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# A Study On The Consequence And Treatment Of Pharmaceutical Components Present In The Discarding Effluents To The Environment And Management Methods Using Biomass.

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**ABSTRACT**

The progress of pharmaceutical industries and their technique has extended its emission of pollution to the environment which affects water bodies. The unused pharmaceutical product and trace of pharmaceutical compounds present in the faeces of human and veterinary consumers like antibiotics, painkillers, contraceptives, and other drugs get disposed of through wastewater which produces an environment effect that disturbs human health and surroundings. These wastewaters mainly consist of contaminants of PPCP compounds in them. Before discharging the compounds to the surroundings this wastewater has to be treated to remove the harmful chemicals present in them. In this study, various studies of Endocrine-disrupting compound (EDC) antibiotics like Ciprofloxacin (CPX), Ofloxacin (OFL) Tetracyclin (TCL), Trimethoprim (TMP), Erythromycin (EM) and Sulfamethoxazole (SFM) were selected and discussed. Normal wastewater treatments like coagulation, sedimentation, flocculation and other techniques are not advisable for the removal of these contaminants present in the Pharmaceutical wastewater treatment. This review explains the various biomass used in the sorption of these components .Waste Biomass is usually disposed of as animal feed which can be treated and used as an effective sorption material. By using this method, volume of solid waste gets reduced with subsequent removal of harmful endocrine disruptors.

**Keywords:** Adsorption, Antibiotics, Biosorption, Endocrine disrupting PPCPs.

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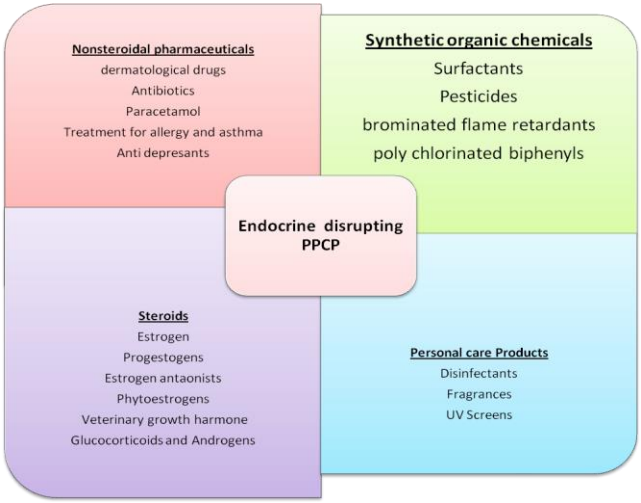
## INTRODUCTION

In recent days Pharmaceutical and personal care products (PPCP's) have influenced human lifestyle in protecting them from harm and retain a healthy life. In the history of medicines, modern technologies started developing after the 20th century. Pharmaceutical products are defined as a prescribed material from the doctor for treating human and animal health and improve the quality of everyday life. In recent days the development of advanced researches and technologies in PPCPs has created a major concern in creating awareness about the impacts and changes caused by them. The concentration of these PPCPs has an impact on water, sediments, and biota which will affect the surroundings. The wastewater treatment (WWT) used in removing this effluent does not remove the entire harmful chemicals present in them. Even the left out trace will slowly create a huge impact in affecting the surrounding environments and human life. A list of pollutants are identified and listed by European Union (EU) and United States Environmental Protection Agency (USEPA) which consist of a wide range of chemicals present in the wastewater and runoff storm waters get connected with the surrounding local bodies and surface water which threatens human life (1). Due to their perceived relative risk, the Environment Agency (EA) of England and Whales have proposed a ranking system of the chemicals which helps in identifying the substances that create a great potential in affecting the water bodies.

The wastewater discharged to the environment will produce an endocrine disrupting effect in humans as well as other living organisms. The impact of PPCPs will create some endocrine-related disease and physiological effects in humans and animal wildlife (2). The Endocrine disrupting PPCPs can be classified into Steroids, Personal care products, and non-steroidal pharmaceuticals. The extensive use of PPCPs has become a major threat in creating an impact on the environment. The Endocrine disrupting chemicals (EDCs) has the recent attraction from the researches about their impacts on human and veterinary medicines. The impact of these EDCs through aquatic environment creates a major concern about the exposure of humans and animals to them. The chemical disinfections produce an unintended effect in producing some health impacts. Even disease and health effects like cancer, immune system damage, inhalation problems, and dermal problems, reproductive and developmental effects can be linked with the effect of hazardous content produced by the chemicals (3). Some of the top components used in preparing PPCPs are aminophylline, lofepramine, clotrimazole, thioridazine, tamoxifen, tramadol, and paracetamol. These components can be classified into three according to their persistence level (Table 1). The 10 pharmaceuticals are categorized into low persistence, medium persistence, and high persistence according to the dissipation time in water or sediment samples (DT50). Hence the degraded pharmaceutical gets discharged constantly would behave as persistent compound (4) Due to the incomplete removal during the treatment the effluent from wastewater consists of EDC and PPCPs in a range of 1.0ng L-1 to 1.0µ L-1 (5). These waters can transmit the chemical to the agriculture field and other water sources. Consumption of this chemicals leads to emerging pollutants to the environment. The Endocrine disrupting PPCP can be classified according to their characteristics and functions (Fig.1). These chemical starts reacting with the water slowly and creates a harmful nature to the water.

**Figure 1: Endocrine disrupting PPCP.**



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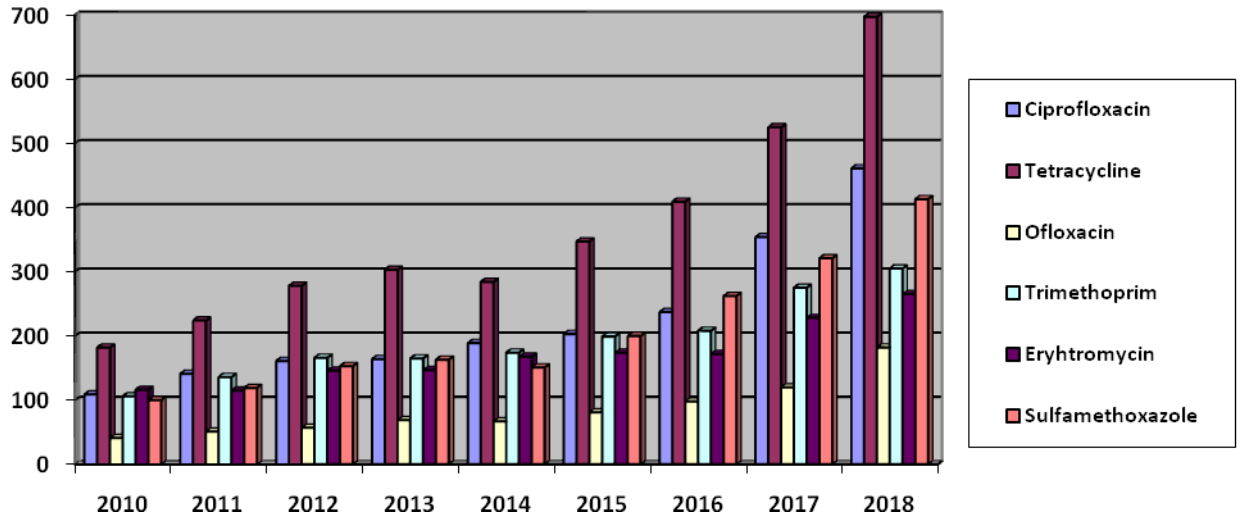
The usage of pharmaceutical products has increased drastically over the past 30 years. Currently, there are more than 3000 compounds are used in the manufacture of PPCPs (6). In PPCP compounds antibiotics is reported as the most commonly used compound which affects the water cycles (7). China leads in the production of antibiotics. They produce 210000t of antibiotics annually. Antibiotics from industries and domestic sources are transported to the wastewater treatment plants (WWTPs). The treated effluents from WWTPs are discharged as a treated effluent to the rivers and other water bodies and sludge produced in the treatment process are used as fertilizers (8). The antibiotics present in this waste get distributed consistently which facilitate the pathogens to threaten the public health. Continues usage and improper discharge of these antibiotics has created a major concern. The occurrence and the fate of residues lead to an impact on human health and veterinaries. The compounds entering the water slowly get decayed and forms harmful to the surroundings (9). The production and consumption of these PPCPs are playing a vital role in depleting the environment slowly. In recent years the extensive use of these products has led to the accumulation of these compounds to the ecosystem and food chains. The PPCPs compound has a tendency to affect directly or indirectly. The compound present in PPCPs water creates a major concern due to its concentration level, toxicity, and emerging contaminants (10).

The current study investigates about various antibiotic compounds such as Ciprofloxacin, Tetracycline, Ofloxacin, trimethoprim, Erythromycin, and Sulfamethoxazole. In recent days various researches and techniques have been done in the removal of these compounds from the wastewater. Apart from various techniques, this study is about various biomasses that can be used as an effective biosorbent in the removal of these toxic compounds from the wastewater. Due to increasing usage of these compounds attention of the researchers have increased in this recently (Figure 2). This paper also explains the disposals and also verdict the proper biosorbent material to treat the compounds present in the waste. This study also describes various characteristics of sorbent materials and its commercial availabilities.

**Figure 2: Recent studies in PPCP treatment using Biosorption**



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## MATERIALS AND METHODOLOGY

### Chemical compounds

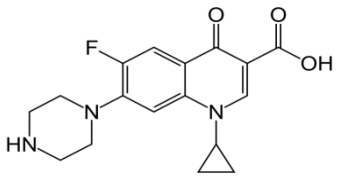
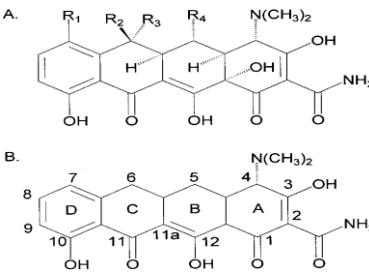
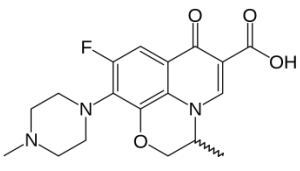
The influents and effluents from the disposal of wastewater samples are collected manually and analyzed according to the guidelines established (11). Pharmaceutical waste is considered to be hazardous waste which can be listed according to their chemical characteristics. Hazardous waste is classified as P- Listed, U-Listed, D-Listed, F-Listed and K-listed chemicals. They depend on the corrosively, toxicity, reactivity nature of the effluent. The persistence level of these compounds can be classified into low persistence, moderate resistance and high resistance these compounds are classified with respect to dispersion time (DT). The different compounds are shown in (Table.1).

**Table 1: Persistence level of compounds**

| Persistance level | Compounds | Dissipation time |
|---|---|---|
| Low persistance | Paracetamol Iburofen 2-hydroxybuprofin CBZ-idol | DT50= 3.1-7 days |
| Moderate persistence | Oxazepam Ivermectin Iopromide | DT50=15-54 days |
| High persistence | Carbamazepine Diazepam Clofibric cis | DT50= 119-328 days |

These harmful chemicals have to be disposed without affecting the environment. Adsorption is the most effective method in removing chemicals from the waste water. This study explains about the adsorption method using various bio mass as a filter medium in removing various chemicals. More than 10000 compounds have registered for preparing public care products (PCPs). In this a large number of compounds are present in the WWTP effluents as a residue. Some common antibiotics present in the effluent of WWTP are ciprofloxacin, tetracycline, Ofloxacin, trimethoprim, erythromycin and sulphamethoxide (Table.2). These compounds used in medicines as an antibiotic prescribed by doctors.

**Table 2: Physiochemical characteristics of compounds**

| | | | | |
|---|---|---|---|---|
| Ciprofloxacin | $C_{17}H_{18}FN_3O_3$ | 331.346 g/mol | Bacterial infections, joint infection, diarrhea, skin infection, typhoid. |  |
| Tetracycline | $C_{22}H_{24}N_2O_8$ | 444.435 g/mol | Cholera, brucellosis, malaria, syphilis |  |
| Ofloxacin | $C_{18}H_{20}FN_3O_4$ | 361.368 g/mol | Pneumonia, urinary tract infection, infectious diarrhea. |  |

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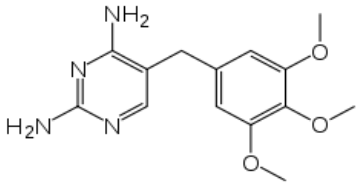
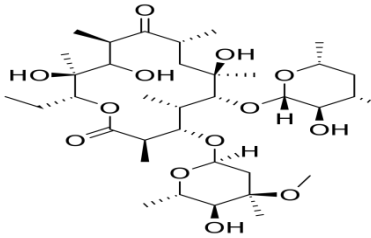
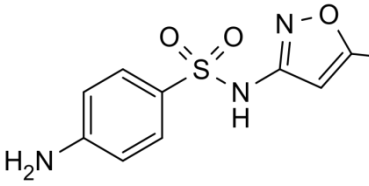
| | | | | |
|---|---|---|---|---|
| Trimethoprim | $C_{14}H_{18}N_4O_3$ | 290.32 g/mol | Bladder infection, ear infection, diarrhea |  |
| Erythromycin | $C_{37}H_{67}NO_{13}$ | 733.93 g/mol | Skin infections, pelvic inflammatory disease, syphilis |  |
| Sulfamethoxazole | $C_{10}H_{11}N_3O_3S$ | 253.279 g/mol | Bronchitis, urinary tract infection, effective against bacteria such as Listeria monocotogenes and E.coli. |  |

These harmful chemicals have to be disposed of without affecting the environment. Adsorption is the most effective method in removing chemicals from the wastewater. This study explains the adsorption method using various biomasses as a filter medium in removing various chemicals. More than 10000 compounds have registered for preparing public care products (PCPs). In this, a large number of compounds are present in the WWTP effluents as a residue. Some common antibiotics present in the effluent of WWTP are ciprofloxacin, tetracycline, Ofloxacin, trimethoprim, erythromycin and sulpha methoxide (Table.2). These compounds used in medicines as an antibiotic prescribed by doctors.

**Table 3: Inputs and outputs from pharmaceutical industry**

| Process | Input | wastewater | Residual waste |
|---|---|---|---|
| Chemical synthesis Reaction | Solvents, catalyst, reactants, e.g. benzene, chloroform, ethylene glycol, hydrochloric acid | Process wastewater with spent solvent, catalyst, reactants. High in BOD, COD, TSS with pH 1-11 | Reaction residue and reactor bottom wastes |
| Separation | Separation and extraction solvents, e.g. methanol, toluene, acetone and hexanes | Spills, leaks, spent solvents | Separation residues |
| Purification | Purification of solvents, e.g. Methanol, Toluene, Acetone and Hexanes | Leaks, spills, spent solvents | Purification residues |
| Drying | Finished active drug and intermediates | Leaks, spills, spent solvents | - |
| Natural product extraction | Plant roots, animal tissues, extraction solvents, e.g. chloroform, phenol and ammonia. | Spills, equipment cleaning, spent solvents and leaks. Low COD, BOD, pH of 6–8 and TSS. | Spent raw materials (Plants, roots, etc.) |
| Fermentation | Inoculums, sugar, starches, nutrient, phosphates, fermentation solvents, e.g. acetone, ethanol, amyl alcohol, methanol, and MiBK, etc | Spent fermentation broth, wastewater containing sugar, nutrients, etc. High COD, BOD and pH 4–8 | Waste filter cake, fermentation residues |

| | | | |
|---|---|---|---|
| Formulations | Active drug, binders, sugar syrups, etc | Equipment cleaning, Leaks, spills and spent solvents, pH range of 6-8, low COD, BOD and TSS. | Particulates, waste packaging, rejected tablets, capsules, etc |

These are the various disposal points of pharmaceutical waste from the industry. These effluents have to be treated effectively before sending out to the environment. After treatment few chemicals can be reused or it can be used for some other process. There are many methods and technologies used to remove contaminants from the disposal like chemical and physical precipitation, solvent extraction, ion exchange, and filter membranes. In this adsorption is the most effective method in the removal of metals (12). The material used in this adsorption process may be high in expenditure, required great energy expenditure to prepare a small quantity of adsorbent. In this case, Biosorption plays a significant role in the removal of these contaminants from the wastewater with the help of natural biomass that is left out as a biowaste (13).

**Different types of Biosorbent**

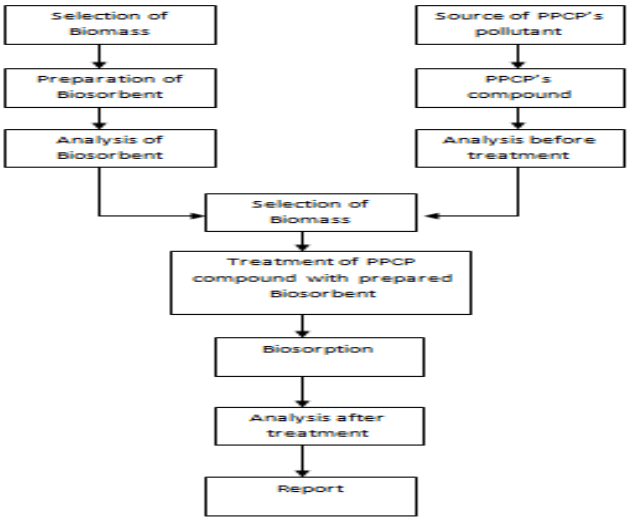
The residues from agriculture or left out biomass are used as various biosorbents in the removal of heavy metals and chemicals present in the wastewater. Rice straw is used as an agro waste biosorbent in the removal of heavy metal (14), removal of copper and zinc by using Chinese cabbage(Brassica campestris), sunflower (Helianthus annuus), reed (Phragmites communis) and cattail (Typha latifolia) (15), aquatic biomass of Indian star grass (Hydrilla verticillata) (16), peanut shell (Arachis hypogaea) (17 ), seaweeds (18), tea waste (19), wood bark (20), spent mushroom waste (Pleurotus ostreatus) (21), almond shells, palm shells (22), marine algal biomass, bagasse fly ash ,sawdust, wool, olive cake, pine needles (23), rice husk (24),pine bark, cactus leaves(25).

**Preparation of Biosorbent**

The collected biomass is cleaned thoroughly to remove the unwanted particles present in them. After cleaning thoroughly with water, the biomass is cut into small pieces. These sliced biomasses are dried under sunlight for few days to remove the moisture content present in them. The dried biomass is kept in an oven for further drying. After drying the material is crushed into powder and sieved using mesh and stored in an airtight vessel (16).

Desorption can be carried out in this for reutilizing the exhausted biosorbent by passing them through proton exchange by means of acids like CaCl2 or EDTA. By this, the capable eluant desorbs the metals completely without deteriorating (26).

**Figure 3: Biosorption analysis**



**Adsorption of compounds**

**Ciprofloxacin:**

Ciprofloxacin (CPX) is the second generation fluoroquinolone antibiotic. It is a very commonly used compound for curing many bacterial infections. Extensive usage of these compounds leads to the existence of these compounds in low concentration. (27). Adsorption is the most preferred technique in removing these compounds from the wastewater. For the adsorption of ciprofloxacin (CIP) some of the natural adsorbents like Moringa oleifera (28) and algae like Scenedesmus obliquus (29), some animal faeces like rabbit manure biochar (30), kitchen waste like potatoes, soybeans (31, 32), rice straws (33), astragalus mongholicus, enteromorpha prolifera (34). Biosorption is a promising technique using this biomass in the removal of the toxic chemical from the wastewater. These biosorbents are low cost, easily available and good removal of chemicals (35). The aim of this study tends to give details about various biomass used in the removal of CPX from the wastewater.

**Adsorption of Ciprofloxacin using Enteromorpha prolifera:**

The enteromorpha prolifera algae are washed and dried under the sun for 6 days. The dried alga is crushed and ground under 80 meshes. It is analyzed using Perkin-Elmer 283B FTIR spectrometer. E. Prolifera is an effective biosorbent in the removal of CPX. Apart from removing CPX, E.Prolifera can also be used to remove metals like lead, copper, and dyes. The good adsorption properties of E.Prolifera are due to its presence of amino carboxyl, hydroxyl, phosphate and sulfate group present in its surface. The experiment is carried out in the batch process (34). After the adsorption process the samples are separated by using a centrifugation process at 800rpm for 8 min. from the separated sample the amount of adsorption taken place can be calculated using

$$Qe= ((I.C-O.C)/M_e )/Vol \quad (1)$$

Where:

I.C-O.C - Initial and equilibrium concentration of Ciprofloxacin.
Vol- Volume of the solution.
$M_e$- Weight of Enteromorpha prolifera in grams.

**Tetracycline:**

Tetracycline (TCL) a residue in aquatic conditions has creates a serious concern in recent years. Since the antibiotic is poorly metabolized and absorbed by humans and animals. A large amount gets excreted through feces and urine (36). As the residues transported to the groundwater and surface water results in the growth of antimicrobial bacteria affects the water quality (37). The trace of tetracycline concentration present in the wastewater varies high up to 216 mg L-1(38). These trace of tetracycline can be removed using low-cost absorption. This study is about various investigations done to find the mechanism of sorption involved in using the biosorption. Tetracycline trace is removed using various biomass like Chitin, Chitosan (39, 40), Canola biomass (41), Pachydictyon coriaceum (42), sponge like Rosa cannia (43), seaweeds (44, 45) agricultural waste sorption material (46), sawdust, rice straw (47, 48). These are some of the biomass used in the sorption of tetracycline from the aqueous environment.

**Adsorption of Tetracycline using seaweeds biomass:**

Seaweeds are collected from the different coast and used as an effective sorption material. These collected seaweeds are washed thoroughly with water and dried under 80-85° overnight. The dried biomass is ground and separated by screening with 100 mesh sieve. The powdered material is then treated with conc. H2So4 for 1 day and washed with dil.NaOH solution. After treating use DI water to neutralize the solution. The resulted solution is dried and stored in a container (44). The prepared biosorbent is added to tetracycline solution in different dosages. The solution is agitated at 170 rpm using temperature controlling shaker for 3 hrs. Agitating the solution is centrifuged to 1000 rpm for 10 minutes. The amount of tetracycline removed is calculated using UV-Visible spectrometer (45).

**Ofloxacin**

Ofloxacin (OFL) antibiotic is used to treat some infections by killing bacteria. Ofloxacine residue present in aqueous solution gets degraded slowly and creates side effects like diarrhea, nausea, and vomiting to the consumer. The intensive use of OFL leads to a widespread occurrence in the ground, surface and sea water (49).

The municipal wastewater effluents consist of high concentration (50). However, due to its limited biological degradation, the residues create an environmental pollution. These residues can be removed by using biochars from various products including bamboo, straws, peanut shells and microalgae (51, 52, 53, 54), Moringa Oleifera (55), spent tea leaves (56), activated sponge from Luffa sponge (57). This biomass is capable of removing OFL residues from the wastewater.

**Adsorption of Ofloxacine using Cassava dreg biochar:**

The collected Cassava dregs were dried in room temperature. The moisture content was removed completely and it is grinded to a mesh size of 1 mm sieve. The powdered cassava dreg is placed in a crucible and made in char at different temperature (350°-750°C) under limited oxygen in a muffle furnace. The biochar produced is passed through 60 mm mesh sieve (58). The ash content is the mass remaining after heating at 750°C for four hours. This is calculated by:

Ash (%) = (Weight of ash content/ Dry weight of biochar) x 100 (2)

Adsorption of OFL solution is determined by using the batch equilibrium method. 50ml centrifuge tube 10 ml of 0.1 MCaCl2 solutions is spiked with 30 mg L-1 of OFL is added with a certain amount of prepared biochar (0.5-0.1 g). The tubes are sealed well and shaken in dark 298 K with 200 rpm for 1day. The solution attains an equilibrium state with the biochar. The equilibrium solution is centrifuged at 8000 rpm for 5 min. high-pressure liquid chromatography (HPLC) is used to analyze the filtrate.

**Trimethoprim**

Past couple of year's diverse type of PPCP residues is detected in the aqueous environment which creates a sensitive risk in the ecosystem (59). Trimethoprim (TMP) antibiotic is prescribed to eliminate bacteria's causing urinary infections. It also has some side effects like vomiting, diarrhea, and stomach upset. The wide usage of these antibiotics has created more attention as water-borne pollutants. It is very difficult to stop consuming these antibiotic agents, so researches have been carried out in the removal of these compounds from water bodies using low-cost biosorbents. The released antibiotics into the environment have a concern due to contamination of raw water, recycled water, and treated water (Rang et.al 1999). The waste biomass chicken feather derived charcoal (60), the biomass of bacteria like Pseudomonas putida (61), kitchen tea waste (62), and the biomass of chitosan. These low-cost biosorbents are capable of removing the toxic content present in the wastewater.

**Adsorption of Trimethoprim using chicken feather:**

Chicken feather is a useful biomass in the removal of TMP. Chicken feathers are obtained from the market and washed with distilled water. The impurities are removed and it is dried at 80°c for one day. The dried feather is crushed into small particles using a high-speed pulverizer. The crushed feather is made into biosorbent (63). Chicken feather consists of hydrophobic keratin which enhances the resistance of polymer-based composites (64). A batch equilibrium studies are carried out to investigate the concentration, temperature, adsorbent dose and strength of adsorption. A UV-visible spectrometer is used to find the maximum adsorption using Chicken feathers as a low-cost biosorbent. The effect of pH and temperature is measured using pH meter and adjusting the solution temperature according to adsorption isotherms.

**Erythromycin:**

Erythromycin (EM) is used for the treatment of certain infection caused by bacteria such as pneumonia, respiratory tract infection, pertussis (Severe coughing), lung infection and diphtheria (throat

infection). EM is called macrolide antibiotics which stop the growth of bacteria. However, these drugs are improperly applied and observed as residues in the wastewater and animal source food such as milk (65). EM is a bio-fermentation residue which can be used as a nutrient source. The contaminants present in the EM residue have to be considered at a suitable level of utilization. Chitosan from shrimp shells are used as biosorbent in the removal of these residues (65), ralstonia solanacearum (66), cashew nut shell, hazelnut shell, and olive stone (67, 68, 69). The reuse of EM residue as a nutrient has reduced the impact towards environment but still, biosorbent can be used in the remove the concentration of EM in the wastewater.

**Adsorption of Erythromycin using Ralstonia solanacearum:**

The experiment is carried out in a batch process by fixing the parameters namely pH, temperature, concentration and contact time. The collected samples are centrifuged at 8000 rpm for 20 min. Prepared antibiotic-impregnated disc was placed on the agar plate and incubated for 1 day at 37°C. The samples were washed using distilled water thrice and mixed with potassium bromide at a ratio of 1:100. Microscopic examinations of loaded and unloaded biosorbent were observed using a scanning electron microscope (SEM) and X-ray spectroscopy (EDX). The samples were separated into pellets and washed with distilled water and dried for 48 hours at 60°C in the hot air oven. The experiment shows a maximum removal capacity of 90% using Ralstonia solanacearum (66).

**Sulfamethoxazole**

The combination of sulfamethoxazole (SFM) and trimethoprim (TMP) is used in infections like a middle ear infection, urinary tract infection, traveler's diarrhea, shigellosis, and bronchitis. Common side effects of using this drug are dizziness, headache, vomiting, and rash. The PPCP antibiotics used in curing these EDCs are distributing to the environmental aquatic system and slowly degrade the water bodies (1). These harmful residues can be removed using various low-cost sorbents like coffee waste, banana peel, coir pith, rice husk (70, 71), and Euphorbia rigida biomass (72). This low-cost biomass is used as an effective adsorption material in removing the concentration of SFM from the effluent wastewater.

**Adsorption of Sulfamethoxazole using Long root Eichhornia crassipes powder.**

The root is washed and dried completely to remove the impurities. The dried root is powdered for further analysis. The batch test of SFM adsorption is carried out by the effect of initial pH, concentration, temperature, reaction time and ion strength. 0.2 g of adsorbent is added to 100 ml SFM aqueous solution in a 250 ml flask. The pH of the solution is adjusted by adding H2SO4 and NaOH solution. The temperature is controlled in a lucifugal oscillator at 195rpm at a given temperature. The sample is filtered and methanol was mixed with the solution at 3:7 volume ratios. The mixture is again filtered through a 0.25µm filter. The removal efficiency is calculated by:

$$\text{Removal efficiency (\%)} = (I.C_e\text{-}O.C_e/Co)*100\% \quad (3)$$

$$Qe = ((I.C_e\text{-}O.C_e)*V)/\ m \quad (4)$$

Where

$I.C_e$-$O.C_e$ (µL-1) was the initial and equilibrium concentration.
Qe (µg g-1) is the adsorption capacity.

In this study long root, Eichhornia crassipes powder is effectively used as an environment-friendly biosorbent in the removal of sulfonamides from the aqueous solution.

**CONCLUSION**

This review presents biosorption studies on antibiotics like CPX, TCL, OFL, TMP, EM and SFM. This paper also explains the detrimental effects of these antibiotics in water bodies and various low cost biosorbents used in the removal of their residues present in the various effluents. This review also discusses about various biomass which can be used as an adsorbent material for the antibiotics mentioned.

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