REMOVAL OF NITRATES FROM POLLUTED WATERS USING BIO-ADSORBENTS

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The sorption characteristics of bio-adsorbents derived from *Annona squamosa*, *Calotropis zygantia* and *Tridox procumbens* in extracting Nitrate from polluted waters were explored. At low pH values, these sorbents showed sensitivity towards Nitrates. The physicochemical parameters such as pH, time of equilibration and sorbent concentrations were optimized. Successful methodologies have been developed to extract good quantities of nitrates. % of extraction with stem powders was found to be more than the respective leaf powders. Fivefold excess of common cations present in waters, have synergistic effect on the % of extraction while other common anions, except sulphate, have marginal effect. The procedures developed were found to be remarkably successful when applied to some real samples of industrial effluents and polluted lakes.

**Keywords:** Nitrates, Pollution control, Bio-adsorbents

INTRODUCTION

Nitrate is the ultimate oxidized product of biodegradation of nitrogenous matter in polluted waters. The sources of nitrogenous matter contamination are both natural and anthropogenic in nature and the main contributions are from agricultural operations, farm runoffs and over usage of fertilizer (Ponde, 1986; Boyd, 1998; Poxton, 1982; and APHA, 1998). The potential anthropogenic sources include sites of disposal of human and animal sewage, industrial wastes related to food processing and munitions and leakages from Septic tanks (Halberg et al., 1993).

Nitrate is a contaminant in drinking water due to its harmful biological effects (Lin, 1996; Virkutyte et al., 2009; 2010; Foley et al., 2010). High concentrations causes, methemoglobinemia and have been cited as a risk factor in developing gastric and intestinal cancer. Infants and elderly people are liable to the risk as their blood composition is directly affected by the reduction of hemoglobin and thereby originating a number of carcinogenic processes. Due to these health hazards, the United States Environmental Protection Agency has fixed health advisory level of nitrate at 45 ppm (APHA, 1998; Gomez et al., 2000).

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There is a great deal of concern in finding effective treatment processes to reduce nitrogen compounds concentrations to safe levels (Lin, 1996; Garbisu, 1992; Emamjomeh, 2009; Reyter, 2010; Sun, 1999, 2000; Abuzaid et al., 1999; D De et al., 2004; Dr’az, 2010; Saleem et al., 2011). Methodologies have been developed based on Ion Exchange (Korngold, 1973; Clifford et al., 1978; and Lauch et al., 1986), Biochemical denitrification (Zajic et al., 1971; Shuval et al., 1977; Environmental Directorate, 1974), Reverse Osmosis (Guter Gerald A 1981; Clifford et al., 1978), Electodialysis (Miquel et al., 1991) and Catalytic denitrification (Horold et al., 1993) to control nitrates in polluted waters. These methods suffer from the fact that they are costly and involve a lot of procedure and are not economically viable methods in developing countries like India, despite of the fact that they produce high quality effluents.

The use of micro–organisms and other agricultural waste products as bio-adsorbents for the removal of polluting ions offer a potential alternative to the existing methods of detoxification and for the recovery of toxic and valuable ions from industrial discharges/ polluted waters (Katsuya Abe et al., 2002; Polatide et al., 2005; Nes.eOzturk et al., 2008; and Ansari, 2009). These biological approaches during the recent past have shown interesting results, which have stimulated continuous and expanding research in this field (Amir et al., 2005; Orhan et al., 1993; Trivedy, 1995; Gerard Kiely, 1998; Baker et al., 1998; Huang et al., 2000; Vaughan et al., 2001; Unnithan et al., 2002; Shukla et al., 2002; Majeti et al., 2000; Tshabalaka et al., 2004; Dinesh Mohan et al., 2006; Boujelben et al., 2008; Sandhya Babel et al., 2003; LuzE. De-Bastan et al., 2004; Khan, 2006; and Meera et al., 2006). Some works in this direction have been done in our research labs (Divya Jyothi et al., 2011, 2012; Hanumantha Rao et al., 2011; and Suneetha, 2012).

In the present work powders of leaves, barks, half-bunt and ashes of plant materials and biomasses have been tried with an object of controlling the concentration of nitrates in the polluted waters.

**MATERIALS AND METHODS**

**Chemicals:** All chemicals used were of analytical grade. Stock solution of Nitrate of concentration 500 ppm was prepared and it was suitably diluted as per the need.

**Adsorbents:** Diverse adsorbents of flora origin were used in this work. But leaves or barks of *Annona squamosa*, *Calotropis zygantia* and *Tridox procumbens* have been found to have affinity towards nitrates.

Leaves or stems of *Annona squamosa*, *Calotropis zygantia* and *Tridox procumbens* were freshly cut or scraped from the trees, washed with tap water and then with distilled water. The leaves were then sun dried. The dried leaves were powdered to a fine mesh of size: <75 microns and then they were activated at 105°C. Thus obtained powders were used for the present study.

**Adsorption experiment:** Batch system of extraction procedure was adopted (Trivedy, 1995; Gerard Kiely, 1998; Metcalf and Eddy, 2003). Carefully weighted quantities of adsorbents were taken into previously washed 1 lit/500 ml stopper bottles containing 500ml/250ml of potassium nitrate solution of predetermined concentrations. The various initial pH values of the suspensions were adjusted with dil. HCl or dil. NaOH solution using pH meter. The samples were shaken vigorously in mechanical shakers and were
allowed to be in equilibrium for the desired time. After the equilibration period, an aliquot of the sample was taken for Nitrate determination. Nitrate was determined spectrophotometrically (Vogel, 1961; APHA, 1998). NO$_3^-$ was reduced quantitatively to NO$_2^-$ using Cd-reduction column. The obtained NO$_2^-$ was determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride to form highly colored azo dye and OD measurements were made at 543 nm spectrophotometrically.

**Effect of Interfering Ions**

The interfering ions chosen for study are the common ions present in natural waters, viz., Phosphate, sulphate, fluoride, Chloride, Carbonate, Calcium, Magnesium, Copper and Zinc. The synthetic mixtures of nitrate and of the interfering ions are so made that the concentration of the interfering ion was maintained at five fold excess to Nitrate ion concentration. 500 ml of these solutions were taken in stoppered bottles and then correctly weighted optimum quantities of the promising adsorbents (as decided by the Graph Nos.: A, B and C) were added. Optimum pH was adjusted with dil. HCl or dil. NaOH using pH meter. The samples were shaken in shaking machines for desired optimum periods and then small portions of the samples were taken out, filtered and analyzed for Nitrates. % of extraction was calculated. The results were presented in the Table 1.

**RESULTS AND DISCUSSION**

The percentage removal of Nitrate was studied under various parameters with various adsorbents derived from *Annona squamosa*, *Calotropis zygantia* and *Tridox procumbens*. The results were presented in the Graph No: A: 1-3; B: 1&2; C:1&2 and Tables 1 and 2. The following observations were significant.

1. % of extractability increases with time for a fixed adsorbent at a fixed pH and after certain duration, the extractability remains constant, i.e., an equilibrium state has been reached (vide Graph A: 1-3)

2. pH sensitivity: The % of extractions were found to be pH sensitive. The % of extractability of nitrate decreases with the increase of pH for a fixed adsorbent concentration (Vide Graph B 1 and 2).

As for example, in the case of leaves powders of *Annona squamosa*, the maximum extractability is found to be: 19.4% at pH: 10, 20.8% at pH: 8; 39.2% at pH: 6; 72.6% at pH: 4 and 95% at pH: 2. In the case of leaves powders of *Calotropis zygantia*, the maximum extractability is found to be: 38.5% at pH: 10, 41.2 % at pH: 8; 53.8% at pH: 6; 62.8% at pH:4 and 82.0% at pH:2. *Tridox procumbens* leaves powders were extracted to an extent of: 21.2% at pH: 10, 37.4% at pH: 8; 43.7% at pH: 6; 59.8% at pH: 4 and 87.0% at pH: 2.

3. With the stem powders, the extractability at pHs: 10, 8, 6, 4 and 2 was found respectively to: 28.2%, 35.5%, 54.7%, 80.5% and 99% for *Annona squamosa*; 40.5%, 44.8%, 56.6%, 82.2% and 94% for *Calotropis zygantia*; 30.1%, 43.2%, 50.5%, 79.8% and 95.0% for *Tridox procumbens*. It can be inferred that the extraction of Nitrate was found to be more in the case of stem powders as sorbents than powders of leaves.

4. Further, the time needed for maximum removal of nitrate was also found to be less in the case of stem powders than powders of leaves. As for example, the maximum extractability of Nitrate is 95% at pH: 2 after an equilibration period of 6 hrs for *Annona squamosa* leaves powders while with its stem powders, the
extractability was found to be enhanced to 99% at pH:2 after an equilibration period of only 5 hrs. With leaves powders of Calotropis zygantia, the maximum extraction of Nitrate was found to be 82% while with its stem powders, 94% of extraction was found at pH: 2 and equilibration period of 6 hrs. Tridox procumbens leaves powders were found to remove 87% Nitrate at pH: 2 after an equilibration period of 7 hrs while with its stem powders, the % of removal was found to be 95% at pH: 2 at equilibration period of 5 hrs.

5. When percentage removal was studied with respect to adsorbent dosage at fixed optimum pH: 2 and at optimum equilibration times, the graphs increase up to certain dosage and from then onwards plateaus were obtained Vide Graph C1 and 2).

With powders of leaves, the optimum sorbent dosage was found to be 1g/lit for Anona squamosa and 4g/lit for Calotropis zygantia and Tridox procumbens (vide Graph Nos: C:1&2).

**Figure 1: Effect of Equilibration Time on the Extraction of Nitrate**
With the powders of stems, the sorbent concentration needed was considerably low. The sorption concentrations needed at optimum conditions of pH:2 and equilibration time were found to be 1 g/lit for *Anona squamosa*, 3 g/lit for *Calotropis zygantia* and *Tridox procumbens* (vide Graph C1 and 2).

**Effect of Interfering Ions**

The extractability of nitrate ions in presence of fivefold excess of the common ions found in natural waters, namely Chloride, Fluoride, Sulphate, Phosphate, Carbonate, Calcium, Magnesium, Copper and Zinc ions has been studied with the successful adsorbents at

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**Figure 2: Effect of pH on the Extraction of Nitrate**

![Graph showing effect of pH on nitrate extraction](image)

**Figure 3: Effect of Sorbent Dosage on the Extraction of Nitrate**

![Graph showing effect of sorbent dosage on nitrate extraction](image)
optimum conditions of extractability. The results were presented in the Table 1.

The extractability of Nitrates in presence of Sulphates were markedly affected. Phosphate, Chlorides, Fluorides and carbonates have marginal effect. It is interesting to note that the extractability was increased in presence of Ca, Mg, Cu and Zn ions. As for example, the % of extraction was 87.0% at pH:2 with powder of Tridox procumbens leaves in the absence of cations, while in the presence of Ca$^{2+}$, Cu$^{2+}$, Zn$^{2+}$and Mg$^{2+}$ the % of extraction was increased to 91.8%, 92.9%, 94.5% and 95.6% respectively (vide Table 1: S. No. 3).

**DISCUSSION**

With the available data, it is not possible to propose sound theoretical grounds for each observation as further probe is needed on the surface morphology. It is beyond the aims of this work. However, the behaviors may generally be understood as follows:

- The functional groups present in the lingo cellulos’ materials like leaves and stems are either –OH/-COOH groups. These groups dissociate at high pH values imparting negative charge to the surface and thereby a thrust for cations prevails on the surface. But as the pH decreases, the functional groups get protinated endowing positive charge to the surface which results in thrust for anions at the surface at low pH. Nitrate being an anion is adsorbed by these materials at low pH and thus results in higher % of removal. As pH increases, the deprotination occurs and hence the affinity of the adsorbent towards the Nitrate

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Adsorbent and its Concentration</th>
<th>Maximum Extractability at Optimum Conditions</th>
<th>Extractability of Nitrate in Presence of Fivefold Excess of (250 ppm) Interfering Ions at Optimum Conditions: Conc. of Nitrate: 50 ppm (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td>SO$_4^{2-}$</td>
</tr>
<tr>
<td>1.</td>
<td>Powder of Annona Squamosa leaves 95.0%; pH: 2; 6.0 hrs; sorbent dosage: 1.0 gm/lit</td>
<td>72.4</td>
<td>92.6</td>
</tr>
<tr>
<td>2.</td>
<td>Powder of stem of Annona Squamosa 99.0%; pH:2;5.0 hrs; sorbent dosage: 1.0gm/lit</td>
<td>61.9</td>
<td>95.2</td>
</tr>
<tr>
<td>3.</td>
<td>Powder of Calotropis Zygantia leaves 82.0%pH:2, 6.0hrs Sorbent dosage: 4.0 gms/lit</td>
<td>60.3</td>
<td>79.5</td>
</tr>
<tr>
<td>4.</td>
<td>Powder of Calotropis Zygantia stems 94.0%pH:2, 6.0 hrs; Sorbent dosage: 3.0 gms/lit</td>
<td>63.5</td>
<td>92.1</td>
</tr>
<tr>
<td>5.</td>
<td>Powder of Tridox Procumbens leaves 87.0%; pH:2; 7.0 hrs; Sorbent dosage:4.0 gms/lit</td>
<td>61.6</td>
<td>83.4</td>
</tr>
<tr>
<td>6.</td>
<td>Powder of stems of Tridox Procumbens 95.0%pH:2, 5.0 hrs; Sorbent dosage: 3.0 gms/lit</td>
<td>60.7</td>
<td>93.4</td>
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</table>

Table 1: Effect of Interfering Ions on the Extractability of Nitrate with Different Bio-Sorbents
decreases and thus resulting in low % removal of Nitrate ions.

- The decrease in the rate of adsorption with the progress in the equilibration time may be due to the more availability of adsorption sites initially and are progressively used up with time due to the formation of adsorbate film on the sites of adsorbent and thus resulting in decrease in capability of the adsorbent.

**Applications**

The methodologies developed were applied to the real samples of diverse nature, and the results were presented in Table 2. It can inferred that the procedures developed were remarkably successful.

**CONCLUSION**

a) The sorption potentialities of bio-adsorbents derived from *Annona squamosa*, *Calotropis*...
zygantia and Tridox procumbens in removing/controlling Nitrate from polluted waters were brought to the lime light.

b) We claim 95%, 82% and 87.0% removal of Nitrate with the powders of leaves of Annona squamosa, Calotropis zygantia and Tridox procumbens respectively from synthetic waters at pH: 2 and at optimum equilibration times and sorbent dosage.

c) With the stems powders of Annona squamosa, Calotropis zygantia and Tridox procumbens, the % of removal of Nitrate was found to be 99.0%, 94.0% and 95.0% respectively at optimum conditions of extraction.

d) % of extraction was more in the case of stem powders than with their respective leaves powders.

e) Fivefold excess of cations like Ca^{2+}, Cu^{2+}, Zn^{2+} and Mg^{2+} are synergistically increasing the extraction. Sulphates were effecting the % of extraction markedly while Cl^-, carbonates, fluorides and phosphates (H_2PO_4^-/H_3PO_4^- ionic forms at pH: 2) marginally effect the extraction at the optimum conditions cited in the Table 1.

f) The procedures developed were found to be remarkably successful when applied to some real sample of industrial effluents and polluted lakes.

REFERENCES


