A Review on Pharmaceutical Compounds in Water and their Removal Technologies

Sanjeevani Parmar[1], Dr. Sarita Sharma[2], Dr. Ashok Sharma[3], Dr. Sanjay Verma[4]

[1]MTech, Research scholar, Department of chemical engineering, Ujjain engineering college,Ujjain 456010 (MP), India

[2, 3, 4]Professor, Department of chemical engineering, Ujjain engineering college,Ujjain 456010 (MP), India

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Abstract - *Recently, the health, economy and reduction of pollution are great cause of concern due to health consciousness of public. The water pollution is directly associated with human health and aquatic ecosystem, and presence of pharmaceutical contamination in the water can leads to the serious harm to environment. Endocrine diseases are found to be mainly due to these compounds.*

This study was conducted to focus on all aspect of the presence of pharmaceutical-derived compounds in water and their removal technologies. Some major pharmaceutical families of drugs present in water and related water pollution issues were analyzed in comparison with their threshold limit. The prime conventional water treatment technologies; Ozonisation and adsorption on activated carbon (from lotus stalks, olive-waste cake, coal, wood, plastic waste, cork powder waste, peach stones, coconut shell, rice husk) were summarized. Performances of alternative processes like oxidation by chlorine dioxide, Nano filtration/reverse osmosis and zeolite filters were also described along with limitation to be used as complementary process in place of major technics. The effect of these treatments on pharmaceutical compounds and capacity of the used adsorbent has been discussed.

The treatment to remove toxic and other harmful substances like pharmaceuticals have gained popularity. This review suggest the research direction to optimized the performance of conventional techniques such as chemical precipitation, carbon adsorption, ion exchange, evaporations and membrane processes are found to be effective in treatment of waste and biological treatment of sewage water

***Key Words*: Pharmaceutical, activated carbon, water treatment, Ozonisation**

1. INTRODUCTION

Pharmaceutical organizations are committed to coming across and growing new drugs with the intention to permit patients to stay longer, healthier and more productive lives. But at the same, they generate each hazardous and nonhazardous waste, and the inadequate remedy of those wastes results in surface and groundwater infection that poses dangers to the health of the aquatic ecosystems and the encompassing surroundings [1]. The pharmaceutical compounds reach the aquatic surroundings as effluents of the hospital systems, pharmaceutical industries, municipal sewage treatment plant, as well as agriculture and breeding residues [2]. Presently, the outcomes of pharmaceutical wastes on aquatic organisms are the apparent essential issue, consisting of inhibition of boom, production of stress hormone, feminization and behavioral modifications [3]. Moreover, ibuprofen, fluoxethin and ciprofloxacin had been shown to reason mortality of fish [4].

Pharmaceutical pills are chemicals used for prognosis, treatment, or prevention of infection of the human body and elements of pharmaceuticals may want to manipulate symptoms in preference to remedy situations. At present, tons of pharmacologically lively materials had been used annually in each human medicine for stopping illness and animal and fish farming as growth promoters or parasiticides [5]. With the addition of new prescription drugs to the already massive array of chemical instructions, maximum of these substances are excreted un-metabolized or as lively metabolites coming into the surroundings [6]. Certainly, pharmaceutical compounds had been detected in sewage remedy plant effluents, surface and ground water or even in consuming water all around the world [7].

The predominant way is through the discharge of sewage from residential locality or medical facilities. Despite the fact that superior remedy techniques are able to obtain better removal rates, they still do not achieve whole removal of pharmaceuticals [7] [8]. After all those diverse discharge routes and next treatment of wastewater, very low mg/L concentrations of pharmaceuticals were detected in consuming water resources [9]. Even through the amount of prescribed drugs and their bioactive metabolites being disposed or discharged into the environment are likely low, their continual enter into the surroundings can also result in a protracted-term, left out unfavorable effect on each water ecosystem and terrestrial organisms [5].

2. TREATMENT TECHNOLOGIES FOR REMOVAL PHARMACEUTICAL DERIVED COMPOUND

The extended attention concerning negative outcomes due to natural micro pollution within the aquatic environment, in conjunction with coming near law, has brought about investigations and improvement of treatment technologies, which can drastically lessen the concentrations of those materials. The technologies that are taken into consideration, oxidation with ozone and adsorption onto activated carbon, had been each commonly utilized in drinking water remedy however by and large for the purposes of disinfection (Ozonisation) and elimination of smell and taste associated organics [10-12]. In the following sections, these technologies are greater thoroughly supplied and some options that have been investigated are briefly described.

2.1 Oxidation with ozone

Ozone is a risky gas due to the reactive nature, persistent exposure to high concentrations can lead to lung harm. The daily exposure restriction is set to a 120 μg/m3 (~0.05 ppm) in the European Union [13]. Defensive measures are therefore required to prevent leakage at some stage in treatment and sufficient removal of residual ozone after treatment. It has two distinct mechanisms of movement; both through direct electrophilic assault by using the ozone molecule itself or in a roundabout way by using hydroxyl radicals form all through ozone decomposition [14]. Ozone without difficulty targets organic compounds with electron donating group, including C=C double bonds, amines or aromatics. This might be discovered in for instance carbamazepine, diclofenac and many antibiotics [15-17]. Hydroxyl radicals (-OH) target molecules non-especially, but simplest increase the general rate of reaction, not the oxidation capability at dissolved organic matter (DOM) stages discovered in effluent wastewater [18]. DOM refers to all dissolved organics which might be found in a solution, of which pharmaceuticals most effective contributes a small fraction in wastewater. DOM is quantitatively represented by using the attention of dissolved organic carbon (DOC). The -OH reaction may be promoted by growing the ozone dose, elevating the pH or via addition of hydrogen peroxide [16, 18]. Moreover, the oxidation of low to reasonably removed substances, which can be more depending on the presence of -OH, is negatively affected by a particularly high DOC, which neutralize the radicals [16, 17]. To some extent an excessive presence of suspended solids can also lead to a reduced performance.

Ozonisation does not complete eliminate molecules completely; however as a substitute degrade into other metabolites. In drinking water treatment, presence of bromide is for Example of difficult consideration that it's effortlessly oxidized to the carcinogen bromate [15]. Oxidation of pharmaceuticals in wastewater leads to loss of toxicity [19, 20]; at the same time as for a few substances an accelerated toxicity has been observed [21-23]. However, it's been indicated that biologically active sand filters could mitigate this accelerated toxicity [24, 17].

2.2 Adsorption with activated carbon

Activated carbon (AC) can be made from a spread of raw substances with high carbon/low ash content material, which includes coal, lignite or coconut shell. The production system is as an alternative power consuming and is typically executed as follows: a gradual elevation of the temperature to 500°C for oxidation and removal of volatile impurities [25]. In addition increase of the temperature to 1000 °C produces steam, which expands the porous structure of the material. For the duration of the activation process a distribution of pores with exclusive length are created which extends from the carbon surface into the particle. Pore sizes are classified into 3 categories in keeping with the diameter of the pore starting; micropores <2 nm, mesopores 2- 50 nm and macropores >50 nm. AC is commercially available in both granular and powdered form, defined therefore: Granular activated carbon (GAC) has a predominantly large particle diameter than 0.2 mm, while powdered activated carbon (PAC) has particle diameters smaller than zero.2 mm, despite the fact that commonly in the variety of 5-50 μm [26, 27].

Many different factors were proven to persuade adsorption related to the adsorbent (AC), the adsorbate (the adsorbed substance) and the water matrix. In the latter, i.e. the wastewater, DOM may have a two-fold bad effect; either pore blockage or direct attack for adsorption sites. The primary is attributed to massive sized DOM that could block the access to micropores and smaller mesopores, suitable for adsorption of organic micro pollutants. Pore blocking became shown to be mitigated through ACs that had a huge distribution of pores in the length between 30 and a 100 nm [28]. Smaller sized DOM directly competes with natural micro pollution for adsorption sites and can therefore boom the AC intake. For instance, it was proven throughout use of PAC that the DOC-normalized dose (mg PAC/mg DOC) turned into higher correlated to the removal efficiency than the volumetric dose (mg PAC /L) [29]. Using DOC-normalized doses has additionally been mentioned in Ozonisation studies [30, 17].

DOC is decreased in the wastewater remedy tiers, often by way of biodegradation as formerly defined and it was additionally proven that dosing PAC to effluent from primary sedimentation led to very inefficient adsorption, attributed to very excessive DOC [31]. Associated with the distribution of pore sizes, a large surface area, which is completed with the aid of a high distribution of micropores and small mesopores, was shown to correlate properly with the average elimination of organic micro pollutants [32]. As at some point of sorption to sludge a better hydrophobicity (log D), turned into well correlated with better adsorption to AC, which has a predominantly hydrophobic surface [33]. In the same look at, presence of hydrogen donor/acceptor and aromatic rings in the molecular shape of the adsorbate was shown to be useful for the adsorption, compared to the absence. Moreover, inevitable adsorption of DOM has a tendency to give negative charge to carbon surface pH [34, 35], which helps in electrostatic interactions. So negatively charged particles are more pronounced to absorb [30, 36, and 37].

Granular activated carbon

Filtration through fixed bed column is usually performed to treatment with GAC. An essential idea for GAC filtration is the mass transfer zone [MTZ], where adsorption takes place within the filter bed. As the GAC will become saturated with the aid of the adsorbate the MTZ moves down [or up] the filter bed. If the MTZ extends past the filter bed, via applying an excessive glide or by way of nearly whole saturation, the adsorbate will pass via the filter. Breakthrough takes place on the factor whilst an undesired ratio of effluent to influent concentration [C/C0] is passed. The bed has then reached its bed life and is changed. The accumulative quantity that has surpassed via the filter bed, the throughput, is generally given in bed volumes [BV] of water that has been treated. Bed lives are normally in the range of several thousand BV. The HRT in a GAC filter bed is often given as the empty mattress touch time [EBCT], i.e. with the imaginary assumption that the GAC is absolutely porous. Some parameters, which have been proven to lessen the bed life, are (high) presence of DOM, shorter EBCT. The other will be achieved with strategic operation including parallel operation of numerous filters out columns or so-referred to as lead lag operation of filters in series [38]. GAC has the advantage over PAC that it could be regenerated for later reuse. That is accomplished in a procedure very much like the activation system, i.e. Thermal regeneration, in the course of which adsorbate are volatilized and degraded. Therefore, the adsorption capability is completely restored, but, on the cost of approximately 10% mass loss [39].

Powdered activated carbon

Adsorption by PAC mainly accomplished in the system composed of one or several contact tanks. After that to prevent AC particles from passing through to the effluent sedimentation and/or physical filtration required. Carbon dose and HRT are main operational parameters of PAC treatment of the water in the contact tanks, i.e. the contact time. Equilibrium can be achieved by increasing contact time and adsorption capacity by increasing carbon dose. Study shows that adsorption equilibrium is reached after 20-48 hours [29, 40, and 41]. As this exceeds even the HRT of many WWTPs, the retention time of the water and the AC should not be equal for efficient adsorption. Nicolet and Rott proposed recirculation of PAC as an approach to this hassle almost many years in the past, when they attempted to attain value-green color removal in wastewater, in a separate pilot system [42]. While the elimination of organic micro pollution at some stage in latest years became an emergent subject matter, this system change became tailored apparently by using default to obtain a suitable elimination [30, 43]. The implication of recirculation in a separate treatment level and the benefit it offers is as a consequence still quite understudied in the large scale [44, 45]. An opportunity to inner recirculation has however been greater explored, regarding recirculation to the organic treatment level [31, 46, 47]. If introduced slightly after the influent to the biological remedy level, wherein DOC is already closely decreased, it become shown that the superior contact time over a separate treatment caused similar elimination, in spite of an overall higher DOC [31]. In complete-scale implementation with a separate treatment stage, spent PAC could continuously be eliminated from the system, then be dewatered, dried and ultimately incinerated to restriction transfer of the pollutants into any other biome.

Activated carbon modification

A few researches have investigated the performance of applications using variants of the traditional activated carbon sorts which were smaller than the defined particle sizes [48, 49]. Those changed ACs gave the benefit of faster adsorption kinetics; as a consequence contact times will be shortened whilst reaching a similar elimination. The adsorption capacity however generally not affected since the AC particles maintained their original pore length distributions. It stays to be seen whether this is possible opportunity in complete-scale applications because the suggested particle sizes presently most effective can be attained thorough grinding of commercially available product.

2.3 Activated carbon vs. Ozonisation

Some studies have as compared the removal of natural micro pollutants with Ozonisation and PAC in bench and pilot-scale [29, 30]. Altmann et al. considered both treatments to be well acceptable for the supposed purpose and showed suitable removal of the crucial materials carbamazepine and diclofenac, even as Ozonisation became greater perfect for the elimination of sulfamethoxazole and PAC could do away with a few materials including benzotriazole higher [29]. Margot et al. desired PAC with the extension of ultra-filtration [PAC-UF] for particle retention, no matter a higher operation price than Ozonisation, PAC-UF caused a better reduction of toxicity in the effluent [30]. Mousel et al. shows Ozonisation is clear winner followed by PAC by comparing energy demand for Ozonisation, GAC and PAC along with energy demand for manufacturing and transportation [50].

For the activated carbon methods it turned into cited that the energy need for manufacturing and transportation have been dominant and in future it should be improve in water treatment.

2.4 Oxidation with chlorine dioxide

Oxidation with chlorine dioxide [ClO_2] is an alternative to Ozonization for elimination of pharmaceuticals. ClO_2 had lower oxidation because it is weaker oxidant and does not generate -OH. However, it had same capacity as ozonization to get rid of substances including diclofenac, sulfamethoxazole, ethinylestradiol, and some different antibiotics, while almost no oxidation took place of carbamazepine and ibuprofen. General, oxidation with ClO_2 show few blessings over Ozonisation, due to less difficult operation and lower operation cost in this kind of setting [51-53].

2.5 Nano filtration/reverse osmosis

Filtration with high-pressure membranes shows removal of pharmaceuticals in wastewater to some extent. Pores or cavities in the membrane allow the permeation of water, but rejects substances based on a combination of size exclusion, adsorption via hydrophobic interaction and via electrostatic interactions [54]. Electrostatic interactions lead to rejection of negatively charged molecules than positively charged, by diffusing through the membrane [55]. Overall, a high removal of pharmaceuticals than AC and Ozonisation, However, the energy demand was 40% higher and additional 20-25% rejection of waste water fraction. Adoption of treatment to prohibit any discharge would further increase the cost of this technology [57].

2.6 Adsorption with zeolites

Zeolites are porous minerals, which like activated carbon, can act as an adsorbent for natural compounds. Zeolites have more or less uniform pore sizes, which can be decided in the range of the favoured molecular diameters. As a consequence, zeolites can take in molecules of a sure size thoroughly. This become shown via de Ridder et al., who similarly shown that organic matter in water did not intervene with adsorption by way of pore blocking off, which can be attributed to a more homogenous surface are than that of AC [58]. In end, it was advocated that adsorption with zeolites must handiest be implemented as a complement to e.g. AC adsorption because of the very restricted affinity limit [58].

3. CONCLUSIONS

An outline of the technology described in this paper is compiled to permit for a rough contrast. An easy end that also has been drawn is that Ozonisation and activated carbon adsorption are the suitable options for treatment operation. Both technologies have the affinity for a high and, broad removal of pharmaceuticals at affordable cost. A number of the other technologies, i.e. NF/RO filtration and zeolites adsorption should doubtlessly be taken into consideration in complement with the two principal options to their limitations. Thus, need of optimizations would be desired to make NF/RO filtration as alternative to the AC and Ozonisation.

Table -1: Summary of pharmaceutical removal by AC

Author	Adsorbent	Pharmaceutical	Observations	Removal or Adsorbent Capacity
Liu[59]	GAC – LS (from lotus stalks)	Trimethoprim, bacteriostatic antibiotic	Four kinds of phosphorus oxyacid's (HxPyOz), i.e. H_3PO_4, $H_4P_2O_7$, HPO_3 and H_3PO_3, were used to activate LS	228mg/g
Baccar[60]	GAC (from exhausted olive-waste cake)	Ibuprofen, analgesic Ketoprofen, antiinflammatory Naproxen, antiinflammatory Diclofenac, antiinflammatory	Activated carbon was produced via chemical activation using Phosphoric acid. Increasing pH gradually reduced the uptake of the four drugs. The increase of temperature in the range 4–40 ^{0}C does not have a perceptible effect on the adsorption processes	33.25mg/g
Cabrita [62]	GAC-B (from coal) -NS (from wood) -PP (from plastic waste) -CC (cork powder waste) -CP (from peach stones)	Paracetamol	Samples prepared by chemical activation of residues showed reasonably high removal efficiencies and fast rate of adsorption	212mg/g
P. Liu, W.J. Liu [61]	Lotus Stalk derivatives	Trimethoprim	Activated with phosphorus oxyacids	79percent
H.R. Pouretedal [63]	Vine woods	Amoxicillin Cephalexin Penicillin Tetracycline	T = 45 C, pH = 2, 0.4 g/l GAC	88percent
I. Cabrita, B. Ruiz [64]	Coal, Wood, Plastic waste Powder waste Peach stones	Paracetamol	T = 30 ^{0}C	74percent 97 percent 60percent 87percent 82percent
Rosal [65]		Ciprofloxacin		98percent

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