-friendly and economical method for the removal of Arsenic from aqueous solution, the present study was carried out using Bagasse, a

sugarcane waste product despite several adsorbents due to its local availability and low cost (Bhagyalakshmi *et al.*, 2015; Ranjan *et al.*, 2009) Bagasse pitch is a waste product from sugar refining industry. It is the name given to the residual cane pulp remaining after sugar has been extracted. Bagasse pitch is composed largely of cellulose, pentosan, and lignin (Bhagyalakshmi *et al.*, 2015) studied on adsorption of Cd (II) and Pb(II) onto functionalized formic lignin from sugar cane bagasse.

## **Materials and Methods**

### **Collection and preparation of adsorbents**

#### **Sugarcane waste bagasse**

Bagasse pitch is a waste product from sugar refining industry. It is the name given to the residual cane pulp remaining after sugar has been extracted. Bagasse pitch is composed largely of cellulose, pentosan, and lignin (Peternele *et al.*, 1999) studied on adsorption of Cd (II) and Pb(II) onto functionalized formic lignin from sugar cane bagasse.

Bagasse was obtained from local sugarcane juice vendors. It was dried in the oven till it turned crispy enough to be ground well. Then the material was ground in a local mill. It was washed with tap water and then with distilled water thoroughly to remove other unwanted solid particles and subjected to other treatment methods.

#### **Treatment with Alkali**

The ground bagasse material obtained after washing was treated with 5N sodium hydroxide and boiled for about half an hour in a hot plate. The NaOH treatment is repeated for atleast 3 times for the complete removal of colour from bagasse, to prevent any colour interference during adsorption and estimation process. Then the material

obtained is washed well with distilled water to remove the alkali completely and oven dried overnight at 60<sup>0</sup>C.

#### **Treatment with Acid**

Another set of ground bagasse material was treated with sulphuric acid to obtain a carbonized ash material. Four parts of raw bagasse was treated with three parts by weight of concentrated sulphuric acid and maintained in an oven at 150<sup>0</sup>C for 36 hours. The carbonized ash material was washed well with distilled water to remove the acid completely and oven dried overnight at 110<sup>0</sup>C. The dried, powdered adsorbent material from both the treatments was stored in air tight containers.

#### **Preparation of Arsenic Standard (1%)**

1 gm of Arsenic trioxide, As (III) (preheated to 110<sup>0</sup>C for 2 hours and cooled) was dissolved in a concentrated solution of sodium hydroxide using a magnetic stirrer, the pH of the solution was adjusted to neutral using hydrochloric acid and the volume was made upto 100ml in a standard flask. From 1% standard solution, 250µl was taken and diluted to 100 ml in a standard flask. Working standards are prepared freshly for each biosorption experiment.

#### **Optimization Protocols**

##### **Optimization of pH**

Working standards in different pH range was prepared (alkaline -10.5)-(neutral – 7) – (acidic -2-4)) for optimizing the pH, where other parameters such as contact time and adsorbent dosage were kept constant.

##### **Optimization of Contact time**

The time of contact of biosorbent with the working solution at 1 hr interval, 18hrs interval and 36 hrs interval was carried out keeping pH and biosorbent dosage constant.

### **Optimization of Adsorbent dose**

Varied amount of biosorbent material i.e., 0.5g/ml, 1.0g/ml, 2.0g/ml and 4.0g/ml of solution was taken and centrifuged at 5000rpm for 10 minutes (after the stipulated contact time) to collect the supernatant and the concentration of arsenic after biosorption was estimated. The concentration was compared with that of the standard working solution.

### **Estimation of Arsenic using Iodometric method (Vogel *et al*, 1978)**

0.1N and 0.05N iodine was prepared. 1% sodium starch glycolate indicator was prepared freshly (diluted from 5% stock). 10ml of the standard working solution without biosorbent was taken in an Erlenmeyer flask and 10ml of the distilled water was added to it. 2g sodium bicarbonate was added to 20ml of the solution and stirred well in a magnetic stirrer till all the sodium bicarbonate dissolved. 2ml of 1% sodium starch glycolate was added to the flask. This was titrated slowly with the iodine solution till the endpoint blue colour was obtained. Titrations are repeated to get the concordant values. From the values obtained and from the normality of the iodine solution, the normality of the working solution and its strength was determined.

## **Results and Discussion**

### **Effect of particle size of Adsorbent**

Particle size is an important parameter that should be taken into consideration for any biosorption experiment. Various forms of bagasse material after treatment with acid and alkali was obtained. Fig1. Shows raw

dried bagasse and Fig.2 shows raw powdered bagasse that developed a strong colour and interfered in estimation

Fig.3 shows alkali treated fibrous bagasse material which showed negligible adsorption. Fig 4. Shows Powdered alkali treated material with adsorption of arsenic i.e., around 14.28% of adsorption after 18 hrs of incubation. Fig.5 depicting acid treated bagasse-finely powdered ash showing a biosorption capacity of 28.58% after 18hrs of incubation.

### **Effect of pH and Contact time**

pH appears to be the significant parameter in every biosorption experiment. At high acidic and alkaline pH, the adsorption was found to be negligible. Adsorption was found to occur at around neutral pH (6.8-7.5). The estimation by iodometric method is effectively possible only at neutral pH. Thus solutions drawn in 1hr intervals for 3 hours showed no change in the concentration of arsenic in the solution, decrease in concentration was observed after 18 and 36hrs of incubation. This result shows that the adsorption increases with increase in contact time but the pH of the solution must be constant throughout the incubation time for efficient adsorption of arsenic.

### **Effect of temperature and adsorbent dosage**

An increase in adsorbent dosage per 100ml of working arsenic solution produced colour. The carbonized ash material discharged a brown colour with high adsorbent dosage. Only solutions with 2g/100ml of adsorbent produced satisfactory results.

**Table.1** Adsorption Effect of different forms of Adsorbent prepared using Sugarcane Bagasse material

Different forms of bagasse material	Biosorption capacity
Raw Bagasse	Developed strong colour, interference in estimation
Alkali treated fibrous Bagasse material	Negligible adsorption
Powdered alkali treated material	14.28% (18 hrs incubation)
Acid treated Bagasse-finely powdered ash	28.58% (18 hrs incubation)

**Table.2** Percentage efficiency of adsorption at different contact time

BIOSORBENT	pH	TEMPERATURE	ADSORBENT DOSAGE (g/l)	EFFICIENCY OF ADSORPTION (%)	
				CONTACT TIME	
				18 HRS	36HRS
Alkali treated bagasse	7.2	27+/-2 <sup>0</sup> C	20	14.28	39.99
Acid treated Bagasse	7.2	27+/-2 <sup>0</sup> C	20	28.58	62.59

**Figure 1: Raw dried bagasse**



**Figure 2: Raw powdered bagasse**



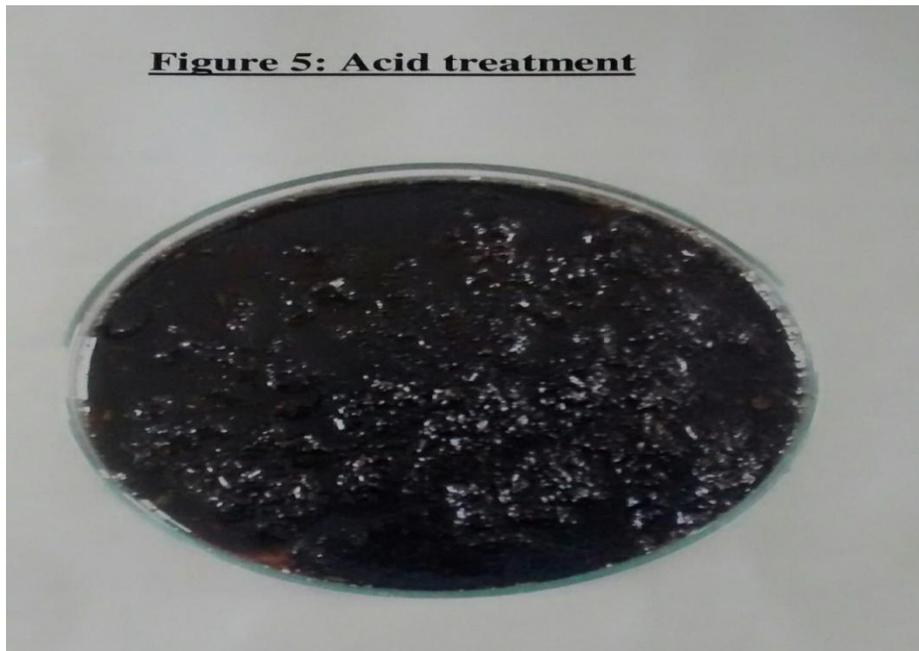
**Figure 3: Alkali treatment**

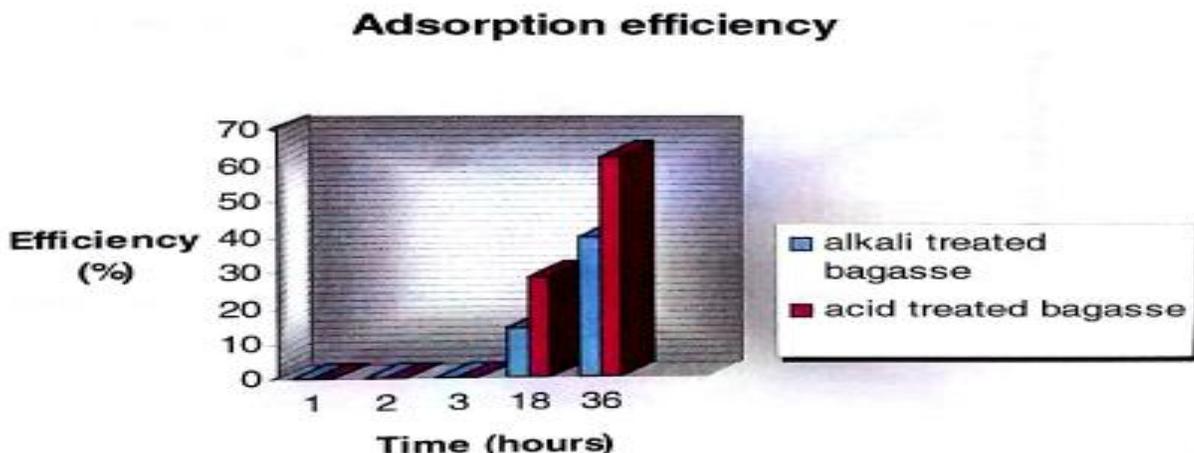


**Figure 4: After alkali treatment**



**Figure 5: Acid treatment**





### Comparison of the adsorption efficiency of Acid treated bagasse ash with alkali treated bagasse ash

The adsorption capacity of acid treated bagasse was found to be 62.59% in comparison with a value of 39.99% increases with increase in contact time with no alteration in the pH of the solution throughout the incubation time for efficient adsorption of arsenic (Table 1 and Table 2)

The results show that alkali and acid treated bagasse can adsorb arsenic from prepared arsenic solutions under appropriate conditions. Acid treated bagasse showed more adsorption than alkali treated bagasse. The adsorption of other metal/dyes on bagasse shows a wide range of percentage of removal depending on the experimental conditions and the pretreatments (Revathi, M., 2005). The major parameters that affect the adsorption of metal ions to the sugarcane waste bagasse are particle size, pH, temperature, Contact time and the initial concentration of the metal ion (Mohan *et al.*, 2002). The removal efficiency increased rapidly with increase in the concentration of the adsorbent due to the greater availability of the exchangeable sites or surface areas at higher concentrations of the adsorbent. In

the present study, raw bagasse was not applicable to be used as such because of the strong colour that it produced in the solution due to the lignocellulosic substances present in it. This colour development strongly interfered with the estimation method. Hence alkali treatment of bagasse was preferred for the complete removal of the colour.

Sodium hydroxide treatment changed the bagasse into a fibrous form due to the large particle size there was negligible adsorption. Powdered fine particles of bagasse was treated with alkali which shows little adsorbing capacity. Treatment of the bagasse with concentrated sulphuric acid converted it into a carbonized material or ash that showed considerable adsorption of arsenic due to large surface area of the ash material. The physiological parameters studied showed that the adsorption increases with increase in contact time with constant pH throughout the incubation period for efficient adsorption.

### Conclusion

The development of economically feasible eco-friendly products from natural plants or agricultural wastes for removal of heavy

metals has found to be efficient owing to their low cost. Arsenic can be removed by adsorption onto many adsorbent materials proving advantageous with acid/alkali treated sugarcane waste bagasse. For efficient adsorption and accurate estimation, further studies using highly sophisticated and sensitive methodologies have to be employed for studying the adsorption and equilibrium kinetics.

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