CONTROLLING OF SO₂ BY KMNO₄ MODIFIED PLANT MATERIAL BY BIOSORPTION

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Abstract:
Adsorption technology has been successfully employed for controlling water pollution. Surface chemistry, surface modification, nature of adsorbent and adsorbate plays a vital role in the Adsorption phenomenon which has been studied by using KMnO₄ modified adsorbents. From the present studies the experiments have been carried out by using KMnO₄ modified plant materials as bioadsorbents and the order of efficiency of removal of SO₂ is found to be Citrus limetta > Abelmoschus esculentu > Hevea brasiliensis > Hibiscus sabdariffa > Bacopa monnieri > Aloe barbadensismiller > Psidium guajava > Nelumbo nucifera > Fenugreek > Amaranthus.

Keywords:
Adsorption; Water pollution; Adsorbent; Adsorbate; Removal of SO₂; Surface modification; Plant materials; Bioadsorbents;
**Introduction:**
Agricultural waste materials are the by-products/residues of various agricultural activities. The efficiency of non-conventional agricultural waste materials for controlling air pollutants depends on their availability, low cost eco-friendly, nature, particle size, the concentration of adsorbate and adsorbent.[1-4] Agricultural waste materials are rich in cellulose and Pectin. In recent studies, by-products of agriculture wastes were successfully utilized for the removal of Chromium, Arsenic and Fluoride ions.[5,6] Taking those studies into consideration studies have been carried out with the agricultural wastes treated with KMnO₄.[7] The agricultural waste studied are Citrus limetta, Abelmoschus esculentus, Hevea brasiliensis, Hibiscus sabdariffa, Bacopa monnieri, Aloe barbadensis miller, Psidium guajava, Nelumbo nucifera, Fenugreek, Amaranthus.

**Selection of Adsorbent:**
1. **Bacopa monnieri:** Common name is Bacopa monnieri which is collected from the village Duvva in West Godavari district of Andhra Pradesh. It is highly grown in marshy areas. These leaves contain Terpenoids, Alkaloids and Bacapasides I-XII.[8]

**Chemical modification of Bacopa monnieri:**[9-11]
The collected Bacopa monnieri leaves/flower leaves are air dried, crushed and packed in air tight bottle. After cleaning/washing/removing color. The stored Bacopa monnieri leaves are treated with 0.01 KMnO₄ for surface modification (KMnO₄ acts as a good oxidising agent to increase oxygen containing functional groups on surface of Bhramhi).

FTIR analysis reveals prominent bands at 3266.82 cm⁻¹, 2915.04 cm⁻¹, 1685.78 cm⁻¹, 1500.35 cm⁻¹, 1416.76 cm⁻¹, 1222.65 cm⁻¹, 1145.51 cm⁻¹, 1010.52 cm⁻¹, 840.812 cm⁻¹, 713.533 cm⁻¹ indicating the presence of various functional groups NH₂, OH, alcohol, aldehyde groups. Many peaks are found in the finger print region which supports the adsorption of SO₂ molecules from aqueous solutions. Not much work is carried out by the modified leaves of Bacopa monnieri so it is checked for adsorption.

2. **Hibiscus sabdariffa (Roselle):** Commonly known as Gongura which is available in two varieties green stemmed variety and red-stemmed variety. It can be grown in sandy and clay soils. Loamy soils are suitable for the growth of Gangura. Gangura leaves are collected from the garden of St. Ann’s college for women in Hyderabad.

**Chemical modification of Gongura:**[12-17]
The leaves were sundried, washed after cleaning. These leaves are treated with 0.01m KMnO₄ for structure modification. The modification has been done to increase oxidising groups which may lead to adsorption of SO₂. FTIR analysis carried out on Gongura leaves showed the presence of ketones, aldehydes aromatic compounds, alkanes, phenols, stretching of oxime/imine group acetyl, acid groups. (Rheological and functional properties of Roselle leaves puree. (Jaga Mohan Meher, Amit Keshav, Beduty Mazomdar potravinarslovsk Journal of food sciences 2019) these were used in the green synthesis of nanosilver fibres.
3. *Citrus limetta*[^18-22] Commonly called Lemongrass. It has many medicinal properties and it belongs to the grass family. It has antiseptic properties and it is good insect repellent. Lemongrass leaves were used in the present study after treating with 0.01N KMnO₄ after preliminary purification. The FTIR studies untreated with KMnO₄ showed a number of absorption peaks indicating complex nature and presence of Carbonyl, Hydroxyl and Amino groups (Comparative study on the biosorption of Pb(II), Cd(II), Zn(II) using lemongrass: Kinetics, isotherms and thermodynamics). Lemongrass has been modified used as an adsorbent for trapping synthetic dye molecules[^18] (Trapping synthetic dye molecules using modified lemon grass adsorbent, for creating from wastewater. lemongrass powder is used as an adsorbent for the treatment of chromium from tannery water for removal of methyl blue, lead ions from wastewater, methylene red dye, taking these factors into consideration they have been used for removal of SO₂ from aqueous solution.

4. *Abelmoschus esculentus* (lady finger)[^23-26]
Most common in India. It grows in tropical and subtropical regions. It consists of vitamins, minerals and proteins. They can be used for the treatment of Goitre as it is an excellent source of Iodine. Ladyfingers are used for the preparation of zerovalent iron nanoparticles, for dye removal, congo red, for adsorption of Cr(VI) azo dyes and fluoride removal. Taking this factor into consideration Abelmoschus esculent is have been successfully used for studying its adsorption capacity of SO₂. Abelmoschus is collected from Monda market, Hyderabad washed, cleaned, dried and powdered followed by treating with 0.01N KMnO₄ for adsorption studies.

5. *Aloe barbadensis miller* (Aloe vera): Aloe vera is a genius of Aloe. It is a green perennial plant widely grown with 500 varieties. Aloe vera was collected from the forest region of Rangareddy district, Telangana. Aloe vera has been used for wastewater treatment, heavy metals removal, dyes removal and other pollutants from the aqueous media.[^27-29] Taking that reason into consideration. Aloe Vera is treated with 0.01 N KMn04 and used for further studies after cleaning, dusting dried with the Aloe Vera leaves.

Lotus scientific name us *Nelumbo nucifera* and it is aquatic plant species of India, Lotus have submerged root systems. They grow in swamps and edges of lakes, rivers. They grow in polluted water also. Taking that factor into consideration lotus root powder has been investigated for controlling SO₂ pollution. Lotus roots contains polysaccharides that are modified for drug delivery. (Extraction, structural modification and characterization of lotus root polysaccharide excipient with potential application in modified drug delivery systems) Lotus roots were modified for better adsorption which were investigation by M.S. Munagapathi aa protonated amine-modified lotus, modified for Chromium(Cr⁶⁺) removal, reactive Rad¹⁹⁵ removal, Cadmium (Cd) removal. Lotus root is treated with KMnO₄ to increases the active sites for adsorption of SO₂.
7. **Hevea Brasiliensis (Rubber leaves)**[33-35]
   Rubber leaves are collected from St. Ann's college garden. They were dried, crushed and made into powders. These powders are treated with 0.001 N KMnO$_4$ solution for surface modifications. Rubber leaves are used as an adsorbent for copper, lead, chromium, methylene blue removal or acid-treated rubber leaves, sequestration of toxic Pb (ii) ions by chemically treated rubber, organic acid modified rubber, phosphoric acid-treated rubber and the hydrogel. Many studies have been carried out which promoted the studies of Rubber leaf as a bio adsorbent.

8. **Amaranthus(Thotakura (red))**: [36-38]
   Amaranthus is a perennial plant and they are summer weeds and are known as pigweeds. They have different types of pigments from the spectrum of maroon to crimson. These Amaranthus leaves are collected during summer from sitafal mandi near the railway tracks areas as they are widely grown in those areas and are considered waste plants. Considering the potential of agro-waste material leaves were cut, dried and made into powder. This powder is treated with KMnO$_4$. It is a novel adsorbent that was not studied in detail.

9. **Fenugreek (Methi)**: [39-42]
   Fenugreek leaves or Methi leaves consists of different vitamins like Vitamin K, Calcium, Vitamin E, Riboflavin and Folic acid. They are highly effective for many ailments. Not much has been studied about these leaves. The present studies so far have shown that these leaves screen out for the adsorption of SO$_2$.

10. **Psidium guajava (Guava)**: [43-45]
    Guava is a traditional plant. It grows in tropical and subtropical areas. Guava leaves are used as adsorbents by various investigations. Depending on the inherent knowledge of Guava leaves it has been modified by 0.01N KMnO$_4$ for removal of SO$_2$.

**Biosorption:**
A stock solution of 100ppm sodium metabisulphite is prepared using distilled water. Batch adsorption studies have been carried out by taking 40 ppm of 100ml aqueous solution of SO$_2$. 1 gm of adsorbent is added to bottles. The initial and final concentration of a solution by using the West-Geek method using a spectrophotometer.[46] The percentage removal of SO$_2$ is calculated.
Bacopa monnieri (Bramhi):
Polymeric in nature of Brahmi and presence of Baco residues I — 'll lead to the adsorption. The KMnO₄ helped in breaking the existing bonds. Due to the breaking of the bond on the surface of Brahmi or bio adsorbent, Brahmi has more active sites with more oxidizing groups. The complex surface mechanism can be ascribed for the removal of SO₂ molecules from an aqueous solution of SO₂. The percentage removal of SO₂ with Brahmi is 50% for a 40 ppm aqueous solution of SO₂.

Hibiscus sabdariffa (Roselle) Gongura:
Per cent removal it 52% Gongura is highly fibrous, polymeric nature. As it consists of C=C, N-H bonds it gets oxidized due to Manganate (III) ions. Oxygen from the oxidizing agent reacts with acidic SO₂ and gets adsorbed by other active sides of Gongura leaves. The reaction follows the biosorption process.

Aloe barbadensismiller (Aloe vera): The percentage of SO₂ from aqueous solution by modified Aloevera leaves is 40%. It was found from previous studies the specific surface of acid/base/oxidizing agent increases which have helped in the adsorption when the Aloevera is treated with the chemicals will have mesopores which were studied by the Barrett-Jaine-Helenda method.

Nelumbo nucifera seed powder:
The percent removal SO₂ with lotus seed powder is 40%. Many studies have been carried out lotus seed for derectutilisation yet no study was performed by chemical modification. The treated surface contains more active groups and leads to successful adsorption.
Hevea Brasiliensis (Rubber leaves):
Modified rubber leaves resulted in 52% adsorption of SO$_2$. It is a promising green adsorbent for successful adsorption. Physical forces/chemical forces may cause the binding of SO$_2$ with Rubber leaves.
The studies on methi leaves showed 12% adsorption, 3% adsorption with Thotakura and 1% with Guava leaves.

Results and discussions
1. The percentage removal of SO$_2$ with KMnO$_4$ modified ladyfingers is 68%. Ladyfinger consists of hemicellulose, lignin, and pectin. The ladyfingers consist of hydroxyl groups forming intra/intermolecular bonding among cellulose molecules. These complex, structural behaviour of functional groups are altered/modified by KMnO$_4$. Due to chemical modifications, many existing bonds are broken producing more active sites. Along with active sites, the number of oxygen-containing groups must have been increased which has led to adsorption of SO$_2$ molecular from aqueous solution.

2. The percentage removal of SO$_2$ with KMnO$_4$ modified lemongrass is 75%. As the lemongrass consists of a number of functional groups it is Polymeric nature which has been modified by KMnO$_4$. This modification has brought more active sites on surface, and may have given to more reactive nascent oxygen groups resulting in oxidation of SO$_2$ in and adsorbing process.

Conclusions
The adsorption capability of KMnO$_4$ modified plant based adsorbents for the removal of SO$_2$ from aqueous medium was investigated using screening tests. The order of removal efficiency is Citrus limetta > Abelmoschus esculentus > Hevea brasiliensis > Hibiscus sabdariffa > Bacopa monnieri > Aloe barbadensismiller > Psidium guajava > Nelumbo nucifera > Fenugreek > Amaranthus.

These screening measures enabled us in assessing the efficacy of the modified biosorbents in preparation for further research.

References:


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