




Phytoremediation of contaminants of emerging concern from soil with industrial hemp (*Cannabis sativa* L.): a review

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Abstract

The presence of contaminants of emerging concern (CECs) in wastewater treatment plant effluents is a significant underlying health risk and environmental concern. CECs consist of a wide variety of contaminants, including pharmaceuticals and personal care products, hormones, steroids, alkyl-phenols, flame retardants and pesticides. Their impact is of particular relevance to agricultural settings due to CEC uptake and accumulation in food crops and consequent diffusion into the food-chain. Meanwhile, marijuana reform is accelerating in the US, based on the scope and pace of legalization efforts and on wider acceptance in polls of voters. In this review, the effectiveness of industrial hemp (*Cannabis sativa* L.) in phytoremediation and hyperaccumulation of organic contaminants (e.g., benzo(a)pyrene, Naphthalene, and Chrysene) and heavy metal (e.g., Selenium and Cobalt) from either aqueous solutions or contaminated soils has been reviewed. The potential of industrial hemp as a renewable resource to biodegrade and/or decontaminate CECs is explored. Disposal strategies of this new phytoremediation crop that promote circular economy are also discussed. According to this current review, we believe the use of industrial hemp for phytoremediation is promising to have a sustainable, environmentally friendly and economically viable future.

Keywords Phytoremediation · Industrial hemp · *Cannabis sativa* L. · Green liver model · Contaminant of emerging concern · Circular economy

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1 Introduction

Considerable attention has been attributed to contaminants of emerging concern (CECs) due to their dramatic blossom in wastewater treatment plants (WWTPs) in recent years. CECs are those synthetic or naturally occurring pollutants detected in water bodies which typically fall outside current environmental regulations (Sauve and Desrosiers 2014). The CECs include, but are not limited to pharmaceuticals and personal care products (PPCPs), hormones, flame retardants, pesticide and disinfection byproducts. CECs along with their precursor compounds and metabolites, are discharged into the WWTPs during manufacturing processes and/or through disposal of used and unwanted products. Due to their continuous input and lack of appropriate removal equipment, they maintain pseudo-persistence during wastewater treatment (Gulkowska et al. 2008). The occurrences of CECs in WWTPs effluent and biosolid/sludge have been repeatedly reported with the detected concentrations at ng L^{-1} to $\mu\text{g L}^{-1}$ and at ng g^{-1} to $\mu\text{g g}^{-1}$ (Alvarez et al. 2014). However, because of the low concentrations of CECs, related regulations in the US have not been well established until there is more firm scientific data (Barbosa et al. 2016). A previous study demonstrated that CECs can cause an extremely wide range of adverse effects to human-beings and various organisms (e.g., chronic, reproductive damage, behavioral changes and accumulation in tissues) even at very low-level exposures (Phillips et al. 2010). For example, veterinary antibiotics exhibited oxidative damage to liver cells of rainbow trout (*Oncorhynchus mykiss*) (Gagné et al. 2006). The exposure of fish and benthic invertebrates to psychoactive drugs altered their behavioral responses (Rosi-Marshall et al. 2015). Therefore, it is urgent to study the fate and transport of CECs and correspondingly, the removal protocols of CECs.

CECs from the WWTPs effluents have been reported to contaminate surrounding agricultural land via different ways. Reuse of wastewater for irrigation purposes contribute significant amounts of CECs to agricultural systems (Becerra-Castro et al. 2015). Sewage sludge, which was recycled as the soil amendment, also brought a portion of hydrophilic CECs to agricultural soil (Kirchmann et al. 2017). In the agricultural subsoil system, the likelihood of CECs transport was affected by several factors. Among them the most important are: its physicochemical properties (e.g., half-life and polarity), the soil properties and climate conditions (e.g., precipitation, seasons). A study showed that the specific surface area and cation exchange capacity of the soil correlated with the adsorption affinities of a reproductive hormone, 17β -estradiol (Casey et al. 2003). A high correlation between specific surface area and sorption was found ($r^2=0.92$) in the experiment. While cationic exchange capacity only partially affect the adsorption affinity because of soil organic matters and clay mineral. Nonylphenol polyethoxylates had fast and complete degradation (initial half time 0.3–5 days). But nonylphenol, the degraded byproduct of nonylphenol polyethoxylates, depredated rapidly in the beginning. 26–35% of them remained in the soil till the end (Sjöström et al. 2008). Those hydrophobic residues were found to be accumulated in the contaminated environments and unable to be further consumed by any plants (Soares et al. 2008). Because of higher precipitation and larger herbicide/pesticide applications, CECs' concentrations in agricultural catchments were found to be significantly higher in summer seasons (Fairbairn et al. 2016). These factors altered the transport of CECs in the subsoil system, which makes the detection and removal even more difficult to conduct.

Among different CECs' decontamination strategies, phytoremediation has received great attention because of its efficiency and cost-effectiveness. It employs plants, crops, and grasses to extract, sequester and eradicate those potentially toxic chemicals in

the soil, water and other environments (Kumar et al. 2017; Jiang et al. 2015). Rather than chasing the limited number of CECs, plants effect and control chemical activities including contaminant transport and metabolisms in soil biota, since its intense root systems and continuous exudes. Industrial hemp (*Cannabis sativa* L.) is one of the widely investigated plants for phytoremediation. The feasibility of in-situ contaminants' removal is mainly credited due to its porous and hydrophilic surface structure, as well as the strong recalcitrance on levels of toxicity. For example, hemp fibers were chosen as the remediator of heavy metal ions (i.e., lead (II), zinc (II) and cadmium (II)). The metal removal efficiencies of hemp that were persuasive ranging from 17.5 to 39% in single/ternary ion metal(s) solutions (Pejic et al. 2011). Campbell et al. (2002) observed large reductions of benzo(a)pyrene (~33.5%), but inconsistent results on chrysene from -50% to 64% in the contaminated soil. It was also estimated that contaminant accumulation was highly selective on hemp parts. For example, the accumulation of nickel, lead and cadmium in hemp leaves were 4–12 times larger than the metal in other parts like fibers, seeds and herbs (Linger et al. 2002). It makes the potential remanufacture/reuse of less contaminated hemp parts possible, which aligns with the circular economy. In addition, the short maturation period and high biomass yield of industrial hemp also extended the utilization to other non-food manufacturing in the rest of a year (Kumar et al. 2017).

However, these benefits were not fully realized until the recent marijuana reform policies. According to search results returned by keywords of "industrial hemp" or "*Cannabis sativa* L." plus "phytoremediation" using the Web of Science database, countries that have most prominently addressed these topics over the last 20 years include Italy, USA, Canada, China and Germany (Fig. 1). The historical importance of hemp in Europe and China leads to the continuous research input in these areas (Salentijn et al. 2015). While in North America, published studies on phytoremediation of industrial hemp evidently exploded until gradual legalization of hemp production in 1990s (Fike 2016). Therefore, industrial hemp is expected to be applied to wider scaled applications with this trend, in which phytoremediation is believed to be a promising answer for CECs removal.

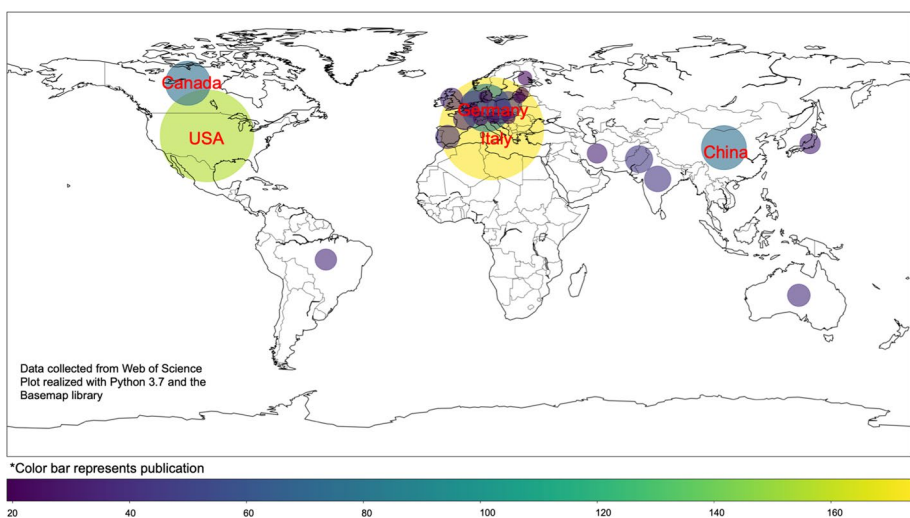


Fig. 1 The global publications of research on industrial hemp phytoremediation from 2000 to 2020

With increasing concerns of CEC contamination, the realization of a low-cost and efficient *in-situ* CECs removal via hemp is a feasible solution. But it is often not lucrative enough to make it appealing for groups of people because of limited data and large uncertainty. Therefore, it is essential to shed light on the viability and great economic benefit of this strategy before action. This review aims to provide more information about the efficacies of CECs remediation by industrial hemp. The detoxification performance of plants reported in previous studies are collected, estimated, compared and the underlying mechanisms of phytoremediation are revealed in the following sections. Major factors such as soil properties and physicochemical properties of contaminants are investigated in order to optimize the decontamination process. Nonetheless, the application of industrial hemp cannot achieve ambitious goals without addressing the issue of residue management after implantation. Therefore, the potential disposal strategies of phytoremediation via industrial hemp under the framework of the circular economy are rigorously advised in this review.

2 Mechanism of CEC decontamination

Numerous CEC phytoremediation studies interpreted its mechanism under the guide of the 'green liver model' theory (Burken 2003). This theory successfully brought the concept of mammalian liver function into plants. Plants and mammals have very similar responses to the xenobiotic molecules, except excretion stages only appear in mammals. Under this theory, the functionality of plants' phytoremediation has been considered as the effort of the whole-plant system instead of sole compartment of plants. The overall detoxification can be divided into three stages: translocation, transformation and/or conjugation and sequestration (Fig. 2). However, this theory seems to only envisage the overall trend of organic pollutant decontaminations. In recent experimental and field studies, the observations do not always follow such theoretical steps, sometimes they only partially align with the theory. Therefore, the theory was updated with new findings collected in recent studies

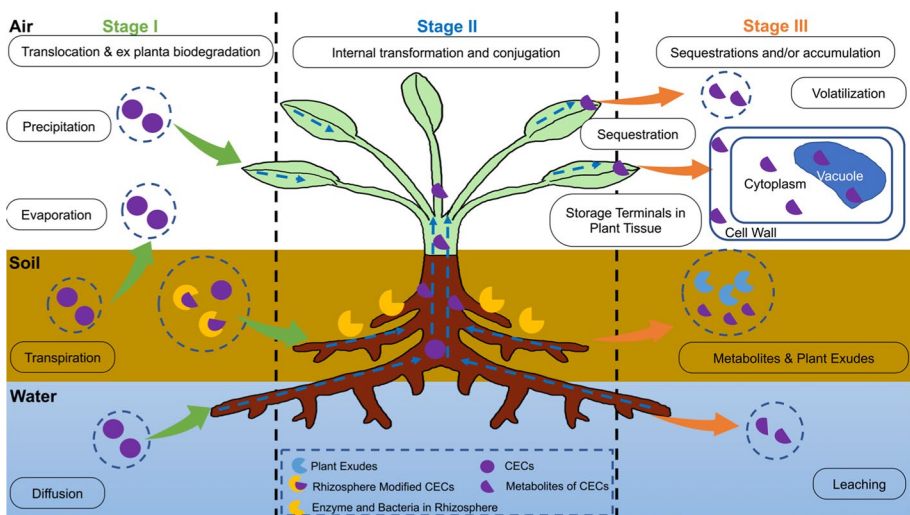


Fig. 2 Schematic phytoremediation pathways of CEC pollutants from contaminated environments (i.e., water, soil and air)

(2005~2020) in order to have a clearer idea of the phytoremediation process, specifically the external CEC-plant-soil interaction.

2.1 Stage I—translocation and ex planta biodegradation

Theoretically, contaminants enter plant tissues by active transport, namely translocation, in the direction opposite of the chemical potential gradient. Such translocation utilizes soil water with a transpiration stream to reach the aerial plant tissues. Besides active transport, passive diffusion was also largely observed in studies which utilized the macrophytes vegetation and/or which were conducted in a hydroponic environment (Tai et al. 2019). In addition, those CECs with semi-volatile characteristics and low molecular weights (MW) were partitioned or adsorbed from the atmospheric air (Gawrońska and Bakera 2015). Volatile organic matter are reported to have two major transports solely or combinedly: partition into waxy cuticle and convey through the surface stomata, followed by the translocation through the phloem (Ferro et al. 2013). A significant portion of CECs has high vapor pressures such as benzene, toluene, ethylbenzene, xylene and methyl tert-butyl ether, which indicates such translocation is very possible. However, the translocation of volatile organic matters is reported less because of current technological difficulties to capture and quantify the contaminants and their metabolites in the air. After plants-CEC interaction, CECs can either be further translocated/transformed or simply adsorbed on plants' waxy cuticles, it is largely dependent on the plants' adsorption capacity and existing enzymatic system.

In recent years, plants were found to be functional externally, namely ex planta phytoremediation. Plant exudes of organic acid are helpful to mobilize those highly hydrophobic contaminants by competing binding sites in a soil matrix. At the same time, plants exude acts as carbon-rich source for the rhizobacteria, which could further detoxify the CECs retained in the soil. Huesemann et al. estimated that highly hydrophobic polynuclear aromatic hydrocarbons were effectively removed (73% decrease) by the eelgrass (*Zostera marina*) phytoremediation, but only 25% removed in unplanted controls (Huesemann et al. 2009). Since only 0.35% of contaminants were detected in the roots and shoots in the initial 60 weeks, the results suggested that plant-enhanced biodegradation in rhizosphere was the major contributor within the plant-amendment environments. Besides the acceleration of in-situ phytoremediation, this 'defense' system of plants was also reported to prevent further phytotoxicity. To protect plants, plant exudes could further inhibit translocation into aerial tissues and increase defense enzymes activity in affected regions. Such uptake inhibition was documented to relate to specific enzymes and metabolite inhibitor, such as protoporphyrinogen oxidase, 2,4-dinitrophenol (2,4-DNP), and iodo-acetate. It was reported that these inhibitors targeted protoporphyrinogen in cytoplasm (Madalão et al. 2012), proton-couple fluxes through the plasma membrane or endomembrane system (Kong et al. 2007). Specifically, hemp was found to produce a significant amount of salicylic acid, which efficiently induced polycyclic aromatic hydrocarbon (PAH) bacteria and increased PAH mineralization (Liste and Prutz 2006).

2.2 Stage II—internal transformation and conjugation

Plants' internal phytodegradation is similar to xenophobic metabolism of mammalian living organisms. The initial metabolic step is transformation, which includes a series of contaminants' mobilization, such as oxidations, reductions, methylation, dehalogenation, hydroxylation and photolysis (Boonsaner and Hawker 2010). Both mammal and plants rely

largely on cytochrome P450 monooxygenases to metabolize exotic chemicals (Nebert et al. 2013). This step increases the hydrophilicity, which serves as the pre-treatment for the following conjugation. Transformation also allows contaminants to be hydrophilic enough to diffuse into the cytoplasm through apoplast pathway (Tanoue et al. 2012). Conjugation is the predominant step in the detoxification, which also serves as a protection system against high oxidative stress caused by xenobiotics. It utilizes enzymes like glycosyltransferase, glutathione S-transferases, peroxidases, and hydrolases to combine the transformed metabolites with natural molecules like sugar, amino acid and malonate. The detected metabolites and conjugates showed the same order with theoretical metabolisms. Since the rapid metabolism and associated conjugation normally happen in a relatively short-time period, these two steps sometimes are investigated together in previous studies (Huber et al. 2009). For example, diclofenac metabolism has been extensively studied, which includes a rapid hydroxylation, followed by the conjugation with glucuronide and/or sulfate. Bartha et al. (2014) found that 4'-OH diclofenac, the product of transformation, were detected only after one day in even higher concentration than diclofenac itself. 4'-O-glucopyranosyl-oxydiclofenac, product of conjugation, was found to have increase concentration after 3 days. However, the frequency and concentration of the detected conjugates are still very limited compared to the transformed metabolites. In the previous example, only 20% of the metabolites have been conjugated in the first 3 days and remained unchanged afterward.

So far, there is still limited information on the contaminant's metabolism. Most of metabolism investigations refer to the similar detoxification conducted in mammalian liver more or less. The difficulty falls in the technological detection of low-concentration, unknown and complexed metabolites as well as resulted conjugates. Additionally, the lack of halogen on these polar contaminants make it even more difficult to detect due to the lack of isotope in mass spectra (Fu et al. 2018). As stated in the green liver model theory, the metabolism is a whole-plant activity. But degrees of metabolisms, involved enzymes, and products can vary. For example, metabolic pathways of carbamazepine (CB) are well-documented, which constitutes epoxidation by cytochrome P450 enzyme, hydroxylation by epoxide hydrolase enzyme, and conjugates with glucuronide (Dordio et al. 2011). Dordio et al. (2011) found that only one of the metabolites, epoxide-CB, was detected in the leaf of *Typha* spp. after 21 days. Mordechay et al. (2018) demonstrated epoxide-CB, which substituted ~60% of parent molecule, was detected in wheat ear after 155 days without the detected dihydroxy-CB. In tomato fruit, dihydroxy-CB replaced ~50% of parent molecule without detected epoxide-CB after 98 days. Only lettuce leaf showed a comprehensive metabolites' distribution which includes epoxide-CB (20%), dihydroxy-CB (20%), and CB itself (60%) after 42 days. None of them have detected the CB-conjugates. Even the same plant would carry out several metabolisms at the same time. For example, Macherius et al. (2012) found that triclosan was rapidly adsorbed up to 95% into the carrots tissue in the first 2 h, and subsequently, followed by a quick metabolism with a 9-h half-life. Eight different metabolites were detected during the triclosan detoxification, which continuously conjugated with saccharides, disaccharides, malonic acid, amino acid and sulfate. Tai et al. (2019) detected a total of 15 metabolites in the root of *Iris pseudacorus.*, 9 of them in shoot, and a confirmed acetyl-conjugate in exposure of sulfonamides. These results proved the metabolisms are largely plant specific. It also revealed the importance of selecting an appropriate plant for phytoremediation.

Xenophobic metabolisms have some similarities among plants. Besides the similarity of involved enzymes (e.g., cytochrome P450 enzyme, glutathione S-transferases and glycosyltransferase), some studies indicated that those contaminants bearing polar functional groups are easier to be detoxified, such as phenolic group, amines and carboxylic acids

(Macherius et al. 2012). Contaminants with lower molecular weight contaminants are easily detoxified than higher molecular weight. But moieties such as chloride, nitro and methyl groups, which have stronger steric hindrance than others, are harder to be transformed (Fu et al. 2017). Amino acid conjugates are consistently detected in quantities contaminants, but sometimes as a side reaction (He et al. 2017).

2.3 Stage III—CECs sequestrations and/or accumulation

The major difference between mammalian and plant metabolism is in the ultimate fate-storage, which is opposite to excretion in mammals. Due to the lack of excretion pathway, most of the metabolites and conjugates are sequenced in the plant tissues, which is also termed as 'excretion storage'. There are at least three terminal fates within the plant tissues for sequestration: storage in cell vacuole, storage in the apoplast, or covalent binding to cell walls (Bartha et al. 2014). And few compounds are reported to be volatilized through stomatal pores on the leaves (Dordio et al. 2009). It was also found that released conjugates and plant natural exudes could be further re-uptaken to enhance the bioavailability of residual contaminants in soil environment (Tai et al. 2019). Some contaminants that are not metabolized or sequestered are released to the atmosphere through stoma on leaves surface (Barbour et al. 2005). Some are partitioned into plant lipids during the translocation without further metabolism (Tai et al. 2019).

3 Phytoremediation potential of industrial hemp

3.1 Performance of industrial hemp for the decontamination of CECs

So far, the fiber production and medical value of industrial hemp have been dominantly recognized. However, because of the long-term illegalization for planting industrial hemp in the North America, its phytoremediation potential has been largely unknown. In the limited industrial hemp phytoremediation studies available, the effectiveness of hemp's ability to remove heavy metals has been repeatedly proven (Tofan et al. 2013; Stonehouse et al. 2020; Praspaliauskas et al. 2020). Compared to other popular phytoremediation species, such as mustard and sunflower, hemp exhibited excellent removal efficiency with heavy metals (Meers et al. 2005). Industrial hemp is ideal for heavy metal removal owing to its large and porous surface structure, low nutrient requirements and high contaminants tolerance. Studies demonstrated that hemp can survive in highly contaminated sites such as landfill leachate, mine area, where very few crop plants could survive (Mihoc et al. 2012). Accumulated heavy metal can be further digested, metabolized and even be exuded as dietary form of heavy metal (Stonehouse et al. 2020). Industrial hemp also performed good clean-up of CECs. CECs with a wide range of molecular weights and solubilities were remediated with hemp (Table 1). Several studies reported that the soil remediation and microbial activity were also enhanced by the hemp cultivation. During the growth of hemp, powerful allelopathic chemicals through its root has been secreted, accelerating the soil remediation (Linger et al. 2002). Similarly, a study conducted on *Zea mays* proved the biogenetic, rather than anthropogenic sources of hydrocarbon contents in soil (Grifoni et al. 2020). Bacteria including *Achromobacter* sp., *Pseudomonas* sp., and *Alcaligenes* sp., which were isolated from hemp, completely degraded the phenol and benzene, indicating great phytoremediation potential of hemp (Iqbal et al. 2018). Co-contaminations

Table 1 CECs and plant species investigated in phytoremediation studies

| Contaminant | LogK _{ow} ^a | Functions of plant and final storage | Plant medium | BCF (g/g wt in plant / wt in initial medium) ^b | Plant type | Refs. |
|---------------------------------------|---------------------------------|---|------------------|---|--|------------------------|
| Total polycyclic aromatic hydrocarbon | – | Hemp promotes the contaminant-degrading enzyme by exuding allelopathic chemicals. | Loamy Sand | 0.150 | Hemp (<i>Cannabis sativa</i> . L) | Liste and Prutz (2006) |
| Naphthalene | 3.30 | During the study, it implanted explanta | Loamy Sand | 0.097 | Hemp (<i>Cannabis sativa</i> . L) | |
| Benzo(b)fluoranthene | 5.78 | biodegradation, especially bacteria-associated degradation | Loamy Sand | 0.061 | Hemp (<i>Cannabis sativa</i> . L) | |
| Benzo(a)pyrene | 6.13 | | Loamy Sand | 0.105 | Hemp (<i>Cannabis sativa</i> . L) | |
| Dibenzo(a, h)anthracene | 6.5 | | Loamy Sand | 0.120 | Hemp (<i>Cannabis sativa</i> . L) | |
| Total petrol hydrocarbon | – | | Loamy Sand | 0.068 | Hemp (<i>Cannabis sativa</i> . L) | |
| Benzo(a)pyrene | 6.13 | The existence of hemp in the watered soil enhanced the bacteria-associated degradation. | Silt Clay Soil | 0 (min) 0.415 (max) | Hemp (<i>Cannabis sativa</i> . L) | Campbell et al. (2002) |
| Chrysene | 5.96 | The influence of plants occur as growing time increases | Silt Clay Soil | 0 (min) 0.190 (max) | Hemp (<i>Cannabis sativa</i> . L) | |
| Cobalt (II) | – | Hemp fiber functioned as a biosorbent to accumulate cobalt | Aqueous Solution | 0.0013 (min) 0.0078 (max) | Dry Hemp Fiber (<i>Cannabis sativa</i> . L) | Tofan et al. (2013) |

Table 1 (continued)

| Contaminant | LogK _{ow} ^a | Functions of plant and final storage | Plant medium | BCF (g/g wt in plant / wt in initial medium) ^b | Plant type | Refs. |
|----------------------|---------------------------------|---|--|--|---------------------------------------|--------------------------|
| Selenium (Se) | – | Major functions of plants include biofortification (i.e., production of dietary products), accumulation, translocation, and conjugation of Se. The dominant detected forms of Se was C-Se-C. Se was stored mainly in leaf vasculature and in the seed embryos | Turf (Gravel Growth Medium) | 0.0013 (max) | Hemp (<i>Cannabis sativa</i> . L) | Stonehouse et al. (2020) |
| Hydrocarbon (C > 12) | – | Although no significant bioadsorption of contaminants, enhanced microbial degradation of hydrocarbons with vegetates was found in the experiments | Sandy Soil | 0 | Corn (<i>Zea mays</i>) | Grifoni et al. (2020) |
| Hydrocarbon (C < 12) | – | | Sandy Soil | < detection limit | Corn (<i>Zea mays</i>) | |
| Carbamazepine | 2.7 | Epoxidation was the major metabolic pathway Contaminant and its metabolites are dominantly stored in lettuce outer leaves. Soil with high organic contents also preserved and degraded a portion of contaminants | Loamy sand Sandy Loam Sandy Clay | 1.5 × 10 ⁻⁴ 1.1 × 10 ⁻⁴ 0.5 × 10 ⁻⁴ | Lettuce (<i>Lactuca sativa</i>) | Mordechay et al. (2018) |

Table 1 (continued)

| Contaminant | Log K_{ow} ^a | Functions of plant and final storage | Plant medium | BCF (g/g wt in plant / wt in initial medium) ^b | Plant type | Refs. |
|---------------|---------------------------|--|-------------------------------|---|---|--------------------------------|
| Acetaminophen | 0.46 | The function of the plant in this study included the accumulation, translocation, and rapid conjugation of contaminants (1 week). Higher metabolism activity was found in the leaves | Hoagland Nutrient Solution | 0.173×10^{-3} (root) 0.11×10^{-3} (leaf) | Indian mustard <i>Brassica juncea</i> L. Czern | Bernadett Bartha et al. (2010) |

Table 1 (continued)

| Contaminant | LogK _{ow} ^a | Functions of plant and final storage | Plant medium | BCF (g/g wt in plant / wt in initial medium) ^b | Plant type | Refs. |
|----------------------|---------------------------------|--|-------------------|---|--|---------------------------------|
| Triclosan | 4.76 | Compounds with carboxylic group exhibited higher uptake rates on the plant. Plant translocation and lipophilic adsorption both appeared in the study | Nutrient Solution | 0.438 | Lettuce (<i>Lactuca sativa</i>) | Calderón-Preciado et al. (2012) |
| Triclosan | 4.76 | | Nutrient Solution | 0.502 | Spath (<i>Spathiphyllum</i> spp.) | Chigbo et al. (2013) |
| Copper (Cu) + Pyrene | 4.88 (pyrene) | The function of plant included the phytoextraction of Cu. Indirect evidence showed accumulation, possible metabolism of pyrene and enhanced photodegradation were presented. The combination of metal and organic pollutants significantly inhibited both the phytoextraction of heavy metal and degradation of pyrene | Topsoil | 0.118 (max pyrene) 3.640 (max Cu) | Black mustard (<i>Brassica juncea</i>) | |

Table 1 (continued)

| Contaminant | $\text{Log}K_{ow}^a$ | Functions of plant and final storage | Plant medium | BCF (g/g wt in plant / wt in initial medium) ^b | Plant type | Refs. |
|-------------------------|----------------------|--|-------------------|---|-------------------------------------|--------------------|
| Iron (II) + Norfloxacin | 0.46 | The function of plant included the phyto-extraction of Fe (II) and norfloxacin. The accumulation of norfloxacin in rice roots was inhibited with the increasing dosage of Fe (II) (0–50 mg Kg^{-1}). But increasing accumulation was found when Fe (II) was in the range of 50–70 mg Kg^{-1} . Norfloxacin was mainly distributed in the root surface, epidermis and stele of the rice root | Paddy Soil | 0.907 (max norfloxacin) | Rice (<i>Oryza sativa</i> L.) | Yan et al. (2017) |
| Oxytetracycline | - 0.90 | The functions of the plant include translocation and metabolism of oxytetracycline. The translocation of oxytetracycline was an energy-dependent process, requiring binding sites | Nutrient solution | 0.142 (min) 0.242 (max) | Alfafa (<i>Medicago sativa</i> L.) | Kong et al. (2007) |

Table 1 (continued)

| Contaminant | Log K_{ow} ^a | Functions of plant and final storage | Plant medium | BCF (g/g wt in plant / wt in initial medium) ^b | Plant type | Refs. |
|-------------|---------------------------|---|--|---|--------------------------------------|-------------------|
| Iopromide | - 2.05 | The functions of the plants include translocation and metabolism of iopromide. Multiple mechanisms (i.e., oxidation and dehalogenation) and transformation products were identified in the leaves, roots and rhizomes. Final storages of iopromide were found in leaves, shoots and rhizome zone. The dominant transformation products were stored in leaves rather than roots and rhizomes | Commercial Potting Soil + Hoagland Nutrient Solution | 1.101 (max) | Bulrush (<i>Typha latifolia</i> L.) | Cui et al. (2017) |

^aData were collected from the online database^bNormalized to the same units according to the information provided in the literatures

of heavy metal and CECs are even more challenging. The phytoremediation results are debatable because of the different functions of heavy metals and the interactions between heavy metal and organic contaminants. Pyrene was reported to facilitate copper penetration into the plant cell, increasing copper accumulation (Chigbo et al. 2013). The competition between heavy metal and organic contaminants, on the other hand, resulted in the limited phytoextraction of residual contaminants. For example, the accumulation of norfloxacin in rice roots was inhibited with the increasing dosage of Fe (II) (0–50 mg Kg⁻¹) (Yan et al. 2017). However, a handful of studies have investigated the contaminants with halogenated functional groups or with larger molecular weights (>400), which are commonly found as CECs. Studies investigating the phytoremediation potential of these CECs are urgently needed as the increasing contamination is found globally (Marsik et al. 2017; Mattes et al. 2018).

3.2 Factors influencing the performance

3.2.1 Physicochemical properties of contaminants

Physicochemical properties (i.e., log K_{ow} , molecular weight and numbers of carbon) of the contaminants are dominant factors to consider during the uptake of xenobiotics. As discussed in Sect. 2, plant uptake of contaminants occurs by passive and/or active transport. Compounds characterized as semi-volatile or volatile can be partitioned or adsorbed from the atmospheric air. These quite different decontamination approaches are resulted from the physicochemical properties, collectively described as octanol-water partitioning coefficient (K_{ow} or D_{ow}) and octanol-air partitioning coefficient (K_{oa}) (Lin et al. 2007). Predictions have been made that nonionic compounds, which log K_{ow} in a range of 0.5–3.5 are lipophilic enough to move through the lipid bilayer of membrane, yet water-soluble enough to transfer into the cell fluid. For passive transport of poorly water-soluble organic compounds, it has been noted that the single and most important plant characteristic is the plant lipid content (Barbour et al. 2005). This might indicate that multiple uptake mechanisms occurred. It has also found that log K_{ow} smaller than 2 exhibited a more diverse bioaccumulation factor (BCF), which represents the uptake efficiency of contaminants from the studied medium (Fig. 3). Plants exhibited complex preferences on remediation of compounds with different molecular weights (MW), especially when MW > 300. In some cases, contaminants with higher molecular weights have more resistance to biodegradation, resulting in decreased accumulations to plants (Liste and Prutz 2006). Some studies showed high BCF (> 3) of compounds with large molecular weight. This result, however, was contributed by multiple factors including optimal growth medium (e.g., commercial potting soil and Hoagland nutrient solution), smaller log K_{ow} and longer study duration (Cui et al. 2017; Boonsaner and Hawker 2010; Yan et al. 2017). And the lower transformation efficiencies ranging from 0 to 0.06 (from root to shoot) were found with these compounds (Cui et al. 2016; Yan et al. 2017). As for weak electrolytes, parameters have different reflections on the plant uptake. D_{ow} is the normalized parameter to K_{ow} considering the effect of ionized functional groups. D_{ow} is largely dependent on the factors such as the acid–base coefficient (pK_a) of the compound and the medium pH. It can be estimated with the following equation: $D_{ow} = K_{ow}(1 + 10^{pH-pK_a})^{-1}$ (Halling-Sørensen et al. 1998). Contaminants transported in phloem was found to be optimal for compounds of intermediate hydrophobicity (Log K_{ow} 1–3) and weak acidity (pK_a 3–6) (Trapp 2004). This indicates the contaminants

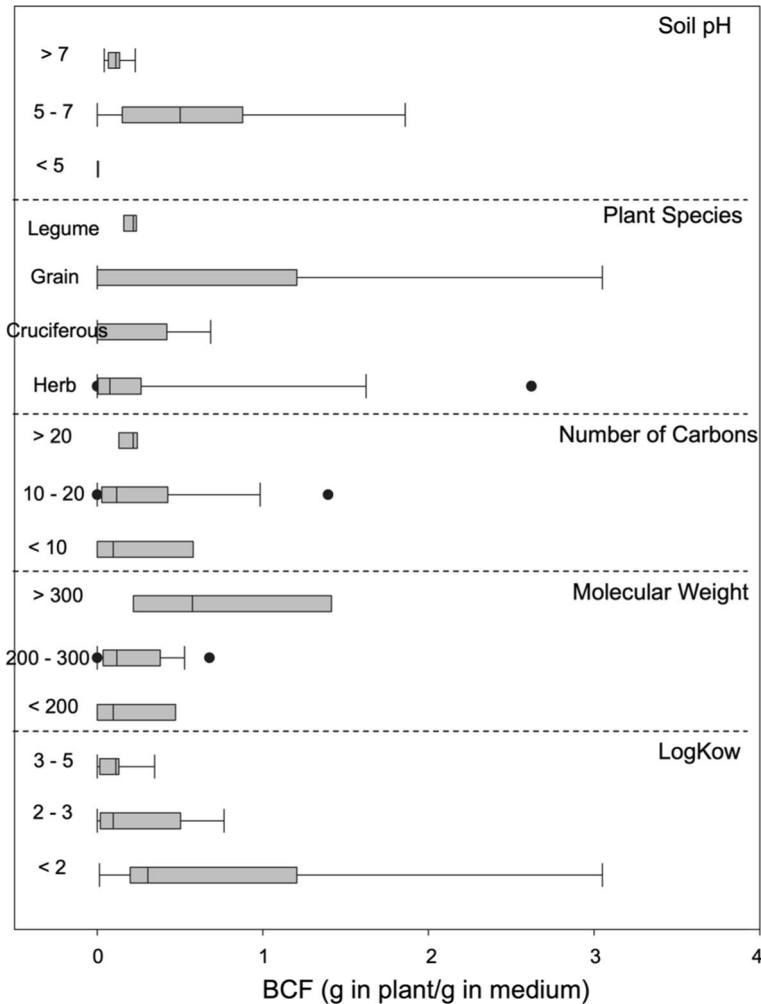


Fig. 3 Influences of Soil pH, plant species, physicochemical properties of contaminants (i.e., number of carbons, molecular weight and LogK_{ow}) on Bioaccumulation Factors (BCF)

with these properties have larger chances to be further metabolized. However, in general, there are still very limited studies investigating the weak electrolyte's phytoremediation.

3.2.2 Plant type and growing medium

Selection of plants as phytoremediators depends on the phytoremediation efficiency. Higher efficiency and more attention have been found with herbs (e.g., mustard and industrial hemp) and grains (e.g., soybean and corn) (Fig. 3). Common characteristics they share are high tolerance to on-site pollution, short life cycles and handling ease. Fibrous root systems are also preferred because of the large rhizoplane surface area, which enriches the microbial population (Escalante-Espinosa et al. 2005). For example, Alfalfa increased the

number of both culturable, aerobic heterotrophic and PAH degrading bacteria in the rhizosphere after 7 weeks compared to bulk soil (Kirk et al. 2005). Uncontaminated soil also showed the increasing amount of large molecular hydrocarbon ($C > 12$) with the growth of maize (*Zea mays*), indicating the biogenic sources of the compounds (Grifoni et al. 2020). Yellow medick (*Medicago falcata* L.) and alfalfa were both effective at on-site remediation of petroleum contaminants, but the number of hydrocarbon-oxidizing microorganisms were larger in the rhizosphere zone of alfalfa (Panchenko et al. 2017). Soil pH and pK_a values of contaminants combinedly decided the neutral or ionic form in the study medium, determining the availability to plants. However, uptake efficiencies and forms of contaminants are not always closely related in studies. For example, in soil (pH=6.5–6.7) fortified with pharmaceuticals, uptake efficiencies were reported the greatest of carbamazepine (neutral) and sulfamethoxazole (ionic) in plant tissue, suggesting that factors other than soil pH affect the uptake (Holling et al. 2012). Similarly, Herklotz et al. (2010) found the largest accumulation in cabbage tissue was correlated to the compound with lowest pK_a , sulfamethoxazole (ionic form in studied medium). Some studies found the metabolism could be independent from environmental factors, such as soil type, carrier medium and solely controlled by the total amount taken up by the plant (Mordechay et al. 2018). Therefore, comparing to medium properties, characteristics of target compounds seem to play larger roles in uptake efficiencies.

4 Circular economy of industrial hemp applications and management

4.1 Hemp potential disposal strategies

It is essential to discuss the disposal strategies of industrial hemp when considering the economic benefits. Industrial hemp is a particularly vigorous annual crop, which can be seeded from late spring when the soil just starts to warm. It has a remarkable growth rate, which has been recorded with heights from 1 to 5 m by August (Ip and Miller 2012). High tolerance of contaminants make hemp valuable in terms of its further application after phytoremediation (Kumar et al. 2017). Estimating from previous studies, contaminants only showed limited effect on hemp quality. For example, Linger et al. (2002) indicated that heavy metal contamination did not show negative effect on the hemp fiber quality (i.e., fineness or strength) or quantity. Revealed by greenhouse experiments, dry biomass of hemp cultivated in a moderately contaminated area decreased up to 40% compared to those in uncontaminated soil (Pietrini et al. 2019). While chlorophyll content and other photochemistry parameter only slightly reduced, indicating the good physiological status of plants. Husain et al. (2019) also demonstrated that the height of hemp in contaminated soil and commercial soil exhibited no significant difference when heavy metal accumulation were detected in all parts of hemp.

So far, industrial hemp, serving as an economical crop, has been extensively applied to the fields including bioenergy, paper, construction etc. (Table 2). Hemp can either be utilized as the whole plant or each individual part, such as hemp fibers, seeds and inflorescences (Table 2). These non-food applications can also be applied to the disposal strategies with appropriate pretreatments and investigations. In order to optimize socioeconomic benefits and limited environmental impact of hemp disposal after phytoremediation, strategies that target each individual part instead of whole plant are suggested.

Table 2 Disposal strategies of industrial hemp

| Scenario | Interested part | Hemp/hemp part treatment | Study method | Environmental impact and/or other concerns | Refs. |
|------------------------|-----------------|--|---------------------|--|-------------------------------|
| Tissue and towel paper | Hemp hurbs | The hemp was retted and decorticated. The obtained hurds were mixed with hardwood chips. It was processed by the following steps simultaneously: separation, washing, refining, screening and pulping | Lab test | – | Náithani et al. (2020) |
| Paper production | Hemp fiber | 1) Whole stalk was processed with thermomechanical and/or chemi-thermomechanical pulping 2) Hemp bark fiber chemical was processed with pulping and bleaching, and hemp core fiber chemical pulping and bleaching 3) Whole stalk chemical was processed with pulping and bleaching | Literature review | (1) Frequency of activity (e.g., chisel, herbicide of pre-plant fertilizer, bedding, seeding, cultivation, and harvesting) on the hemp plantation is much higher than tree plantation (2) Environmental footprints are much higher than tree plantation (3) It is commercially uncompleted | Bowyer (2001) |
| Bioethanol production | Hemp hurbs | Enzymatic hydrolysis which converts lignocellulosic biomass into ethanol | Life-cycle analysis | (1) Global warming (CO ₂ , NO _x , SO _x) has increased shifting from conventional gasoline to ethanol blend due to the nitrogen fertilizer usage and agricultural machinery (2) It is commercially uncompleted | González-García et al. (2012) |

Table 2 (continued)

| Scenario | Interested part | Hemp/hemp part treatment | Study method | Environmental impact and/or other concerns | Refs. |
|---|-----------------|--|-------------------|---|------------------------|
| Reinforced or chemical additive | Hemp fiber | Recycled polypropylene/hemp fiber composite was dried at 105 °C for 2 h prior to moulding and then processed with the injection moulding | Lab tests | (1) Hemp fibers decreased the impact on global warming, acidification, photochemical oxidation, eutrophication, and abiotic depletion (2) Analysis is not highly representative | Bourmaud et al. (2011) |
| Heat, power and vehicle fuel production | Hemp | 1) Spring-harvested baled hemp pressed into large square bales and combustion 2) Spring-harvested briquetted hemp was heat small-scale domestic boilers, (80% thermal efficiency) for energy supply purposes.; 3) Autumn-harvested, chopped and ensiled hemp was converted to biogas in an anaerobic digester, the byproduct is the nutrient-rich digestate 4) Autumn-harvested, chopped and ensiled hemp was converted to be refined to vehicle fuel | Literature review | (1) Environmental analysis was made that changing fuel to renewable sources could reduce CO ₂ emission considerably (2) Other competitors such as sugar beet, maize, willow, and reed canary grass 3) Technology development is required to improve energy yield | Prade et al. (2012) |

Table 2 (continued)

| Scenario | Interested part | Hemp/hemp part treatment | Study method | Environmental impact and/or other concerns | Refs. |
|---|---------------------|--|---------------------|--|------------------------------------|
| Wastewater remediation and desertification strategy | Hemp | – | Literature review | (1) Reduction of greenhouse emission as the fertilizer needs, energy use and chemical pollution from wastewater treatment are minimized (2) Difficult balancing between hydraulic loading and contaminants remediation (3) Deterioration of soil quality; (4) Low public and stakeholder's acceptance | Barbosa et al. (2015) |
| Insecticide and pest management | Hemp inflorescences | The extraction of essential oil was made by fresh hemp inflorescences (monoecious cv. Felina 32) by steam-distillation | Lab tests | It was the environmental safety to non-target invertebrates | Giovanni Benelli et al. (2018a, b) |
| Biodegradable pot material | Hemp fibers | Hemp fibers was soaked into sodium alginate water solution and shape into pots | Lab and field tests | It completely biodegraded in 16 days | Schettini et al. (2013) |

Table 2 (continued)

| Scenario | Interested part | Hemp/hemp part treatment | Study method | Environmental impact and/or other concerns | Refs. |
|---|-----------------|--|---------------------|--|----------------------|
| Wall construction material | Hemp shiv | Hemp bales decortification, which mechanically removes fibers from the straw. It was then separated to fiber, shives and dust. Hemp shives are used for lime-hemp wall and other parts are collected to other applications | Life cycle analysis | (1) Hemp was the key parameter to reduce the greenhouse gas emission. (2) Analysis did not precisely represent the real scenario because of the limited data | Ip and Miller (2012) |
| Long-term phytoremediation and bioenergy production | Hemp | – | Literature review | (1) Phytoremediation is decided by metal tolerance of selected plants; (2) The toxicity of biofuels is doubted because of enriched metal; (3) The disposal residue biomass is uncertain | Liu et al. (2012) |
| Hemp based thermal insulation in construction | Hemp fiber | – | Literature review | (1) It reduces CO ₂ in buildings (2) It is biodegradable and nontoxic to people (3) The hygrothermal performance is doubted (4) There is a potential risk of producing a monstrous hybrid mixture of materials both technical and biological (5) There is health issue considering the usage of nanoparticles | Latif et al. (2010) |

Table 2 (continued)

| Scenario | Interested part | Hemp/hemp part treatment | Study method | Environmental impact and/or other concerns | Refs. |
|----------------------|-----------------|--|--------------|---|------------------|
| Biodiesel production | Hemp seed | Hemp seed oil was processed to biodiesel through a base-catalyzed transesterification reaction | Lab test | Because of the high portion of unsaturation fatty acid in hemp seeds, the oxidation stability of biodiesel will be poor | Li et al. (2010) |

4.1.1 Hemp fibers

Hemp fibers have been largely employed in bioenergy, paper construction sectors (Bowyer 2001). In terms of bioenergy production, it has been recognized as an economic option with low environmental impacts. High cellulose content (~44%) as well as high biomass yield ensure hemp a suitable crop for bioenergy production (Kumar et al. 2017). Nowadays, 36% of the global energy consumption is in the form of conventional liquid fuels including petrol and diesel (Staples et al. 2017). Therefore, the utilization of bioenergy (e.g., bioethanol, biodiesel, biobutanol, and biogas) instead of conventional energy resources exhibits environmental, energy-saving and socioeconomic advantages (González-García et al. 2012). Bioethanol, as recorded, can be produced from the cellulose and lignocellulosic biomass, such as agricultural residues, herbaceous crops or forestry residues (Hou et al. 2020). These materials are abundant and inexpensive, as promising bioenergy production resources. Hemp fiber can also be utilized for paper production. However, there is no record of 100% hemp-based paper production (Naithani et al. 2020). It was also not economically or environmentally competitive comparing to conventional tree plantation (Bowyer 2001).

4.1.2 Hemp hurds

During hemp fiber separation, hemp crops also produce large amount of byproducts: hemp and dust (González-García et al. 2012). Hurds are non-fiber components obtained by retting hemp stem (Scrucca et al. 2020). The chemical contents of hemp hurds are very close to that of wood species, with a high portion of cellulose and hemicellulose. Therefore, it has mainly contributed to the animal bedding production and construction sector. Several studies also estimated the feasibility of converting hemp hurds into bioethanol (Barta et al. 2010; González-García et al. 2012). But hemp hurds-related technologies are relatively new and still under development.

4.1.3 Hemp shiv

Hemp bales are shopped and decertified. The bales are then separated to hemp shiv, hemp fiber and hemp dust. Hemp shiv have been implemented in hemp-lime wall construction. At the same time, hemp fiber and hemp dust are recycled in use of other products. The dust can be utilized as filler in plastics, lime render or compressed for use as fuel logs (Ip and Miller 2012). Hemp-lime wall has been used in Europe early from 1990s, but not commonly accepted (Evrard and De Herde 2010). Nowadays, due to increasing efforts being made on environmental protection and greenhouse gas (GHG) emission reduction, hemp-lime construction is striking globally. Hemp, serving a part of construction material, significantly enhances construction status from different aspects, such as high levels of airtightness, improved air quality and lower energy consumption because of latent thermal capacities of hemp-lime wall (Shea et al. 2012). It was estimated that hemp-lime wall would be able to last over 100 years, or at least as durable as traditional wall (Cripps and Fovargue 2004).

4.1.4 Hemp seeds

Biodiesel is clean production as an alternative to petroleum-based diesel fuel. Biodiesel production has already been commercialized by utilizing crop oils such as sunflower, palm tree and soybean (Meher et al. 2006). Although not largely commercialized, industrial hemp is one of the most promising sources. It has a high yield of oil and biomass, indicating potential production of both biodiesel and bioethanol simultaneously (Li et al. 2010). Li et al. successfully convert the oil of hemp seed to biodiesel through the base-catalyzed transesterification with the conversion yield of 97% (Li et al. 2010). Yang et al. (2010) used a one-pot process, which combined transesterification and selective hydrogenation, converted hemp seed oil to biodiesel with a yield of 96%.

4.1.5 Hemp inflorescences

Industrial hemp has the potential to be employed as insecticides because of its inflorescences. Glandular hair, which exuded oleoresin (a barrier entrapping plant enemies), are accumulated on its inflorescences (G. Benelli et al. 2018b, a). Benelli et al. estimated that the essential oil extracted from hemp inflorescences via hydrodistillation is efficient as natural insecticides for the control and management of mosquito vectors, houseflies and moth pests (Giovanni Benelli et al. 2018a, b). Additionally, the essential oil exhibited protection for earthworms, which are major contributor to the consumption of biodegradable materials and organic waste, which could be converted to vermicast, unlike synthetic insecticides that kill almost all earthworms instantly (Pavela 2018).

4.2 Outlook: implications for industrial hemp based on circular management

In the last few years, the circular economy (CE) has emerged as an initiative facing resource depletion and global climate change (Manriquez-Altamirano et al. 2020). Protocols (e.g., alternatives, technologies and practices) that allow substituting non-renewable natural resources to resources recovered from 'waste' thereby achieve socioeconomic and environmental goals of the CE concept (Lieder and Rashid 2016). In addition, CE system would also positively affect local by-product demand if managed properly. For example, using locally produced and homogenous feedstock can alleviate the economic and environmental concerns caused by long-range transportation and complicated materials supply, subsequently assisting local businesses and employment (Bolognesi et al. 2019). Therefore, industrial hemp after phytoremediation should be re-considered as a 'resource' instead of 'waste' by implanting a more holistic circular economy model (Fig. 4). Before the conduction of such system, pot trial and field trial are required in order to examine the toxicity of hemp/hemp parts and feasibility of the proposed strategy. According to the characterization of contaminants and meso/macro level tests, appropriate amounts of industrial hemp would be applied for the phytoremediation purpose. After 120 days of growth, mature hemp would be qualified by the amount of biomass, volume, height and level of phytotoxicity. Hemp, with higher quality will be continuously processed for further recycling/remanufacturing/reusing processes. While hemp with lower quality would be pyrolysis/digested on-site depending on the treatment efficiency and local conditions. It can also serve as an energy supply to local industries. Nonetheless, the CE system cannot achieve its ambitious goals without addressing residue management after all the steps (Peng and Pivato 2019).

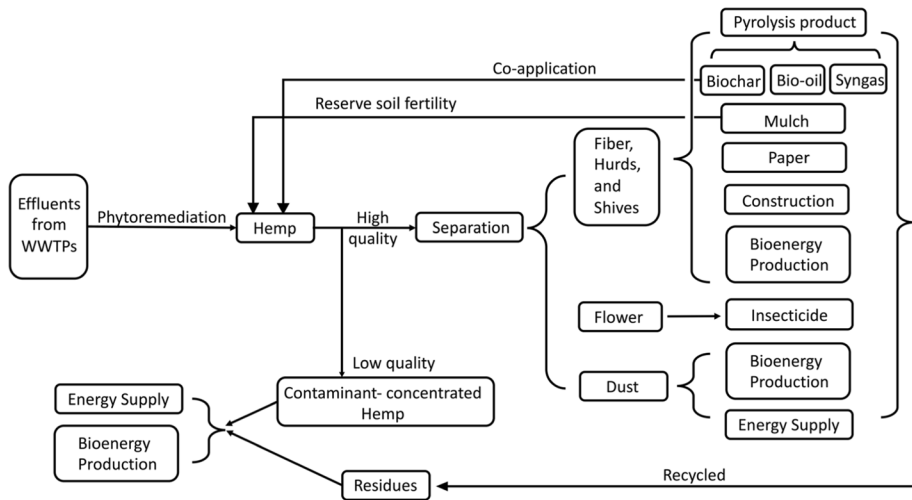


Fig. 4 Proposed local-dominated industrial hemp production line under the framework of the circular economy

Those residues (e.g., ashes and dust) and contaminant-concentrated hemp could be sent back to the domestic boilers for heating purposes with the goal of reducing treatment costs as well as energy consumption.

4.3 Challenges

Recent studies discussed previously shed light on the potential disposal strategies of hemp crops after phytoremediation. But the challenges of industrial hemp utilization remain unsolved. Studies investigating disposal strategies of industrial hemp achieved different results on aspects of the economic and environmental performance mainly due to the lack of a commercial production line. Most of the study methods are limited to the literature review, life-cycle analysis (LCA) and lab-scaled experiments. In addition, the estimations such as LCA are largely based on the literature instead of experimental data, reasonable assumptions, and results of similar crops, making the estimates less accurate.

The application of industrial hemp might negatively affect the environment during crop growth. It was demonstrated that bioenergy production significantly increases greenhouse gas emissions, acidification, and eutrophication because of the feedstock cultivation (Martin et al. 2014). González-García et al. (2012) indicated that 85% blending of ethanol with fossil fuels contributed more than 2 times of GHG to global warming than conventional fuel energy. The study, which investigated the environmental impacts of hemp and flax for non-wood pulp mills showed 80% of greenhouse gas emissions are contributed by fertilizer usage during hemp cultivation (Gonzalez-Garcia et al. 2010).

Not all the hemp parts are feasible for recycling. For example, the recycling strategy of hemp ashes as mineral fertilizer is still under discussion because ash can only replace a minor portion of fertilizer and requires a similar amount of energy. However, ash recycling is an important tool for closing nutrient cycles considering phosphorus deposit depletion (Prade et al. 2012). In addition, it is uncertain whether the ashes are non-toxic serving as mineral fertilizer. In fact, some studies have determined that the heavy metal contaminated

biomass are not only reduced in weight, but also concentrate the heavy metals in ash/char fraction. Nevertheless, their individual pyrolysis fraction, i.e., bio-oil/tar and gas, are both heavy metal free (Liu et al. 2012). Therefore, the utilization of ashes are doubtful, but the valorization of metal might be feasible.

Last but not least, some strategies are commercially uncompetitive. For example, bio-fuels are less acceptable worldwide because the technology is still being developed. Even though the biomass is relatively abundant and inexpensive, not all of them can be utilized for biofuel production, mainly due to the difficulty of effective hydrolysis in terms of cost and energy consumption (González-García et al. 2012).

5 Conclusions

With increasing attention and legalization policies on industrial hemp, comprehensive utilizations of this precious crop have been studied in recent years. This review estimated the phytoremediation potential of CECs and the underlying mechanism of industrial hemp. The Green Liver Model precisely described CECs uptake and detoxification with several steps: transformation, translocation, conjugations and final storage. Studies in recent years (2005–2020) were found to further complete this theory by adding several transformation pathways, final storage terminals and *ex planta* biodegradation. Contaminants physico-chemical properties were found to play a more significant role than soil or plant properties in regards of the phytoremediation performances. However, there are still limited studies available that employ industrial hemp for organic compound decontamination. The circular economy system has been applied in the disposal strategies, in order to optimize the socioeconomic as well as environmental benefits of industrial hemp. In addition, circular economy protocol can also promote local business development and employment if well managed. Future research is urgently required on performance aspects of hemp on phytoremediation and realization of its circular disposal/recycling managements.

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Compliance with ethical standards

Conflict of interest The authors have no conflict of interest in relation to this work.

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