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FABRICATION OF ULTRAFILTRATION MEMBRANE USING ADDTIVE TO EXTRACT HORMONE FROM POULTRY WASTEWATER

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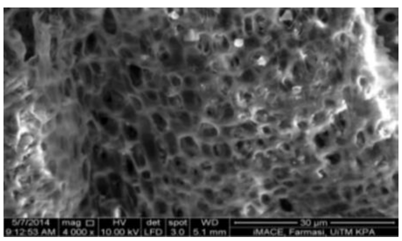
Graphical abstract



Abstract

Steroidal hormones such as 17β-estradiol produced by humans and animals are regularly being released into the environment in their active forms. As the demand of chicken is increasing nowadays, there is a need to evaluate and assess the concentration of hormones in the poultry wastewater. In this study, a simple ultrafiltration membrane was fabricated to extract the hormones in the poultry wastewater from Kuala Garing, Rawang Selangor. Self-doped, sulfonated forms of polyaniline-polyvinylpyrrolidone (PANi-PVP) are blend into polysulfone (PSf) and N-methyl-2-pyrolidone (NMP) ultrafiltration membranes to enhance the hydrophilicity and fouling resistance. The Sulfonated Polyaniline-Polyvinylpyrrolidone (SPANi-PVP) polymer was dedoped at varying concentrations of PANi-PVP additive. Their concentrations vary from 0.5% of PANi-PVP, 1% PANi-PVP, 1.5% PANi-PVP, 2% PANi-PVP to 2.5% PANi-PVP. These newly fabricated ultrafiltration flat sheet membranes which containing increasing amounts of PANi-PVP was than tested for tap water permeability and hormone 17β-estradiol filtration from the poultry wastewater. The result of the study justify that, as the PANi-PVP concentration increased, the rejection of solute increased while the permeate flux decreased. The highest rejection of 17β- estradiol (E2) from the poultry wastewater was 92.5% with the mass of 17β- estradiol retained is 0.37ng/L. This was obtained from the highest amount of PANi-PVP concentration in the membrane which is 2.5wt%. However, the permeate flux for this 2.5wt% of PANi-PVP membrane was to slow compared to other membranes that has lower amount of PANi-PVP concentration. This is due to the higher the PANi-PVP concentration, a thicker and denser membrane skin layer was formed.

Keywords: Ultrafiltration membrane, additive, hormone, poultry wastewater

1.0 INTRODUCTION

Many studies have reported that hormones concentrations such as estrogenic and androgenic compounds in the surface waters were critically high due to cattle farming, swine excretions and poultry land use. According to some studies, hormones are naturally excreted by humans and animals and have been consistently detected in surface water in the range of ng/L. Furthermore, several studies have documented that hormones such as androgens could contribute to reproductive abnormalities in fish at similarly low concentrations [1]. In the aquatic environment, the presence of these androgens and other hormonally active agents has become an issue of general concern [2]. Furthermore, numerous hormones namely estrogens, androgens, and progestin are known to act as reproductive pheromones in fish at the concentrations of ng/L. Moreover, hormones are also known to cause the endocrine disturbance in sensitive aquatic organisms at low ng/L concentrations, although the lowest observable effect level (LOEL) differs by species and compound [3]. For example, E1 hormone was found to twist sex ratios toward females and encourage vitellogenin production in zebrafish at concentrations similar to or lower than those of 17β-estradiol (E2) hormone [3].

Steroidal hormones that are present in the environment may affect not only wildlife and humans but also plants [4]. Even though knowing that aquatic ecosystems are particularly vulnerable to hormone residues, the fate and transport of hormones in animal agriculture remain poorly understood. Despite the fact that other sources related to animal agriculture has the potential of becoming the main source of steroid hormones in certain watersheds, most research to date are focusing more on the role of municipal wastewater treatment plants for steroid hormones. The lacking of analytical sophistication of the analytical methods employed and the limited scope of the research make it difficult to assess the importance of these sources although the possibility that animal agriculture could act as a strong source of steroid hormones to the aquatic environment was raised decades ago [5] with continued research in the past decade [3, 6].

Nowadays, due to the demand of increasing population, intensive animal agriculture operations has been representing as one of the possibly important source of steroid hormones to the aquatic environment. The compounds of hormones are known to be originating from a multiplicity of sources, including wastewater effluent from sewage treatment plants, animal feed-lot effluent, and agricultural runoff. There is a concern from the surrounding of the poultry wastewater and the use of poultry litter as fertilizer could leads to contamination of the aquatic environment, via agricultural runoff, through the release of steroid hormones. Recent data documented has indicated that Maryland Eastern Shore poultry litter contains 17β-estradiol which also known as E2, as well as other forms contaminants including historic pesticides, metals and antibiotics. The common of estrogens hormones that are excreted by poultry are such as estriol, estradiol (E2) and estrone (E1) [7]. In addition, the estrogens hormones can be detected in receiving surface waters at biologically significant concentrations of (5–85 ng/l) even after a few months of field litter applications. There is a determination of an average E2 hormone concentration of 3500 ng/l in the runoff from a postural land applied from 5 Mg/ha of manure of the poultry litter.

Since there is relatively high and biologically active levels of E2 and androgens have been previously detected in poultry litter samples collected from various studies, there should be further investigations into the effect of large-scale poultry production on population dynamics within aquatic habitats. The extraction of these steroids is of importance for current knowledge regarding steroids and contaminants from poultry waste, since they may serve as endocrine disrupters in the freshwater ecosystems where agricultural runoff drains into aquatic habitats. One of the most widely applied membrane technology for production of safe drinking water, food, and dairy processes, reverse osmosis pre-treatment, and mainly to recover the water quality with respect to organic and microbiological contaminants is the ultrafiltration (UF) membrane techniques [8]. A polymer namely Polysulfone (PSf) are well known for its extensively application in the UF membrane as a material in many industrial fields because of its high mechanical strength, resistance to compaction and heat, chemical stability, and the ability to perform in a wide range of pH values [8].

Furthermore, ultrafiltration (UF) membranes which is pressure driven made from polysulfone (PSf) provide not only efficient but also cost-effective method for removing pathogens, macromolecular natural organic matter, and inorganic colloidal particles from the wastewater [8]. Unfortunately, the inherent hydrophobic nature of a Polysulfone (PSf) membrane may results in the adsorption and deposition of solute on the membrane surface, which subsequently may causes irreversible fouling that significantly and reduces the reduces membrane permeability during the water treatment operation [9, 10]. As the result to regain lost of performance, Polysulfone (PSf) films are exposed to hydraulic backwashes and aggressive cleaning agents that eventually degrade the membranes, increase the operating costs, and shorten the membrane life [11, 12].

Previous studies have documented that Polysulfone (PSf) membrane that leads to irreversible fouling is a result of the hydrophobic interactions between the fouling and the membrane polymer. The fouling resistance and hydrophilicity are pointedly important for polymeric membranes since they are both the important issues liaising in the membranes modification [13, 14, 15]. Blending of nanomaterials as hydrophilic additive has been widely considered because of the unique of the nanomaterial's to the physicochemical properties that vary from bulk materials or molecular structure [16].

Recently, a conjugated polymer that is polyaniline (PANi) has been integrated into the Polysulfone (PSf) membranes to perform as a hydrophilic modifier [17, 18]. Sulfonated polyaniline (SPANi) is a unique performing polymer known for its self-doping characteristics. Providing a sulfonation degree of near to 0.5 (sulphur: nitrogen) ratio, SPANi give a color of dark green powder which is insoluble in both organic and aqueous solutions [19].

2.0 EXPERIMENTAL

Dope formulation is going to be prepare by using Polysulfone as the polymer, NMP as the solvent and PANi-PVP as the additive. PANi-PVP will be synthesize through a dispersion polymerization method by using APS as the oxidant and PVP as the steric stabilizer in aqueous HCl medium at 0 °C, according to the procedure mentioned in the references [19, 20].

The content of PSf to total solution will be kept constant at 15 wt %. The contents of PANi–PVP nanocomposite and NMP will be added up to 85 wt %, with varying PANi–PVP nanocomposite contents from 0.5 to 2.5 wt %. There will be five category of Sulfonated PANi-PVP (SPANi-PVP) dope formulation and each will be prepare in 1L mixing of solution. The five different dope solutions will be prepare based on composition of formulation as in Table 1 below and cast on a flat glass plate using SOLTEQ ® Pneumatically Controlled Flat Sheet Membrane Casting Unit (Model: TR 31-A) will be used. Basically, component gel, it is easy to modify the molecular structure of either of the two components.

Table 1 Composition of Formulation

Dope solution	Composition in weigth (%)		
	Psf	*NMP*	*PANI-PVP*
SPANi-PVP 1	15	84.5	0.5
SPANi-PVP 2	15	84.0	1.0
SPANi-PVP 3	15	83.5	1.5
SPANi-PVP 4	15	83.0	2.0
SPANi-PVP 5	15	82.5	2.5

The prepared newly fabricated membranes that need to be examined will be cut into small dimension. This morphology of the newly fabricated membrane will be conducted by using Scanning Electron Microscopic (Quantum SEM 430). All analyses were performed using a 6890 series gas chromatograph (GC-MS) equipped with a split/splitless injector, auto sampler and a 5973-N mass spectrometric detector (Agilent Technologies, Palo Alto, CA, USA). GC–MS for 17β -estradiol expected limit of detection range from 0.1ng/L to 1.5ng/L.

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The newly prepared ultrafiltration membrane will be cut into spherical figure before it is being placed in the Flat Cross Membrane Cell. Then, with the capacity of 25litre, the poultry wastewater sample will be poured into the feed tank. This would enable permeate to go through the membrane at the constant pressure consisting of two bars by using the pumping system. The feed and permeate of the poultry wastewater solution before and after the filtration process will then be taken to determine its concentration.

The poultry wastewater effluent that permeates through the newly fabricated membrane prepared is basically known as flux. This flux process is conducted for tap water and hormone 17β- estradiol hormone. These permeate is then going to be analyse for its concentration using GC-MS. These fluxes will competitively analysed by focusing on the 17β-estradiol hormones extraction. Once the filtration process is over, the treated poultry wastewater will be collected to measure the concentration of the 17β-estradiol hormone removal.

3.0 RESULTS AND DISCUSSION

In this research, the emphasis would be on the emission of natural hormone 17β-estradiol that is well known as E2 in the sample of poultry wastewater. By using GC-MS, the E2 hormone is detected at the average of 0.4ng/L from various concentrations of the poultry wastewater. From the visualization of top surface morphology of the different amount concentration of PANi-PVP, it is shown that all the flat sheet membranes have fine pore structure with nanometer dimensions range. The membranes consist of a dense top layer and a porous sublayer which enriched with the microvoids which is a typical structure of ultrafiltration membrane. The result was similar to the previous work by [21] showed the membranes consist of a dense skin layer at top surface and short finger-like structure.

By increasing the PANi-PVP concentration, the number of microvoids will also start to increase and become bigger as shown in Figure 2 to Figure 6. Increasing the concentration of the PANi-PVP in the casting solution would eventually improve the interconnection of the pore and hence producing a smaller pore size [19].

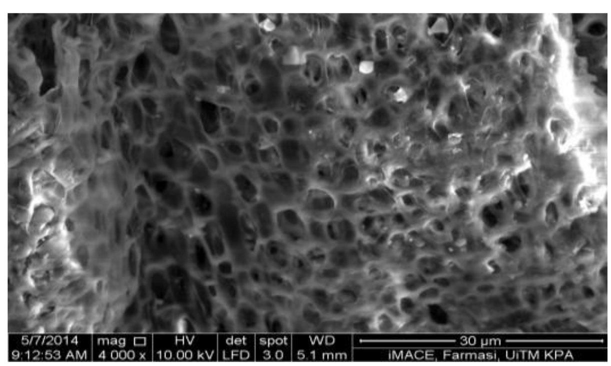

Figure 2 Top surface for PANi-PVP 0.5%

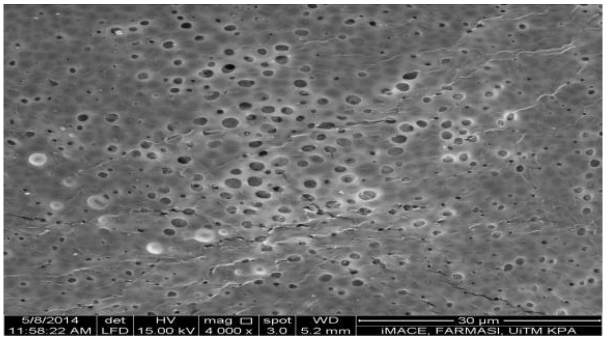

Figure 3 Top surface for PANi-PVP 1. 0%

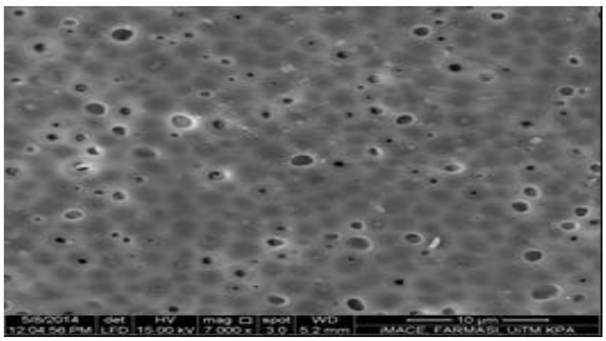

Figure 4 Top surface for PANi-PVP 1.5%

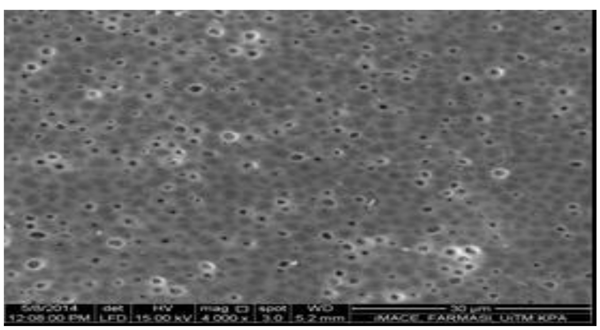

Figure 5 Top surface for PANi-PVP 2.0%

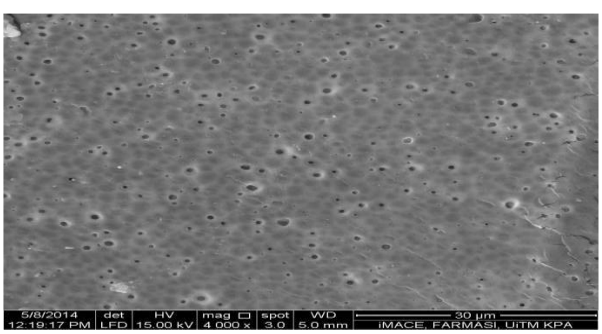

Figure 6 Top surface for PANi-PVP 2.5%

There are five types of PANi-PVP concentration from the casting membranes that were tested for its tap water permeability flux performance. The membranes that had been casted were performed using a constant operating pressure of two bars. Table 2 shows the tap water permeability analysis. It can be found that membrane surface pore sizes decrease with increasing PANi–PVP content. Increasing the PANi-PVP concentration, the number of microvoids will also start to increase and become bigger. Increasing the concentration of the PANi-PVP in the casting solution would eventually improve the interconnection of the pore and hence producing a smaller pore size [19].

Table 2 Tap Water Permeability Flux Performances

Membrane ID	Tap water Permeability (L/m2.h.bar)
PANi-PVP 0.5%	107.7
PANi-PVP 1.0%	102.8
PANi-PVP 1.5%	94.3
PANi-PVP 2.0%	90.5
PANi-PVP 2.5%	93.8

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Figure 7 represents the flux versus the concentration of PANi-PVP for the prepared membranes with application of two bars pressure. The flux values for various percentages of PANi-PVP concentrations which stars from 0.5wt%, 1.0wt%, 1.5wt%, 2.0wt% to 2.5wt% were107.7, 102.8, 94.3, 90.5 to 83.8 L/m2.hr respectively. It can be analyse that the flux was found to be decrease with the increasing of PANi-PVP additive concentration. From this result, the lowest concentrations of additive PANi- PVP which is 0.5wt% are showing the highest permeate flux which is 107.7 L/m2.hr. This eventually, proving that the membrane skin layer of the highly flux value is thin and porous due to the decreased of the polymer concentration whereas, membrane will become thicker and denser with the increasing of polymer concentrations [20].

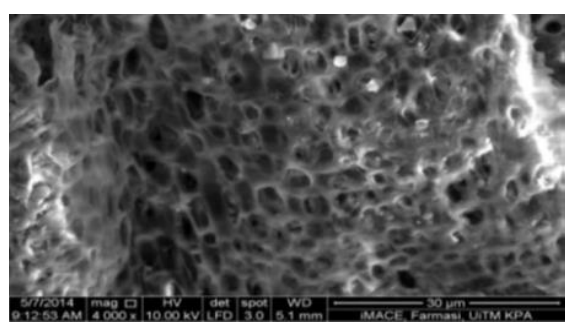

Figure 7 Effect of PANi-PVP on tap water permeability flux performance surface for PANi-PVP 2.0%

Analysis was conducted to investigate the potential of different PANi-PVP additive concentrations for the membrane separation performance of 17β-estradiol (E2) hormone from the poultry wastewater. The permeate concentration of E2 was tested by Spectrophotometer DR5000. The percentage of 17β-estradiol (E2) removal over different additive concentration is shown in Figure 8 whereas; the mass removal of 17β-estradiol (E2) in ng/L is shown in Figure 9. The removal percentage is 22.5%, 42.5%, 67.5%, 77.5% and 92.5% for the membrane with 0.5wt%, 1.0wt%, 1.5wt%, 2.0wt% to 2.5wt% of PANi-PVP respectively. The mass of 17β-estradiol that retained are 0.09ng/L, 0.17ng/L, 0.27ng/L, 0.3ng/L and 0.37ng/L with the increasing amount of PANi-PVP concentrations in the membranes respectively. The highest membrane rejection is the one with 2.5wt% of PANi-PVP membrane which the percentage removal is 92.5% with the mass of hormone retained is 0.37ng/L.

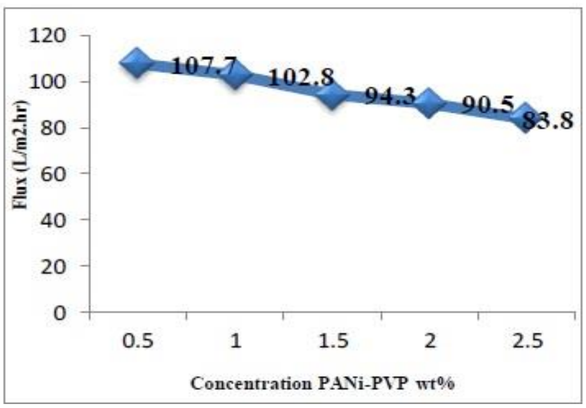

Figure 8 17β-estradiol rejection (%)

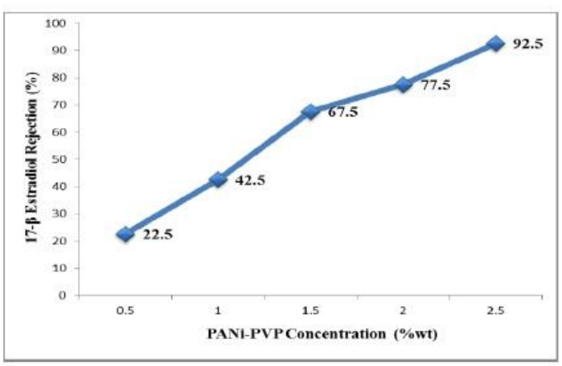

Figure 9 Mass of 17β-estradiol (ng/L)

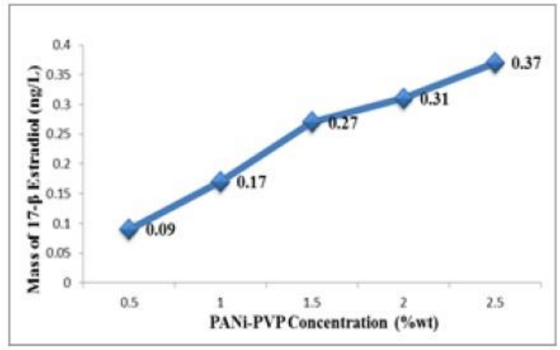

Figure 10 Permeate Flux

The lowest percentage removal is 22.5% which is using 0.5wt% of PANi-PVP concentration with mass of hormone retained giving only 0.09ng/L. From the analysis, it is found that the higher the additive concentration of a membrane, the rejection performance would be greater giving a higher mass of retaintate. In Figure 10, the permeate flux value using the two bars pressure application are decreased from 55.3 L/m2.hr of 0.5wt% of PANi-PVP to 53.8 L/m2.hr of 1.0wt% of PANi-PVP followed by 51.6 L/m2.hr of 1.5wt% of PANi-PVP then 49.3 L/m2.hr of 2.0wt% of PANi-PVP and 48.2 L/m2.hr of 2.5wt% of PANi-PVP. This showed that the higher of the additive of PANi-PVP concentration, the value of the flux would decrease. This result is due to the thickening of the structure of the membrane skin layer which subsequently becoming more selective but less productive for a membrane separation.

From the result above, the flat sheet membranes using increasing amount of additive which is the PANi-PVP shows its efficiency in reducing the concentration of E2 from the poultry wastewater. The analysis shows that, it is found that the highest PANi-PVP concentration percentage which is 2.5 wt%is the most efficient membrane for carrying separation process in this study.

4.0 CONCLUSION

As a conclusion, this aim of this study is to develop an ultrafiltration dope formulation using additive of PANi-PVP, to fabricate the membrane using different concentrations of the additive and to evaluate the Psf/PANi-PVP membrane performance for the removal of hormone E2 in the poultry wastewater. Based on the result, it can be concluded that:

1. Three newly formulation of ultrafiltration membrane using various concentration of PANi-PVP are successfully developed in the range of 0.5wt% - 2.5wt%. The experimental outcomes showed that the rejection of solute increased with the increase of PANi-PVP concentration while the result of permeate flux decreasing due to the increased of polymer concentration.

2. The membrane performance was successfully characterized in this study where the highest of tap water and 17β- estradiol rejection is by using the membrane which consisted of 2.5wt% of PANi-PVP. The Psf/PANi-PVP molecular chains become more aligned and closer to each other at this concentration value giving a better rejection performance. The morphology of these membranes was also successful characterized using the SEM method.

3. The highest rejection of 17β- estradiol (E2) from the poultry wastewater was 92.5% with the mass of 17β-estradiol retained is 0.37ng/L. This was obtained from the highest amount of PANi-PVP concentration in the membrane which is 2.5wt%. However, the permeate flux for this membrane was to slow compared to other membranes that has lower amount of PANi-PVP concentration. It can be concluded that, as the PANi-PVP concentration increased, the rejection of solute increased while the permeate flux decreased. This is due to the higher the PANi-PVP concentration, a thicker and denser membrane skin layer was formed.

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