

# Adsorption of Selenite on Heat Treated Sea Nodule Residue

<sup>1</sup>P.K.Satapathy, <sup>2</sup>T.R.Mohanta, <sup>3</sup>A.K.Sahoo

<sup>1</sup>P.G. Department of Chemistry, North Orissa University, Baripada

<sup>2</sup>Department of Chemistry, F.M. Junior College, Balasore

Email: [pramoda\\_satapathy\\_70@yahoo.com](mailto:pramoda_satapathy_70@yahoo.com)

**ABSTRACT:** - The present study was carried out to investigate the adsorption characteristics of sea nodule residue (SNR) heated at 400 °C towards aqueous selenite. Physico-chemical characterization revealed that the leached residue was a complex mixture of oxides of mainly manganese and iron along with MnCO<sub>3</sub>. Adsorption studies were carried out at varying the pH, selenite ion concentration, SNR dosage and in presence of competitive ions. It was found that the selenite adsorption increased with pH reaches maximum at pH 5.0 and then decreased. Further it was found that the percentage of selenite adsorption increased with increasing amount of adsorbent (SNR) and decreased with increasing initial concentration of selenite. It was observed that the percentage of adsorption of selenite decreased with increasing concentration of externally added ions. The overall effect of competing ions on adsorption of selenite follows the order Cl<sup>-</sup> < NO<sub>3</sub><sup>-</sup> < SO<sub>4</sub><sup>2-</sup> < CO<sub>3</sub><sup>2-</sup>.

**Key words:** - Sea nodule residue, selenite, adsorption.

## I. INTRODUCTION

The selective extraction of strategic metals like Cu, Co and Ni along with Mn and Fe leaves behind more than 70% residue as wastes for disposal. These leached residues containing oxides/oxyhydroxides of Fe, Mn, Al and Si showed reasonable high porosity and surface area. Moreover, Fe and Mn in these residues are present in variable oxidation states. In view of above characteristics, one can envisage the use of leached residues as an effective adsorbent for a variety of toxic anions.

Selenium is an important element of environmental, biological and toxicological significance. Though recognized as an essential nutrient in animal and human diets, selenium in high dosage can be toxic with undesirable physical manifestation[1]. There is a very narrow range between deficient and toxic levels of selenium in animals, which necessitates a clear knowledge of the processes affecting Se distribution in the environment. The toxic effects of selenium are highly variable and depend on chemical species, type of organism, and duration of exposure.

Adsorption of selenite/selenate on hydrous oxides of iron, manganese, and aluminum [2, 3-6] appears to be an efficient and inexpensive method for removing trace contaminants. Selenite adsorption on manganese nodule surface was also studied by Parida et al[7]. However adsorption of selenite has not yet been studied using heat treated sea nodule residue. So the present study is an attempt to use 400°C heated sea nodule residue sample as adsorbent towards adsorption of selenium.

## II. EXPERIMENTAL

### • Materials

Leached residue sample (SNR), generated after reduction roast-ammoniacal leaching process were collected from Pilot plant operated at Hindustan Zinc Limited, Udaipur, India. The parent Indian Ocean manganese nodule (SN), which generates the residue after leaching process, was also collected for comparison of activity. The samples were air dried for several days, mixed thoroughly and kept in airtight bottles for characterization and further use. In order to remove loosely associated metal ions/anions, the leached residue was washed with distilled water. In a typical lot 50 g of the leached residue was dispersed in 500 ml distilled water (solid: liquid ratio = 1: 10) and stirred for 2 h at room temperature. The content was filtered, washed with distilled water for further removal of sulphate and then air dried to get the washed sea nodule residue (WSNR). The air-dried samples are further heated at 300°C and 400°C. for 4 hours using a tubular furnace fitted with programmable temperature controller. These heat-treated samples are studied for their characterization and adsorption experiment.

### • Chemicals

Stock solutions of Selenite were prepared in distilled water. Working solutions were prepared by suitable dilution of stock with distilled water.

### • Chemical analysis

Chemical analysis for major and minor constituent's adsorbents was done as described earlier (8) by conventional wet chemical methods and by atomic absorption spectrometry respectively.

- Adsorption Experiments

Adsorption of selenite on manganese nodules was carried out in acetic acid-sodium acetate buffer medium. Adsorption experiments were carried out in 100-ml stoppered conical flasks by taking appropriate amounts of sodium selenite solution and manganese nodules (2 g/liter). The pH of the solution was maintained by adding acetic acid-sodium acetate buffer. The final volume was invariably kept at 50 ml, and the ionic strength was maintained at  $0.1 \text{ mol dm}^{-3}$  using KCl. The flasks were shaken mechanically at the desired temperature ( $30.0 \pm 0.2^\circ\text{C}$ ) in a thermostatic bath for 3 h. The contents were filtered through Whatman No 42 filter paper, and the concentration of selenite in the filtrate was determined spectrophotometrically by following the procedure of Afsar et al. (36), in which 2-mercaptoethanol is used as the reductant as well as the ligand to form a zero-valent selenium complex. The percentage of selenium adsorbed was determined from the ratio of selenium in the solution and particulate phases,

$$\% \text{ of se adsorbed} = \frac{S_{e_{in}} - S_{e_{eq}}}{S_{e_{in}}} \times 100 \quad [1]$$

Where  $S_{e_{in}}$  and  $S_{e_{eq}}$  are the initial and equilibrium concentrations of selenium respectively.

Each run was made at least twice. All spectrophotometric measurements were made with a Chemito 2500 recording UV-visible spectrophotometer using 10-mm matched quartz cells. The pH of the solutions at the beginning and end of experiments was measured, and average pH values are reported. All pH measurements were made under atmospheric conditions with an Elico digital pH-meter (Model LI 120) using a combined glass electrode (Model CL 51). The pH-meter was standardized with NBS buffers before any measurement. The adsorption experiments under varying conditions of pH, adsorbate and adsorbent concentration were carried out using the heat treated sea nodule residue sample.

### III. RESULT AND DISCUSSION

- Preliminary observations

Preliminary studies with varying initial selenite concentration ( $10\text{-}100 \text{ mg L}^{-1}$ ) at fixed pH  $\sim 5.0$  and adsorbent dose ( $1 \text{ g L}^{-1}$ ) shows the adsorption process is relatively slow and the equilibrium is attained within 10 h. No further change in equilibrium concentration was seen up to 30 h. The time required to reach the equilibrium appears to be independent of initial selenite concentration. Hence the equilibrium time is kept 10 h for all further adsorption experiments. The adsorption experiment was done using heat treated sea nodule residue sample taking adsorbent dose ( $1 \text{ g/L}$ ), selenite concentration  $10 \text{ mg/L}$  and at fixed pH  $\sim 5.0$ .

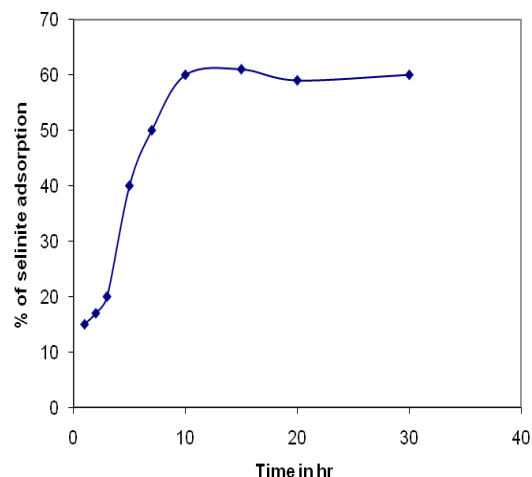


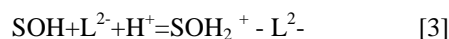
Fig.1.Effect of contact time on adsorption of selenite ions at pH ca.5 with initial Selenite concentration ( $10 \text{ mg/L}$ ) and adsorbent dose  $1 \text{ gm/L}$ .

- 3.2. Effect of pH: -

Figure 2 shows the adsorption of selenite as a function of equilibrium pH at a fixed selenite concentration. It is evident that the adsorption of selenite increases with increasing pH, attains a maximum value at pH 5 and then decreases progressively on further increase in pH up to 8. Similar behavior was reported for the adsorption of anionic species on metal oxides/oxyhydroxides [3,5,9]. Based on infrared and kinetic studies [3, 9] it has been suggested that strongly binding anions like selenite adsorb on metal oxides by ligand exchange mechanism. This mechanism involves exchange of aqueous ligand for a surface hydroxyl group, resulting in the formation of inner-sphere complex. The formation of inner-sphere complex involves the reaction:



Where S-OH is a surface hydroxyl group and  $\text{SL}^{-}$  is the ligand adsorbed species. In contrast, more weakly binding anions such as chloride and nitrate, adsorb through an electrostatic attraction with the surface. An outer-sphere complex is formed where a water molecule is retained between the surface site and adsorbed ligand.



According to the anion adsorption reactions given in Eqs. [2] and [3], an increase in pH should cause a decrease in the amount of selenite adsorption. These trends are indeed observed in selenite adsorption data on heated sea nodule residue samples and are consistent with previous results of anion adsorption on metal oxides [3,4].

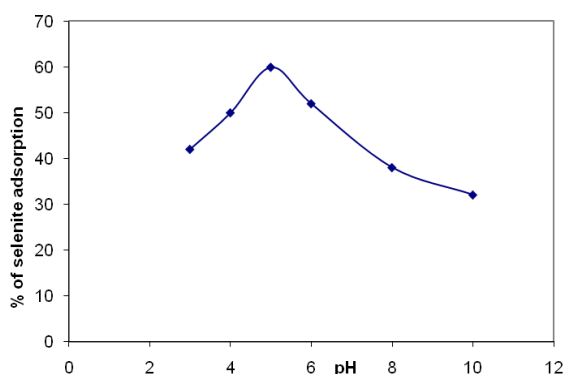


Fig-2. Adsorption of selenite on heat treated SNR sample as a function of pH

- Effect of adsorbent dose and initial adsorbate concentration:

The results of selenite adsorption with varying amount of adsorbent sample (0.4 – 2 g/L) and initial selenite concentrations (10-100 mg L<sup>-1</sup>), keeping all other parameters fixed, are illustrated in Fig. 3 and 4 respectively. It is found that the percentage adsorption of selenite increases with increase of amount of adsorbent then remain almost constant. The first increase in adsorption concentration due to increase of active sites. The adsorption percentage remain constant for further increase of the amount of the catalyst is due to the fact that the fixed selenite ions are not sufficient to adsorb on higher number of active sites. On the other hand the percentage of adsorption decreases with increase of initial concentration of selenite at a constant amount of adsorbent which probable due to availability of more selenite ions for a constant number of active sites on the surface.

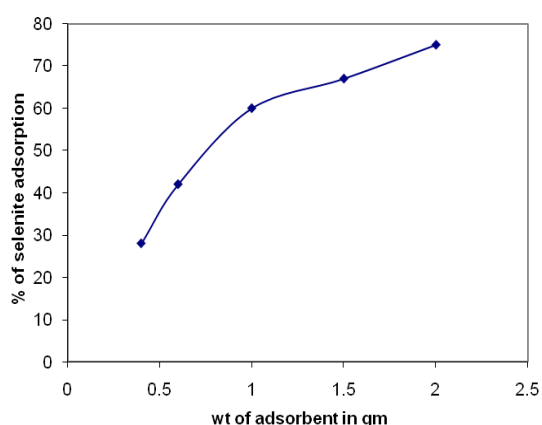


Fig-3. Effect of adsorbent dose on percentage of selenite adsorbed, with initial selenite concentration, 10mg/L and pH 5.0.

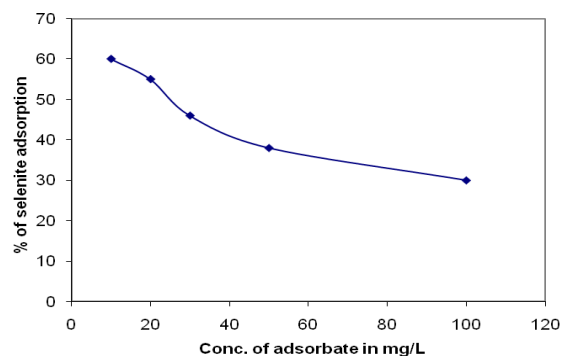


Fig-4. Effect of initial selenite concentration (10-100mg/L) on percentage of selenite adsorbed, with amount of adsorbent, 1g/L and pH 5.0.

- Effect of Competitive ions

The effect of different competitive ions such as Nitrate, Chloride, Sulphate and Carbonate on the adsorption of selenite was studied at pH-5.0 taking 1g/L of adsorbent and 10mg/L selenite concentration (Fig-5). The concentration of each electrolyte is taken as 40mg/L. It was observed that the percentage of adsorption of selenite decreased with increasing concentration of externally added ions. The overall effect of competing ions on adsorption of selenite follows the order  $\text{Cl}^- < \text{NO}_3^- < \text{SO}_4^{2-} < \text{CO}_3^{2-}$ .

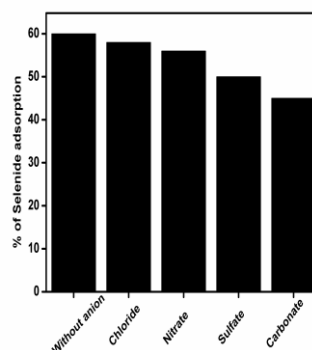


Fig-5. Effect of added electrolytes on adsorption of selenite over heat treated SNR samples

#### IV. CONCLUSION

The potential of Heat treated Sea nodule residue samples for removal of selenite from its aqueous solution was studied. This sample was found effective as an adsorbent for selenite adsorption at pH 5.0. It was found that the percentage of selenite adsorption increases with increasing amount of adsorbent and also decreases with increasing initial concentration of selenite.

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