Different types of peels, seeds and natural waste material used for the treatment of toxic ions in effluent.

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Abstract- *Growth of several industrialization has responsible for dumping of toxic metal ions into the environment. Copper, cadmium, lead, zinc, mercury, and chromium all toxic metals present in effluent. Various harmful metal ions entered into the water bodies through industrial activities. Different types of methods used for the treatment of toxic ions. Some methods are physiochemical or some natural methods. Physiochemical methods are coagulation, reverses osmosis, chemical precipitation etc. are used for the treatment of toxic ions. Different types of agricultural peels, fruits peels, industrial wastes etc. used for the removal of harmful ions. Adsorption is the best process for the treatment of toxic ions/metals. Two types of adsorbents are used in adsorption method like commercial adsorbents or low cost natural adsorbents. Low cost adsorbents are easily available and inexpensive for the removal of metal ions. This review paper will help for our research work to remove of somr toxic ions from ultramarine blue industrial effluents through natural adsorbents.*

Keywords: Industrialization, Treatment, Toxic metals, Adsorption, Effluent, Environment, Coagulation.

1. INTRODUCTION

Toxic metals have been excessively released into the environment due to the rapid industrialization and have created a major problem all around. Effluent produced industrial treatment plant contains significant toxic metal ions contaminants. Ultramarine blue industrial effluent is also responsible for the water and soil pollution because these industries produced every year large amount of toxic ions and these ions is harmful for our environment. Rapid industrialization has responsible for dumping of toxic metal ions into the environment[1]. Various harmful metal ions entered into the water bodies by industrial. Adsorption, coagulation, reverses osmosis, chemical precipitation, nanofiltration, electrochemical treatment, ultra filtration, etc are physicochemical methods includes. One of this method adsorption is the most inexpensive and effective because of their relative low cost. For the removal of toxic metal ions from industrial effluent adsorption method is mostly used by many researchers. Adsorption is one of the safest, easiest and most cost-effective methods for the removal of these metals from industrial effluent. Throughout the food chain toxic metal ions are accumulating in living tissues and it is poisonous and harmful for all living beings and environment[2].

Copper plays an important role in animal metabolism. But the too much ingestion of copper is harmful. Toxic symptoms of copper ion like vomiting, cramps, convulsions or even death[3].

For the physiological function of living beings Zn plays an important role. It is a trace element. But large quantity of Zn can cause various health problem like stomach cramps, skin problems, vomiting, nausea, and anaemia[4].

Mercury is a more toxic element. It can cause damage to the central nervous system and it is neurotoxin. Kidney function, chest pain, dyspnoea, and impairment of pulmonary etc. are affected through high concentrations of mercury[5].

Excessive amount of Nickel is serious for lung and kidney problems. Pulmonary fibrosis and skin dermatitis and gastrointestinal are affected. Nickel is also known as human carcinogen[6].

For human health severe risks is exposed to Cadmium. Cadmium is harmful for kidney functions and high levels of exposure will result in death.

Lead can cause central nervous system damage, kidney, liver and reproductive system, basic cellular processes and brain functions. Irritability, insomnia, dizziness, weakness of muscles, headache hallucination, anaemia, and renal damages are toxic symptoms[7].

Chromium present in aquatic environment mainly in two types; Cr(III) and Cr(VI). Cr(VI) is more toxic than Cr(III). Cr (VI) affects human physiology, accumulates in the food chain and causes severe health problems ranging from simple skin irritation to lung carcinoma[8].

2. VARIOUS CONVENTIONAL METHODS USED FOR WASTE WATER TREATMENT

I. CHEMICAL PRECIPITATION

Chemical precipitation method is simple and inexpensive technique. This method is mostly used in various industries for treatment of effluents[9]. In precipitation processes, chemicals react with heavy metal ions and form insoluble precipitates.

Precipitation methods are two types:-

A. Sulphide Precipitation - Sulphide precipitation is an effective process for the treatment of toxic heavy metals ions. Advantages of using sulphides are that the solubility's of the metal sulphide precipitates are dramatically lower than hydroxide precipitates. Sulphide precipitation methods are used for removal of Cu^{2+}, Cd^{2+}, and Pb^{2+} metal ions[10].

B. Hydroxide Precipitation - Hydroxide precipitation is a type of chemical precipitation technique and its relative simplicity, low cost and ease of pH control[11]. Metal hydroxides minimized pH range is 8.0-11.0 depends on solubility's. Flocculation and sedimentation methods are used for the removal of metal hydroxides. Due to the reason of low cost and easy handling different variety of hydroxides has been used[12]. By Hydroxide precipitation Cu^{2+}, Cr^{4+} metal ions removed from waste water[13].

II. ION EXCHANGE

Due to their many advantages, such as high removal efficiency, fast kinetics, and high treatment capacity ion exchange method is suitable for adsorption. Ion-exchange processes have been mostly used to remove heavy metals from wastewater[14]. Materials used in ion exchange processes, synthetic resins are usually preferred effective to nearly remove the heavy metals from the solution[15]. Due to their low cost and high abundance of natural zeolites and synthetic resins, naturally occurring silicate minerals etc. were used for the removal of toxic ions from aqueous solutions. Zeolites and montmorillonites used as ion-exchange resin for removal of metal ions, they are limited at present compared with the synthetic resins.

III. MEMBRANE FILTRATION

Ultrafiltration, reverse osmosis, nanofiltration and electrodialysis are the membrane processes used to remove metals from the wastewater. Membrane filtration technologies show great promise for heavy metal removal for their high efficiency, easy operation and space saving.

IV. ULTRAFILTRATION

For the removal of colloidal and dissolved material in ultrafiltration membrane technique used low pressures. Micellar enhanced ultrafiltration was studied for the treatment of multivalent metal ions and dissolved organic compounds and from aqueous streams[16] investigated the removal of zinc from synthetic wastewater by using Micellar enhanced ultrafiltration and Sodium dodecyl sulphate method.

V. REVERSE OSMOSIS

The reverse osmosis (RO) process uses a semi-permeable membrane, allowing the fluid that is being purified to pass through it, while rejecting the contaminants. RO is one of the techniques able to remove a wide range of dissolved species from

water[17]. $Cu^{2+}$and Ni^{2+}ions were successfully removed by the RO process and the rejection efficiency of the two ions increased up to 99.5% by using Na_2EDTA[18].

VI. NANOFILTRATION

Nanofiltration (NF) is the intermediate process between UF and RO. NF is a promising technology for the rejection of heavy metal ions such as nickel, chromium, copper, and arsenic from wastewater[19-22].

VII. ELECTRODIALYSIS

Electrodialysis (ED) is another membrane process for the separation of ions across charged membranes from one solution to another using an electric field as the driving force. This process has been widely used for the production of drinking and process water from brackish water and seawater, treatment of industrial effluents, recovery of useful materials from effluents and salt production[23]. Cu^{2+} and Fe^{2+} metal ions removed through electrodialysis method[24].

VII. COAGULATION AND FLOCCULATION

Coagulation and flocculation methods depend on sedimentation and filtration. This method is also working to remove heavy metal from wastewaters. By Coagulation soluble heavy metals and insoluble substances both are removed from waste water.

IX. FLOTATION

At the present time extensive use of flotation method is applied for wastewater treatment. This method employed to separate heavy metal from a liquid phase using bubble attachment, originated in mineral processing[25]. Cd^{2+}, Cu^{2+} and Pb^{2+} metal ions removed by Flotation method from dilute aqueous.

The process of ion flotation is based on imparting the ionic metal species in wastewaters hydrophobic by use of surfactants and subsequent removal of these hydrophobic species by air bubbles[26].

X. ELECTROCHEMICAL TREATMENT

In electrochemical treatment metal ions was removed on cathode surface. This method is expensive and desired large amount of electricity and investment for removal of metal ions. So it is not easy for applied. Zn^{2+}, Cu^{2+}, Ni^{2+}, Ag^{+} and $Cr_2O_7^{2-}$ removed through electrochemical methods[27].

3. ADSORPTION

Adsorption is the adhesive of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of the adsorbent.

Some important applications of adsorption are as under:-

Manufacture of gas mask, removing of colouring matter From Sugar Juice & vegetable oil, dehydration & purification of gases, dyeing of clothes, creation of high vacuum in laboratory, heterogenous catalysis, ion-exchange resins, chromotography, qualitative inorganic analysis and drugs.

On the basis of nature of forces which hold molecules of adsorbate to the surface of the adsorbent, adsorption is classified into two types as under:-

I. **PHYSICAL ADSORPTION OR PHYSIOSORPTION**:-

Physical adsorption does not depend upon the chemical nature of substance which is adsorbed. Physical adsorption increases with increase in pressure. This type of adsorption, the molecules of adsorbate are held by the weak vanderwaal's forces of attraction.

II. CHEMICAL ADSORPTION OR CHEMISORPTION:-

This type of adsorption mainly depends upon the chemical properties of gas and the adsorbent. For the formation of surface compound in chemical adsorption chemical linkage is formed between surface of adsorbent and the adsorbed molecule.

4. ADSORBENTS-

An adsorbent material causes a substance, usually a gas, to form a very thin layer on its surface. Different types of adsorbents are used for removal of toxic metals ions, its depend on industrial requirements.

I. COMMERCIAL ADSORBENTS- Different types of commercial adsorbents are used -

(i). **Silica gel**

Silica gel is mainly present in three forms– regular, intermediate, and low density gels. This gel is considered as a good adsorbent in many industries. [28, 29] For acidic medium silica gel shows high surface area and regular density.

(ii). **Activated alumina**

As an adsorbent activated alumina is receiving renewed attention and a wealth of information has been available[30-34] on its desorption character. Activated alumina is used to remove water from in organic liquids.

(iii)**. Zeolites**

Si and Al present in Zeolites ratios between one and infinity. There are 40 natural and over 100 synthetic zeolites. They are also considered as selective adsorbents. For the removal of pollutants[35-38] various zeolites have been engaged. Recently, observed natural zeolites is an effective adsorbents in water and wastewater treatment[39].

(iv). **Activated charcoal (Adsorbent)**

Activated carbon is the most popular, suitable and inexpensive used adsorbent in wastewater treatment all over the world. Charcoal, is the predecessor of modern activated carbon has been accepted as the oldest adsorbent known in wastewater treatment.

Economical adsorbents preparation from waste materials we got various advantages in economic and environment. Different waste materials utilizing such as agricultural, industrial and municipal wastes extensive variety of low-cost adsorbents have been prepared.

II. LOW-COST ADSORBENTS-

(i) Agricultural wastes

Cellulose containing agricultural materials shows probable sorption capacity for various pollutants. Due to its reasonable hardness and low ash content [40] agricultural wastes is rich source for activated carbon production. So, the exchange capacity of agricultural wastes into low-cost adsorbents is a hopeful substitute to decrease the preparation costs and to solve environmental problems.

(ii). Rice and Wheat waste

For maximum adsorption HNO_3, HCl, H_2SO_4 and $HClO_4$ was reported on treatment with 0.01 mol/L. Rice husks were used for arsenic removal from water[41]**.** Adsorbent (1 g) is used for 5.97×10^{-3} mol/L of arsenic in 5 min.

The adsorption behaviour of rice husks for antimony ions from aqueous solutions has been investigated[42]. The adsorption was studied as a function of appropriate electrolyte, equilibration time, hydrogen ions, amount of adsorbent, concentration of adsorbate, effect of diverse ions and temperature. Quantitative adsorption of antimony from aqueous solutions on rice husks was achieved within a short contact time of 10min. The reaction was found to be endothermic and occurred in presence of a variety of anions, with maximum adsorption in the presence of 0.01M HNO_3. The same researchers also studied the removal of Pb(II) and Hg(II) using rice husk as an adsorbent[43-44].

The adsorption of Pb(II) ions from aqueous solutions on wheat bran has also been reported[45]. For the adsorption of dye, Reactofix Navy Blue 2 GFN, from aqueous solution[46] activated wheat husk has also been found as an adsorbent. To achieve equilibrium conditions contact time 40min was sufficient. Furthermore, low pH and low temperature were found appropriate for maximum adsorption.

(iii). Tea and Coffee waste

Nickel, Iron, Lead and Zinc is easily removed from water through tea leaves wastes[47]. Lead is more adsorbed compare than iron, zinc and nickel from 5-100 mg/L of metal solution. Adsorption of copper by tea wastes was also determined[48].

Adsorption of heavy metal ions through tea leaves wastes is mostly depend on pH, contact time, initial concentration and adsorbent dosage of toxic ions. Adsorption capacities maximum is 6.65 and 2.59 mg/g for binary system, and 8.64 and 11.29 mg/g for single were determined of Cu (II) and Cd (II) respectively. As a low-cost adsorbent for the removal of zinc[42] were carried out by batch adsorption studies[49].

For water treatment coffee industry wastes as a adsorbents have been explored. Adsorption nature of heavy metals on arabica and robusta roasted coffee beans was investigated[50].

In the preparation of powder activated carbon coffee residue used as raw material by chemical activation with zinc chloride for the sorption of Pb(II) from dilute aqueous solutions[51]. Initial concentration of Pb(II), contact time, , solution pH, ionic strength and temperature are determined through batch adsorption experiments.

(iv).Coconut Waste

For the removal of various pollutants from water used coconut wastes like coconut husk, copra meal, coir pith, male flowers of coconut tree, and coconut bunch wastes etc. as adsorbents. Pb(II) ions removed by Coir pith wastes from aqueous solution[52]. For Pb (II) removal adsorption capacity was reported to be 263 mg/g. This capacity is increase with increasing pH from 2 to 4 and remained stable up to pH 10. From aqueous solution methylene blue removed by coconut bunch waste (CBW)[53]. The monolayer adsorption ability was originated to be 70.92 mg/g at 30°C. The pseudo-second order kinetic model is fitted very well for obtained kinetic data at different concentrations.

(v). Peanut or groundnut waste

For the removal of different pollutants, harmful germs, waste materials from waste water used adsorbents peanut/groundnut's husk/hull. The removal of cadmium and lead ions from aqueous solutions by groundnut husks was examined through equilibrium sorption studies at 29°C[54]. For Cu^{2+} and Pb^{2+} removal is possible through peanut hulls[55]. The influence of initial pH (3-5) was evaluated and set between 4.0 and 4.5.

By chemical activation with $ZnCl_2$ below optimized conditions groundnut shell was used as an adsorbent and its comparative characterization was carry out with commercially available powdered activated carbon (CPAC) for its adsorption, chemical and physical properties[56].

(vi) . Peels of different Agricultural Waste

Different types of agricultural wastes like cassava, mango, orange, banana, watermelon, etc. were used for the treatment of different various industrial pollutants. Ni (II) ions was examined from electroplating wastewater by orange peels[57].

(vii). Agricultural Waste Shell

Several researchers used various agricultural products shells as adsorbents for the removal of toxic pollutants from water. For the preparation of activated carbon Bael fruit shell was used as an efficient low-cost adsorbent to remove Cr (VI) from aqueous phase[58]. Maximum chromium removal was found at pH 2.0 and equilibrium time at 240 min. Capacity is 17.27 mg/g. was found in Langmuir monolayer sorption.

(viii). Stem, Seed, Seed Coat and Stalk of Different Agricultural Products

Several agricultural products like seed, stem, and seed coat as low-cost adsorbents for the removal of heavy metals since industrial waste water. Many researchers investigated that papaya seeds (PS) is good adsorbent for the methylene blue adsorption[59]. To study the effects of initial concentration (50-360 mg/L), pH (3-10), adsorbent dose (0.05-1.00g) and contact time batch adsorption methods were applied. Methylene blue (MB) removable temperature is 30 ◦C. The Langmuir model present well fitted data at maximum adsorption capacity of 555.55 mg/g. For the adsorption of MB and PS with good correlation by pseudo-second-order kinetics fitted well. From aqueous solutions Cr (VI) ions removed by Tamarind seeds as adsorbent[60]. For methylene blue removal from aqueous solution pineapple stem waste, was investigated as low-cost adsorbent[61]. As an adsorbent sunflower stalks were used for the removable of methylene blue and Basic red 9 dyes[62].

(ix). Municipal and Industrial Wastes as low-cost Adsorbents

Large amount of Solid waste materials as by-products produced in common industrial activities. But this solid waste material proper utilization is not doing by industries. This industrial waste material is available almost free of cost and causes major disposal problem. As a low-cost adsorbents solid wastes provide two advantage to environmental pollution, the low-cost adsorbent if developed can reduce the pollution of wastewaters at a reasonable cost and the volume of waste materials could be partly reduced.

(a) Fly ash

Many researchers used fly ash for the treatment of cu^{2+} ions and confirmed adsorption data with the help of Langmuir kinetic model. In fly ash the high percentage of silica and alumina is good for use as a reasonably priced adsorbent for bulk use[63].

(b) Wastes of Steel industry (sludge, dust and blast furnace slag,)

Blast furnace slag, dust and sludge, etc. all are steel industries wastes and all these wastes have been used as adsorbents[64]. Researchers investigated un granulated blast furnace slag for the removal of Zn^{2+} ,Cu^{2+}, and Ni^{2+} ions from waste water and examined that slag alkalizing activity creates positive conditions for adsorption through hydroxocomplex formation and colloidal particles of silicic acid. Use hard and soft granulated slag for removal of phosphate. Soft granulated slag is good adsorbent and hard granulated slag described the permeability of adsorbent.[65-69]

(c) Red Mud

For the treatment of fluoride ion Red mud is used as adsorbents[70]. For wastewater, solid waste product of aluminium industry is also used[71].

(d) Fertilizer industry waste

In aqueous solutions Cu^{2+}, Cr^{6+}, Hg^{2+}, and Pb^{2+} was removed through fertilizer industry wastes[72] and it showed excellent adsorption capacities for the studied metal ions. Carbon slurry waste has also been investigated for the removal of dyes, phenols, anions, pesticides, etc. from water and found to be promising adsorbent[73-76].

(e). Paper industry wastes

Today paper industry also produces a large number of by-products in huge quantities. These products generate severe disposal problems and degrade the surrounding environment[77].

They used waste newspaper for the production of activated carbon as raw material. Paper industry wastes (sludge from virgin pulp mill and de-inking paper sludge) were used for the treatment of Cu^{2+} from waste water[78].

5. Adsorption Capacity of Different Activated Agro-waste Materials

S. No.	Toxic metal (ions, dyes and organic pollutants)	Agro waste (low cost adsorbents)	Optimum efficiency
1.	Cd(II) toxic ions	NaOH and $NaHCO_3$ treated rice husk	8.58 mg/g[79]
2.	Ni(II) ions	H_3PO_4 trated rice bran	102mg/g [80]
3.	Cr(VI), Methylene blue, Acid yellow 36, Indigo carmine Safranine, Acid blue-15, Acid red-119, Acid violet-49, Acid violet-54, Acid violet-17, Basic blue-9	Rice Husk Ash	45.5 mg/g 312 mg/g 86.9 mg/g 29.3-65.9mg/ 838mg/g 99.4-155mg/g 19.83 mg/g[81-86]
4.	Cu(II), Pb(II)	Tea waste	48-65 mg/g[87]

5.	Cd(II) Cr(II) Pb(II) Methylene blue Methylene orange Congo red	Banana peel Banana peels Mango peels Banana peels Banana peels Orange peels	35.52 mg/g 131.56 mg/g 99.05 mg/g 15.9 mg/g 17.2 mg/g 7.9 mg/g[88-95]
6.	Zn(II)	Tea factory waste	8.9mg/g[96]
7.	Cu(II) Ni(II) Zn(II)	Mango peels	46.06mg/g 39.75mg/g 28.21mg/g[97]
8.	Methylene blue	Garlic peels	82.64-142.86 mg/g[98]
9.	Pb(II)	Hazelnut shell Almond shell	28.18 mg/g 8.08 mg/g[99]
10.	Cd(II) Cd(II) Pb(II)	Sugargane bagasse Grape bagasse	38.03 mg/g. 0.774 mg/g 0.428 mg/g[100-101]
11.	Basic dye Acid dye 2,4-dichlorophenol	Maize cob	160 - 94.7 47.7-41.4mg/ 17.94mg/g[102-103]
12.	acid blue 264, basic blue 69, basic blue 9	Pinewood	1176 mg/g, 1119 mg/g 556 mg/g[104]
13.	remazol black B	Cotton stalk	35.7 mg/g[105].
14..	methylene blue	Pearl millet husk	82.37 mg/[g106]
15.	Lead, Cadmium, Zinc, Copper, and Nickle	black gram husk	19.56-49.97 mg/g.[107]
16.	Methylene blue Cr(VI) o-cresol	papaya seeds Tamarind seeds palm seed coat	555.55 mg/g 29.7 mg/g 19.58 mg/g[108-109]
17.	Cu(II), Hg(II), As(V), phenol, 4-Chlorophenol, 2, 4- Dichlorophenol	Fly ash	1.39 mg/g 2.82 mg/g 19.46 mg/g f5.58 - 6.48 mg/g 8.62-10.0mg/g 8.16-8.72[110-114].

18.	Pb(II), As, Cr(VI), Zn, Cd	blast furnace slag	40mg/g 1.40mg/g 7.5mg/g 17.66mg/g 18.72mg/g[115-116]
19.	Cu^{2+}, Zn^{2+} Ni^{2+} Cd^{2+} Pb^{2+} Cr^{6+}	Red mud	19.72 mg/g, 12.59 mg/g, 10.95 mg/g 10.57 mg/g. 64.79 mg/g 35.66mg/g[117-118]
20.	As (VI), Cr (VI).	Solid waste from leather industry Iron complexes leather industry waste	26 and 133 mg/g. 51mg/g[111-120].

6. CONCLUSION –

Through the preparation of this review paper it will be observed that various types of agriculture wastes, fruit peels, vegetables peels, clays, natural adsorbents, fruit seeds, agricultural waste Shells, fly ash, Industrial wastes etc. were used for the removal of toxic ions and pollutants. Different types of parameters such as pH, equilibrium time, doses, concentration etc. obtained. For the treatment of heavy metals ions and pollutants used several methods such as chemical precipitation, coagulation, flocculation, flotation, ion exchange, reverse osmosis, membrane filtration etc. But the use of low cost adsorbents and biosorbents is more effective and reasonable for removal of toxic metal ions.

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